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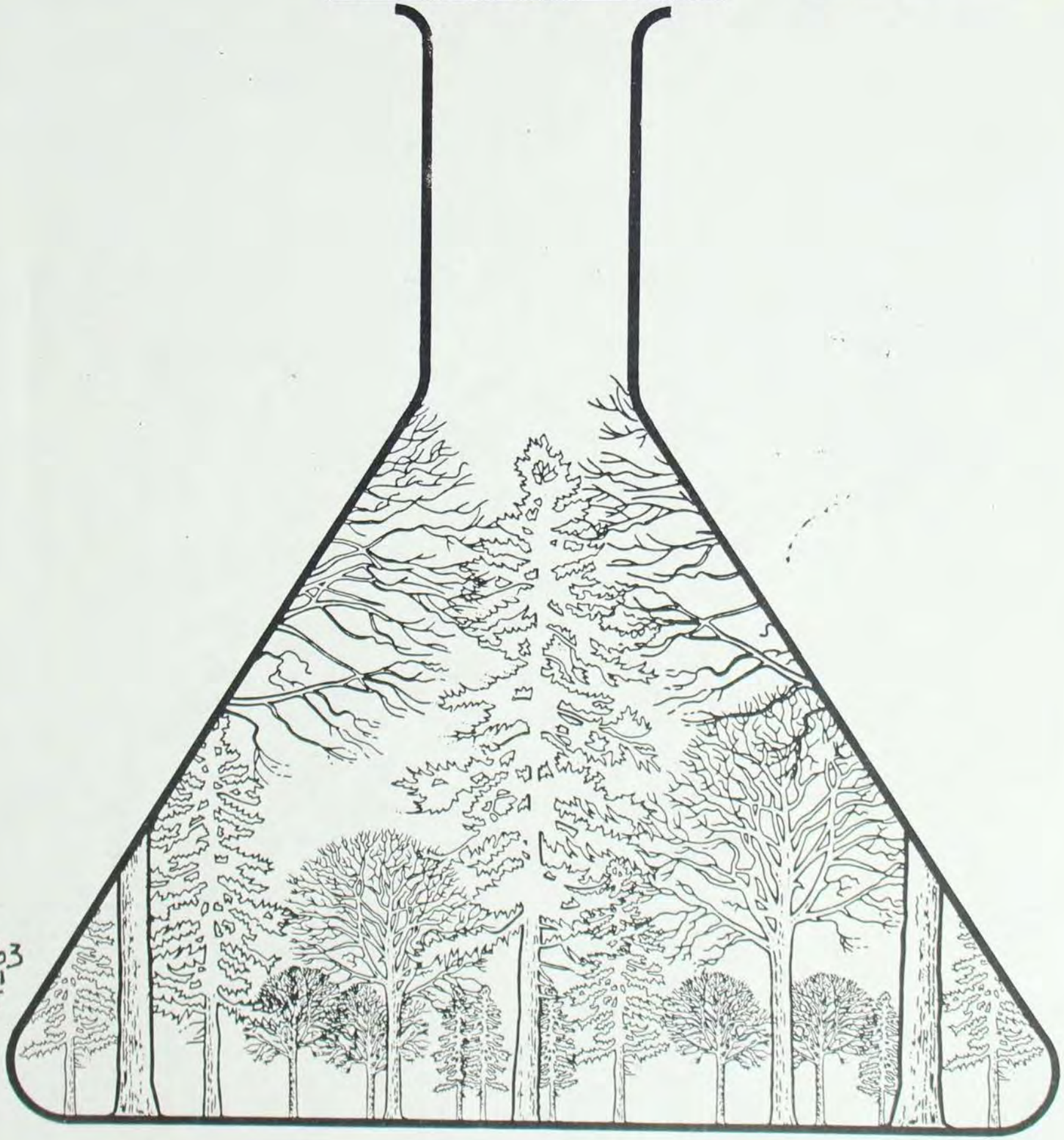

CONTENTS

INDEX TO AUTHORS

HYDROLYSIS OF CELLULOSE IN WOOD WITH CONCENTRATED HYDROCHLORIC ACID IN THE PRESENCE OF LITHIUM, CALCIUM AND ZINC

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ABSTRACT

The kinetics of hydrolysis of cellulose in wood with concentrated hydrochloric acid (37%, ~12N) in the presence of lithium, calcium and zinc chlorides has been studied at moderate temperatures (20-50°C). The first order reactions go virtually to completion in as rapidly as 10 minutes, although in the absence of the salts cellulose is resistant to hydrolysis at this acid concentration. Other variables studied included salt concentration, lower acid concentrations, and wood particle size. The effect of the salts by weight on rate of hydrolysis decreases in the order Li > Zn > Ca.

KEYWORDS: Cellulose, Hydrolysis, Concentrated HCl, Salts.

INTRODUCTION

During studies of the hydrolysis of cellulose with superconcentrated hydrochloric acid (>40%) in this laboratory it was found that in the presence of certain cations (Li^+, Ca^{++} and Zn^{++}) hydrolysis will proceed to completion at lower concentrations of hydrochloric acid that are incapable of hydrolyzing cellulose in the absence of the salts (1). Similar observations were noted by Beardsmore (2). The effect of the variables of acid and salt concentrations, temperature and degree of agitation for the hydrolysis of cellulose by hydrochloric acid enhanced with lithium chloride has been recently reported (3). The present paper represents the extension of these studies to the hydrolysis of cellulose in the presence of calcium and zinc and the hydrolysis of wood in the presence of all three cations.

RESULTS

Cellulose (filter paper, Wiley-milled to pass 60 mesh) was hydrolyzed at 50°C with 12N (37%) HCl containing 2g LiCl per g cellulose or equimolar quantities of $ZnCl_2$ (6.43g) or $CaCl_2$ (5.24g). Table I compares the rates of hydrolysis. Lithium is most effective on a weight basis, but zinc is most effective on a molar basis. The rate constant for lithium is essentially the same as that previously reported for 16N HCl in the absence of salts (1).

Table I

EFFECT OF SALTS ON HYDROLYSIS OF CELLULOSE WITH 12N HCl AT 50°C

Salt (g/g cellulose)	$k(min^{-1})$	Time (min.) for 90% hydrolysis
$ZnCl_2$ (6.43)	-2.561	2
LiCl (2)	-0.425	6
$CaCl_2$ (5.24)	-0.042	56

The effect of salt concentration on hydrolysis of cellulose in ground prehydrolyzed sweetgum wood (~63% cellulose, 37% lignin) is shown in Table II.

It is apparent from the table that the hydrolysis of cellulose during this fixed period of time increases with increasing ratios of salt to wood, reaching more or less constant values near a LiCl:wood ratio of 1.8:1, $CaCl_2$:wood ratio of 2.9:1 and $ZnCl_2$:wood ratio of 3.6:1. These ratios of salt to wood were used in the subsequent experiments reported in this paper. While the optimum weight ratio of salt to wood increases with the molecular weight of the salts, equivalent ratios of each salt accomplished aproximately the same extent of hydrolysis. Of course, these optimum ratios are only approximate since the increments for Ca and Zn shown in Table II are quite large.

Table II

EFFECT OF SALTS ON HYDROLYSIS OF CELLULOSE IN PREHYDROLYZED SWEETGUM WOOD WITH 12N HCL AT 50°C

Salt	Salt/wood ratio (wt.)	Cellulose hydrolyzed (1hr.)(%)
LiCl	1.00:1	69.6
	1.25:1	77.0
	1.50:1	82.4
	1.75:1	88.8
	2.00:1	89.1
$ZnCl_2$	1.21:1	53.0
	2.42:1	79.3
	3.63:1	85.9
	5.13:1	85.3
$CaCl_2$	1.23:1	69.2
	1.96:1	74.3
	2.94:1	83.3
	3.92:1	84.4

Equivalent weights corresponding to 1.8:1 for Li would be 2.4:1 for Ca and 2.9:1 for Zn.

The kinetics of hydrolysis of cellulose in prehydrolyzed sweetgum wood with 37% HCl in the presence of lithium, calcium and zinc chlorides was studied at 20°-50°C. The results at 50°C for ground wood are shown in Table III.

Table III

EFFECT OF SALTS ON HYDROLYSIS OF CELLULOSE IN PREHYDROLYZED SWEETGUM WOOD WITH 12N HCl AT 50°C

Salt g/g wood)	k (min^{-1})	Time (min) for 90% hydrolysis
LiCl (1.8)	- 0.200	9
$ZnCl_2$ (3.6)	- 0.118	15
$CaCl_2$ (2.9)	- 0.020	99

With this substrate the rates were slower than for pure cellulose (Table I) and for 16N HCl (1). Actual salt to cellulose ratios were 2.9:1 for Li, 5.8:1 for Zn and 4.7:1 for Ca. In this series, although all the rates were retarded compared to pure cellulose, the rate with zinc was retarded to a much greater extent. Activation energies and extent of reaction followed the pattern previously reported (1, 3); high activation energies (> 20 kcal/mol) and complete reaction for ground wood, low activation energies and incomplete hydrolysis for chips.

Additional studies were carried out at lower acid concentrations. With 30% HCl at 50°C and the same salt concentrations the rates of hydrolysis were reduced twentyfold. However with 24% HCl at 70°C the hydrolysis rates increased sharply at critical salt:wood ratios of 4:1 for Li, 5:1 for Ca and 8:1 for Zn. Under these conditions 87% of the cellulose was hydrolyzed in one hour with 5.2:1 LiCl, 81% with 6:1 $CaCl_2$ and 79% with 10:1 $ZnCl_2$.

In a final study the substrate used was southern pine wood to determine the effect of the system on an unprehydrolyzed softwood. A holocellulose content of 64% was used for the calculation of carbohydrate hydrolysis. The kinetics of hydrolysis of holocellulose was studied at 20°-50°C with 37% HCl. The results with ground wood at 50°C are shown in Table IV.

In this series also the rates were retarded compared to pure cellulose, but the rate with zinc was not affected as much as in the sweetgum case. Activation energies and the influence of particle size showed behavior similar to that in the hydrolysis of prehydrolyzed sweetgum wood, as did the extent of hydrolysis with 24% HCl at 70°C.

Table IV

EFFECT OF SALTS ON HYDROLYSIS OF HOLOCELLULOSE IN SOUTHERN PINE WOOD WITH 12N HCl at 50°C

Salt (g/g wood)	k (min^{-1})	Time (min) for 90% hydrolysis
$ZnCl_2$ (3.6)	- 0.866	5
LiCl (1.8)	- 0.221	10
$CaCl_2$(2.9)	- 0.037	55

CONCLUSIONS

In the presence of lithium, zinc and calcium pure cellulose and cellulose in both hardwoods and softwoods can be hydrolyzed to glucose in good yield at hydrochloric acid concentrations as low as 24%, although in the absence of the salts cellulose is resistant to hydrolysis at these acid concentrations. At 37% HCl, still below the critical concentration for cellulose hydrolysis without salts, the hydrolysis with salts requires less salt and lower temperatures than at 24%.

The most rapid rates of hydrolysis were obtained with zinc, but since the influence of the salts on extent of hydrolysis corresponded to their equivalent weights lithium proved to be most effective on a weight basis. The presence of lignin in wood retards the rates of hydrolysis compared to pure cellulose. This retarding effect was much greater for zinc than for the others, and much more apparent for the hardwood, sweetgum than for the softwood, southern pine.

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THE COLLOID CHEMISTRY OF WASTE PAPER DEINKING

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INTRODUCTION

In the process of waste paper deinking colloid chemistry plays an essential role in a number of distinct steps. The most important of these are: i) the detachment of ink from the fibres, ii) the dispersion of the ink into small particles, iii) the redeposition of ink particles onto fibres, iv) the elimination of the ink particles from the pulp suspension by flotation or by washing and v) the clarification of recycled process water. In the present investigation we have studied steps no. ii)-v) under conditions typical for a flotation deinking plant. The objective of the work has been to elucidate the mechanisms of the processes involved and to determine the influence of different factors on the performance of each step.

Dispersion (1)

The dispersion of the ink was studied in laboratory scale deinking experiments. Old newspapers were slushed with deinking chemicals and the size distribution of the ink particles in the pulp was determined with a computerized image analyser.

In one series of experiments newspapers with different printing inks were slushed. The results then showed that those offset inks which cause problems in deinking after aging, disperse into smaller particles than other inks. In another series the influence of different chemical factors on the dispersion was studied. The most striking effect here was that calcium stearate, which is usually added as collector for the flotation, increases the mean diameter of the ink particles considerably when present in the pulper. A probable explanation for the phenomenon is that the calcium stearate induces agglomeration of the ink particles simultaneously with the dispersion.

Flotation (2,3,1)

The flotation experiments were performed on model dispersions of ink particles in sodium stearate solutions. To these dispersions the chemicals present in a deinking plant were added. Flotation was then performed in a Hallimond tube (a simple glass device normally used for mineral floatability studies). Afte flotation the remaining ink particle concentration was determined. In one series the size distribution of the remaining ink particles was also determined.

A flotation kinetics experiment showed that the ink particle removal followed pseudo-first order kinetics to a good approximation. It was also found that the first order rate constant increased exponentially with the particle diameter. This behaviour was later confirmed in laboratory scale deinking experiments with a waste paper pulp.

With calcium stearate as collector, the floatability was improved with increasing calcium and stearate concentrations. There was also a clear correlation between floatability and zeta potential of the ink particles, such that the flotation rate was highest when the zeta potential had been decreased from -85 mV to about -40 mV by addition of at least 2 mmole/l Ca^{2+}. The floatability also improved with increasing concentration of sodium chloride but decreased with increasing concentrations of nonionic surfactants or kraft lignin.

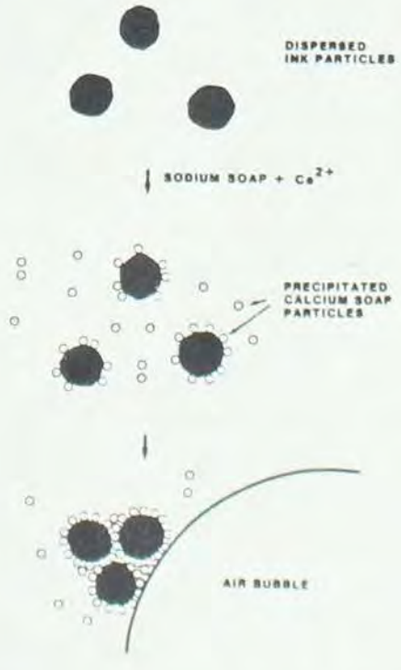

Figure 1. Suggested collector mechanism of calcium stearate

Examination of the ink dispersions by light and scanning electron microscopy revealed that the calcium stearate was precipitated as a layer of discrete particles on the surface of the ink particles. This observation and the floatability results above form the basis for the collector mechanism of calcium stearate suggested in figure 1. In the pulper the ink particles obtain a high negative zeta potential due to adsorption of soaps and ionization of acidic groups in the ink surface. The negative potential promotes the detachment of the ink and provides stability to the dispersion. However it gives rise to a repulsion between the ink particles and the negatively charged air bubbles and thus prevents flotation. When calcium soap is precipitated it forms a layer of small particles around the ink particles and thus give them the surface properties of the calcium soap. In the presence of an excess of calcium they then become hydrophobic and obtain a low zeta potential so that they can easily attach to the air bubbles. The calcium soap also induces agglomeration of the ink particles. This increases their effective diameter which is beneficial for the flotation rate.

Redeposition (4)

To study the deposition of ink particles onto fibres, model ink dispersions were mixed with the long fibre fraction of a thermomechanical pulp. They were then washed under stirring in a specially designed filter cell to remove all non-deposited ink particles from the pulp. The amount of deposited ink was then determined by measuring the reflectance of the pulp.

The results show that under certain conditions extensive deposition of ink particles may occur. However, the deposition can be efficiently prevented by nonionic surfactants normally added as dispersants. Waterglass has a certain effect in preventing deposition, which can be related to its ability to precipitate aluminate ions present in the pulp.

Clarification of process water (5)

Process water from the pulper loop of a flotation deinking mill was clarified by microflotation in laboratory and pilot scale. Three flocculation systems were tested: i) a conventional system consisting of a low molecular weight cationic polymer and a high molecular weight anionic polymer, ii) a water soluble phenol-formaldehyde resin and high molecular weight poly(oxyethylene) and iii) alkali-activated montmorillonite clay and a high molecular weight polyacrylamide.

With the cationic/anionic polymer system high amounts of cationic polymer had to be added in order to neutralize the dissolved anionic material in the water. This made the system considerably less cost effective than the two other systems, which both performed well at reasonable addition levels.

CONCLUSIONS

In the process of flotation deinking the demands on colloidal stability are somewhat contradictory. During the first part of the process a high colloidal stability is necessary for the detachment of the ink and its dispersion into particles of suitable size. A certain stability is also needed throughout the process to prevent the detached ink particles from redepositing onto the fibres. The stability must however be lowered before the pulp reaches the flotation cells in order to facilitate attachment of the ink particles to the air bubbles.

The washing process appears to be simpler from the colloid chemistry point of view. Here a high colloidal stability should be maintained throughout the actual deinking operations to facilitate detachment and dispersion of the ink to small particles and preventing redeposition. However, pollution laws in most countries require that the process water be recirculated. The recirculation then involves a clarification process and here the colloidal stability must be broken to make the suspended material flocculate.

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CHEMICAL CHARACTERIZATION OF KRAFT LIGNIN AND KRAFT LIGNIN PRODUCTS

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ABSTRACT

Lignins isolated from pine kraft black liquor were fractionated and purified by ultrafiltration. The fractions were characterized using gel permeation chromatography and ^{13}C-NMR spectroscopy in combination with chemical methods including GC-MS analysis of the mixture of aromatic carboxylic acids obtained by permanganate oxidation of methylated lignins and lignin products. Gel permeation chromatography of the unfractionated kraft lignin revealed that approximately 50% was less than 5,000 $\overline{M}_w$ and about 30% was less than 1,200 $\overline{M}_w$. The ether-soluble fraction possesses an average molecular weight of 600. Methoxyl content (%) of kraft lignin fractions was found to decrease with decreasing molecular weight. Phenolic hydroxyl content was found to increase while aliphatic hydroxyl groups decreased with decreasing kraft lignin molecular weight.

The ionization $\Delta\varepsilon$ absorption curves of kraft lignin and kraft lignin fractions indicate vast differences in the types and quantities of chromophoric structures between fractions. Results indicate that the relative amount of p,o'-stilbene structures and phenolic hydroxyl content increases with decreasing molecular weight.

Signal assignments in the ^{13}C-NMR spectra were made on the basis of substituent shifts observed in model compounds. Kraft lignin fractions were found by ^{13}-C-NMR to contain xylan fragments apparently covalently bonded to the lignin. Unsaturated vinyl structures were found to be present in all lignin fractions; however, based on some key ^{13}C signals, it is believed that the majority of p,o'-stilbene structures are present in the low molecular weight fractions.

Gas chromatography-mass spectroscopy (GC-MS) analysis of the mixture of aromatic carboxylic acids (methyl esters) formed following permanganate oxidation of kraft lignin fractions showed significant differences in the yields of the major oxidation products between high and low molecular weight fractions which may indicate a nonrandom lignin formation in woody plants.

The chemical characterization was extended to kraft lignin preparations obtained by hydroxymethylation, sulfomethylation and oxidative sulfonation. A number of hydroxymethylated, sulfomethylated and oxidatively sulfonated lignin model compounds were synthesized to study the chemical shifts in ^{13}-C-NMR as related to the lignin preparations.

The use of ^{13}C-enriched formaldehyde in hydroxymethylated and sulfomethylated kraft lignin preparations assisted in monitoring structural changes in various sites of the lignin polymer by clearly defined shifts due to signal enhancement in the ^{13}C-NMR spectra. Alkaline-formaldehyde treatment for hydroxymethylation of unetherified guaiacyl moities in kraft lignin was found to be most effective at 55°C introducing approximately 0.42 $-CH_2OH$ per OCH_3. ^{13}C-NMR spectroscopy showed that hydroxymethylation occurred mostly at C-5 in unetherified guaiacyl moieties with little or no modification of alkyl side chains. GC-MS analysis of permanganate oxidation products indicates an eightfold increase in isohemipinic acid, originating from C-5 hydroxymethylated unetherified guaiacyl moieties, with a corresponding decrease in veratic acid.

Alkaline-formaldehyde treatment at high temperature (150°C) did not result in a significant degree of hydroxymethylation of either unetherified guaiacyl moieties or alkyl side chains as evidenced by ^{13}C-NMR and hydroxyl group analysis.

^{13}C-NMR spectroscopy revealed that the lignin product did, however, contain many structures characteristic of alkaline condensation reactions.

Sulfomethylation of softwood kraft lignins using a two-step procedure, hydroxymethylation at 55°C followed by sulfonation at 150°C, was found to be much more selective resulting in higher product yields than the conventional one-step sulfomethylation procedure. ^{13}C-NMR analysis of ^{13}C formaldehyde-enriched two-step sulfomethylated lignin revealed almost quantitative (92%) sulfonation of hydroxymethyl groups attached to C-5 of unetherified guaiacyl moieties.

^{13}C-NMR analysis of lignins subjected to one-step sulfomethylation showed major modification to alkyl side chains presumably due to Tollens and Prins reactions at the high temperature in addition to formation of aromatic and aliphatic carboxylic acids. The origin and mechanism of formation of the carboxyl structures is not known.

Oxidative sulfonation of softwood (pine) kraft lignins resulted in complete solubilization of kraft lignin in water at both alkaline and acidic pH. The degree of sulfonation was shown to increase with decreasing molecular weight. Approximately 0.07-0.10 equivalents of sulfonic acid groups and 0.9-1.4 equivalents of oxygen per C-9 unit were introduced. The increase in oxygen content reflects the introduction of oxygen-containing groups such as carboxylic acids as a result of autoxidation. Gel permeation chromatography of oxidatively sulfonated lignins reveals a marginal increase in overall molecular weight apparently due to competition between oxidative degradation (fragmentation), oxidative coupling and condensation reactions.

The ^{13}C-NMR spectra of kraft lignin revealed major structural changes due to introduction of sulfonic acid groups predominantly at C-5 position of unetherified guaiacyl moieties and formation of aliphatic carboxylic acid groups. Results from model compound experiments and GC-MS analysis of permanganate oxidation products support the involvement of radical processes in both sulfonation and oxidation, with sulfite radicals in some cases being the sulfonating species.

THE FRENCH EXPLODED WOOD PROJECT

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Extended Abstract

Steam explosion was first introduced more than 50 years ago by MASON. Using steam at about 280°C, the MASON Process explosively defibrated wood waste to give a brown hydrolyzed pulp suited to the manufacture of particule board. In recent years, the intrinsic simplicity of the process has attracted the attention of a number of workers to examine means of employing the same principle for many other applications.

The possibility of producing dissolving pulp from wood by this method was investigated. The purpose was to find the proper conditions which would lead to a pure cellulosic residue of acceptable quality and at the same time to a high value lignin by-product.

Five laboratories were involved in this project in order to define the effect of the processing parameters (mainly chip quality, temperature and time) on the hydrolysis of hemicellulose, cellulose and lignin. A 50l capacity steam explosion reactor was built at CTP. The process was quite similar to the IOTECH explosion process. The maximum operating pressure was 60 bars. Aspen chips were supplied by a mechanical pulp mill located close to Grenoble. Analysis of the effect of the parameters was performed using a seond order, central composite design. The quadratic response surfaces were calculated. Exploded wood samples were extracted with distilled water at room temperature for analysis of hemicellulose, sugar and low molecular weight phenols. Lignin was extracted by a dioxane-water (82:18 , V:V) mixture from the water-extracted product and analyzed for functionality and molecular weight. The quality of the cellulosic residue was assessed by its degree of polymerization and lignin content.

Heat transfer appared to be a limiting factor when using industrial wood chips (3.5mm mean thickness). Reducing chip thickness or mechanically dividing the chips significantly increased the extent of hydrolysis.

Steam pressure (or temperature) were varied from 20 bars to 50 bars and time from 10 sec to 240 sec. Both parameters equally affected the severity of the treatment so that the same result could have been obtained either at low pressure and long time or the contrary.

Quality of the cellulosic residue and the structure of the various products varied continuously with the severity of the treatment.

pH of the water extract decreased from 6 to 3.5 when the severity of the treatment increased. The liberation of acetic and p.hydroxybenzoic acid was found to be responsible for the pH decrease. Depolymerization of hemicellulose was correlated with the treatment conditions by GPC analysis of the water extract.

Depolymerization of cellulose and lignin took place simultaneously so that it was not possible to get a cellulosic residue of DP higher than 200 containing less than 10% lignin. As an example, when the steam explosion was processed at 40 bars for 120sec, the DP of the cellulosic residue was 150 and its lignin content was 8 %. A DP around 600 was obtained after hydrolysis at 30 bars for 90 sec. Then, the lignin content was 13 %. Elimination of hemicellulose occured almost completely in both cases. Other organic solvents and caustic soda were tested in order to replace dioxane-water for lignin extraction without success.

Characterization of the lignin fraction by ^{13}C NMR revealed that the cleavage of βO4 ether linkages was closely related to the yield of extractable lignin and to the treatment severity. A continuous decrease from an estimated value of 0.6 per C_9 unit in MWL to 0.1 after steam hydrolysis at 45 bars for 180sec was observed. Simultaneously, the OH phenolic groups increased from 0.2 (per C_9 unit) to a maximum of 0.7 after steam hydrolysis at 35 bars for 150 sec) and then decreased, indicating that for the most severe conditions either condensation occured or that small lignin fragments of high OH phenolic content were lost to a great extent with the water extract. Reduction of the number of aliphatic OH groups was also observed. Stilbene structures and carbonyl groups were detected. Demethylation did not appear to be extensive (from 1.4 per C_9 unit in MWL to a miminum of 1.1) giving

rise to the formation of some catechol groups. The number average molecular weight of the lignin fraction varied from 1000 to 2000 g/mole without any direct correlation with the process conditions. The yield of aldehydes liberated upon alkaline oxydation was minimal for the most drastic conditions indicating a probable condensation of phenolic rings.

Modified (sulfonated and oxidized) steam explosion lignins, recovered after processing at 40 bars for 80 sec, were tested as dispersants and sequestrants. The results did not appear to be very promising. Other applications should be contemplated.

Chemically modifying the lignin prior to or during steam hydrolysis seems to be the only chance of getting a pure cellulosic residue with acceptable DP.

THE INFLUENCE OF NaOH AND Na_2SO_3 ON THE QUALITY OF CHEMITHERMOMECHANICAL PULPS OF HARDWOODS

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ABSTRACT

Chemithermomechanical pulping of 4 hardwoods (white birch, grey birch, aspen and red maple) was carried out using NaOH and Na_2SO_3 in the treatment of chips prior to pressurized refining. The results indicated that the NaOH had significant effect upon the pulp quality, whereas the Na_2SO_3 was of limited importance .

KEYWORDS: Pretreatment, Refining, Betula, Populus, Acer.

INTRODUCTION

This paper deals with the pretreatment of hardwood chips with NaOH and Na_2SO_3 in the production of chemithermomechanical pulps (CTMP). Pulping trials were carried out with a Sunds Defibrator 300CD refiner. The chemical pretreatment of chips was performed by means of the PREX impregnator which is integrated in the digester.

The following is an account of our experiences in producing CTMP from 4 hardwoods: white birch, grey birch, aspen and red maple.

RESULTS AND DISCUSSION

EFFECT OF NaOH

The NaOH had remarkable influence on all pulp properties studied. In fact the strength characteristics of the pulps were improved with an increase in the level of NaOH addition. Meanwhile the bulk of the handsheets and the brightness of the pulps decreased as the usage of NaOH augmented.

It was observed that the pulps made from the chips pretreated with 5% NaOH gave excellent properties. Further increases in NaOH above this level did not seem to be economically justified and at higher levels of NaOH treatment the improvement in pulp quality was marginal (Figs. 1, 2 and Tables 1-3).

EFFECT OF Na_2SO_3

Concerning the influence of Na_2SO_3, little improvement in the pulp properties was noted, except for the brightness which increased with an increase in the level of Na_2SO_3 when the usage of NaOH was also relatively high, 5% or more. It was, hence, necessary to add Na_2SO_3 to the liquor to maintain a certain level of brightness.

It was also noted that the specific energy consumption was generally decreased as the application of chemicals increased (Fig. 3, Table 1). This could imply that the softening of lignin by the action of Na_2SO_3 accompanied by the swelling of fiber walls caused by NaOH, facilitated fiber separation during refining. The chemical energy was traded for thermal energy with a concomittant improvement in the properties of the pulps.

CONCLUSION

It is concluded that the usage of NaOH is essential in making good quality chemithermomechanical pulps from hardwoods. The Na_2SO_3 helped maintain the brightness of the pulps and reduce the refining energy.

Table . TMP and CTMP produced from grey birch

NaOH, %	0	5	0	5
Na_2SO_3, %	0	0	5	5
Spec. energy MJ/kg	7.24	5.04	6.0	4.96
C.S.F., mL	310	131	424	138
Brightness, %	50	42	61	49
Tear index $mN.m^2/g$	1.80	7.09	1.81	7.76
B. length, km	1.07	3.72	0.92	4.22

Table 2. CRMP produced from red maple

NaOH, %	3	5	5	5	5
Na_2SO_3, %	0	0	3	5	6
C.S.F., ml	163	248	190	179	206
Brightness, %	37	34	34	41	43
Tear index $mN.m^2/g$	2.31	2.45	2.78	3.33	2.86
B. length, km	1.70	1.96	3.34	3.25	2.99

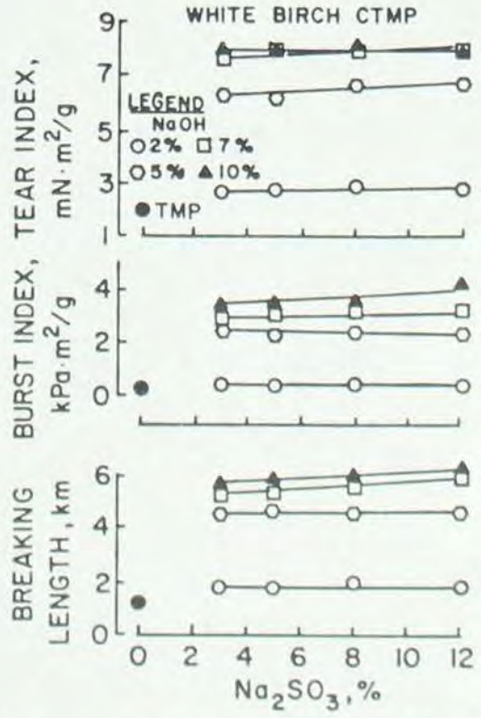

Fig. 1. Effect of NaOH and Na_2SO_3 on the strength properties of white birch CTMP.

Table 3. RED MAPLE CTMP PRODUCED FROM FRESH CHIPS

NaOH, %	5	5	5	5	5	5	8	8	8	8	8	8
Na_2SO_3, %	0	0	5	5	8	8	0	0	5	5	8	8
SPECIFIC ENERGY, MJ/kg	4.34	5.17	2.48	5.10	2.86	5.41	3.30	5.26	2.79	4.56	3.08	5.13
FREENESS, ml	86	86	228	139	275	138	200	76	229	126	255	100
BULK, cm^3/g	3.06	2.83	3.16	2.91	3.20	3.05	2.94	2.65	2.89	2.62	2.95	2.57
BRIGHTNESS, %	39.3	36.1	44.1	45.6	49.8	48.5	34.3	31.0	38.3	38.5	45.7	43.7
OPACITY, %	98.9	99.1	96.5	96.6	94.5	95.9	98.8	99.3	98.0	97.9	95.5	96.9
BURST INDEX, $kPa \cdot m^2/g$	0.77	0.76	0.40	0.54	0.41	0.53	0.62	0.91	0.60	0.84	0.69	0.96
TEAR INDEX, $mN \cdot m^2/g$	2.79	2.33	2.24	2.27	2.10	2.17	2.24	2.20	2.24	2.18	2.44	2.66
BREAKING LENGTH, km	2.23	2.18	1.72	2.10	1.70	2.06	1.87	2.49	1.90	2.41	1.98	2.53

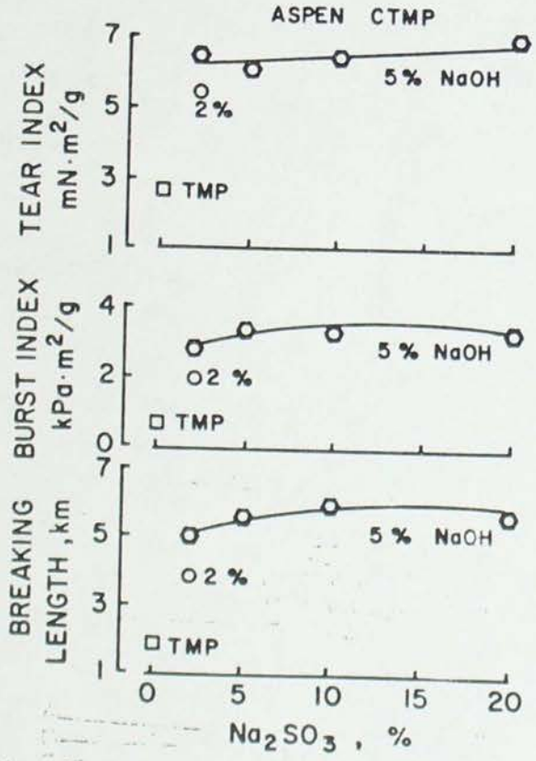

Fig. 2. Effect of NaOH and Na_2SO_3 on the strength properties of aspen CTMP.

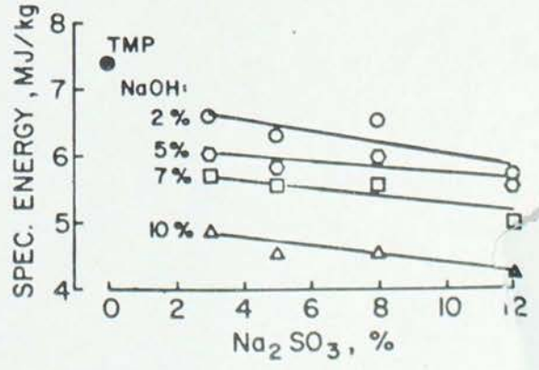

Fig. 3. Effect of NaOH and Na_2SO_3 on the specific refining energy.

STUDY OF LIGNIN STRUCTURE BY SILICON-29 NMR SPECTROSCOPY

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ABSTRACT

Silicon-29 NMR spectra of trimethylsilylated spruce dioxane lignin as well as softwood kraft lignin and its derivatives are reported. The observed resonances are interpreted with the aid of data obtained in model compound experiments. The utility of the method for analysis of lignins and lignin derivatives is discussed.

KEYWORDS: Silicon-29 NMR Spectroscopy, Dioxane Lignin, Kraft Lignin

INTRODUCTION

In some classes of hydroxyl-containing compounds, e.g. saccharides (1), Si-29 NMR spectroscopy of trimethylsilyl derivatives was found to be rather sensitive to structure variations. The aim of this work was to examine whether or not the method can be of use in lignin structural analysis. For this purpose, we measured Si-29 NMR spectra of trimethylsilylated softwood dioxane lignin (see also Ref. 2), kraft lignin and its several derivatives. The assignment of the peaks in the lignin spectra was based on data obtained using more than 30 ligrin model compounds

METHODS AND MATERIALS

The model compounds used represented the phenolic and aliphatic OH groups in native lignin structures (β-O-4, β-5, β-β , β-1, biphenyl 5-5 and end coniferyl alcohol and arylglycerol structures) as well as in modified and degraded lignin strutures (stilbenes, styryl aryl ethers, pyrocatechols, 5- and 6-condensed guaiacyl structures, and hydroxycarbonyl structures). A series of substituted arylcarboxylic and arylalkylcarboxylic acids was also examined.

Trimethylsilylation of model compounds and lignins was carried out with a mixture of bis-(trimethylsilyl)acetamide and chlorotrimethylsilane in a usual manner. Completeness of lignin silylation was confirmed by IR spectra and purity of silylated model compounds was checked by C-13 NMR spectroscopy.

Si-29 NMR spectra were measured in $CDCl_3$ solutions on a Varian XL-200 spectrometer at operating frequency of 39.7 MHz for Si-29 nuclei. INEPT Technique was employed as described in detail elsewhere (3). The FIDs were recorded with proton decoupling, acquisition time was 1 s and delay between the successive pulse trains was 5 s. Typically, 128 scans were accumulated in model compound experiments and 3000--6000 scans were required for lignins. Assignment of Si-29 NMR spectral lines in model compound spectra was facilitated by the SPINEPTR technique (4). The model compound experiments showed good proportionality between the signal intensity and the molar ratio of the corresponding Me_3SiO-groups.

RESULTS

In our set of trimethylsilylated lignin model compounds, the δ values in Si-29 NMR spectra were influenced primarily by electron density at oxygen atom of Me_3SiO-groups and decreased in order $COOSiMe_3$ > aryl-$OSiMe_3$ > alkyl-$OSiMe_3$. Pronounced steric influence was observed only in aryl-$OSiMe_3$ groups derived from guaiacyl moieties substituted in position 5.

The spectrum of trimethylsilylated spruce dioxane lignin (Fig.1.) shows two groups of signals corresponding to aryl-$OSiMe_3$ ($\delta \sim 20$ - - 21) and alkyl-$OSiMe_3$ ($\delta \sim 17$ - 19) groups. The local maxima at δ = 20.4 and 18.7 correspond to the structures of β-O-4 type.

The spectrum of trimethylsilylated softwood kraft lignin (Fig.1.) reflects more complex structure and increased significance of phenolic OH groups in kraft lignin. The resonances in region $\delta \sim$ 23.0 - 24.5 prove the presence of a certain portion of $COOSiMe_3$ groups. The band at $\delta \sim$ 21.8 - 22.6 corresponds to aryl-$OSiMe_3$ groups derived from vanilloyl moieties. The dominating band of resonances produced by aryl-$OSiMe_3$ groups shows local maxima at δ = 21.0 and 20.3 corresponding to guaiacyl nuclei in stilbene and/or styryl aryl ether structures and to guaiacyl nuclei with α-deoxy side chain, respectively. The resonances in the region $\delta \sim$ 19 - 20 can be ascribed to aryl-$OSiMe_3$ groups sterically shielded by substitution in ortho-position like in 5-condensed guaiacyl structures. The peak at δ = 18.6 shows that β-O-4 structures are much less important than in dioxane lignin. The weaker bands at $\delta \sim$ 16.5 - 18.0 revealed the presence of a variety of primary and seconda-

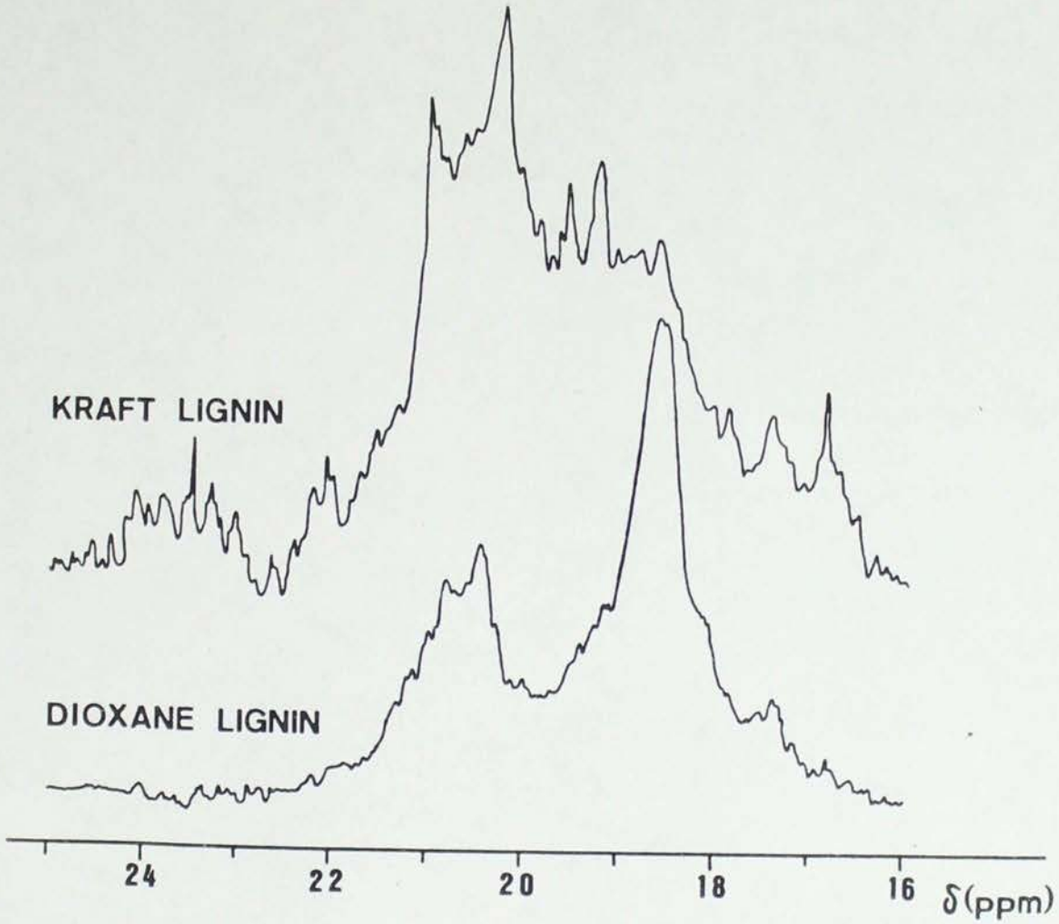

Figure 1. Silicon-29 NMR spectra of trimethylsilylated softwood lignins

ry alkanol groups different from those in native lignin structures.

Kraft lignin was then modified by $NaBH_4$--reduction, catalytic hydrogenation, dimethyl sulfate methylation, MeOH-HCl methylation, and carboxymethylation; Si-29 NMR spectra of the resulting lignin derivatives after trimethylsilylation are also presented and interpreted.

CONCLUSIONS

Reproducible Si-29 NMR spectra of trimethylsilylated lignins and lignin derivatives can be obtained using modern measuring procedures at reasonable demands on measuring time and sample amount ($\sim$ 100 mg). Spectra afford, at least, semiquantitative information on distribution of OH and COOH groups and reflect also the structure of arylalkyl units in lignin macromolecule.

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Delignification using hydrogen peroxide and oxygen under acidic conditions - the PO_s-treatment

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ABSTRACT
At a pH-level below 4, hydrogen peroxide reacts as an electrophilic agent and cleaves the lignin molecule. In the presence of oxygen, the reaction becomes very efficient. At pH 2 with hydrogen peroxide and oxygen, the kappa numbers of sulfite pulps are reduced to 50 % of their initial levels.

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The best and most efficient chlorine-free delignification process for sulfite pulps is a hydrogen peroxide-supported oxygen delignification in the presence of sodium hydroxide (1). Nevertheless, this method will not be in the focus of this presentation. the most recent development in pulp bleaching is the delignification with hydrogen peroxid in the presence of oxygen under acidic conditions. We use the initials PO_s for peroxide, oxygen and sour, or acidic, conditions. The procedure was developed in 1984 on a laboratory scale by Degussa AG und PWA Waldhof. Pilot plant trials started at Waldhof in February this year. After an initial phase with one ton of pulp per hour, temporarily the full capacity of the older production line with 100 tons of spruce per day was delignified.

The aim of this paper is to describe the

- development of the procedure,
- the reaction parameters,
- the mechanism of delignification,
- the process's advantages and drawbacks,
- results of the pilot plant trials.

1) Development of H_2O_2/O_2-delignification under acidic conditions

At constant temperature and oxygen pressure, the rate of delignification plotted against the pH-value shows a steep decrease leaving strong alkaline conditions and coming close to neutrality.

While delignification rates of more than 50 % are obtainable under strong alkaline conditions, only poor effects can be achieved at lower pH- values.

With MgO, a pH of only 9 to 9.5 is obtained. Consequently, under mild conditions only poor results are the result of oxygen treatment in the presence of magnesium oxide.

With neutral or acidic conditions a delignification with oxygen is nearly impossible. There is only a poor effect under very acidic conditions. Mostly, it is the result of a washing procedure during the treatment, and of acidic hydrolysis.

Hydrogen peroxide behaves a bit differently. Similar to oxygen, there is a steep decrease of the delignification rate if the pH-value drops from alkaline to neutral conditions. At lower pH-values, the delignification rate rises again. The lower the pH-value, the higher is the decrease of lignin content in pulps. The first figure illustrates the effect of pH-value on delignification for oxygen and hydrogen peroxide.

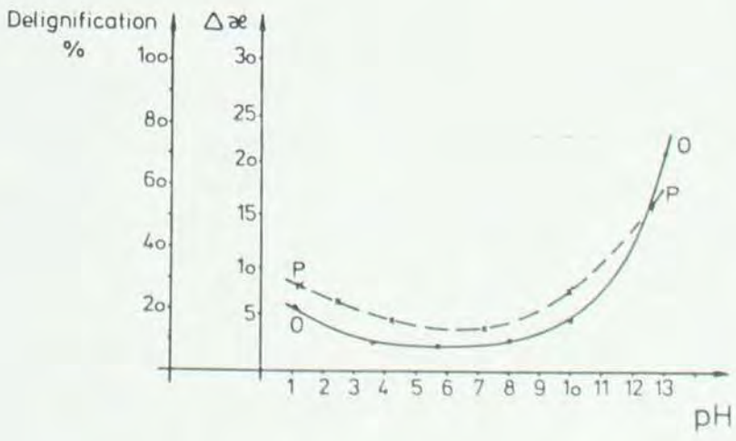

Figure 1. Delignification of sulfite pulp with oxygen or hydrogen peroxide as a function of the pH-value. (20 % cons. 95° C, 1 h, 1 % H_2O_2, 0.3 MPa O_2)

This effect was reported in literature (2) several years ago. The mechanism of delignification is an electrophilic attack of the hydroxonium ion on the aromatic nuclei. Some patents (3) claim special effects for hydrogen peroxide delignification under acidic conditions. For example, a specific effect of heavy metal ions on the delignification process is claimed. Another patent describes the application of chelating agents to reduce viscosity losses, and claims no effect of heavy metals on the delignification process.

In all of these application cases, hydrogen peroxide reacts with significantly lower delignification intensity compared with strong alkaline conditions.

If the application of hydrogen peroxide and oxygen is combined, the curve for the delignification rate in the alkaline area is very close to those for oxygen and hydrogen peroxide as single compounds. Acidic conditions result in a significant increase of the delignification rate. Figure 2 illustrates this effect.

In fact, at low pH-values delignification with H_2O_2/O_2 is nearly as efficient as in the presence of alkali. A 50 % decrease of lignin content is achieved, as figure 2 shows.

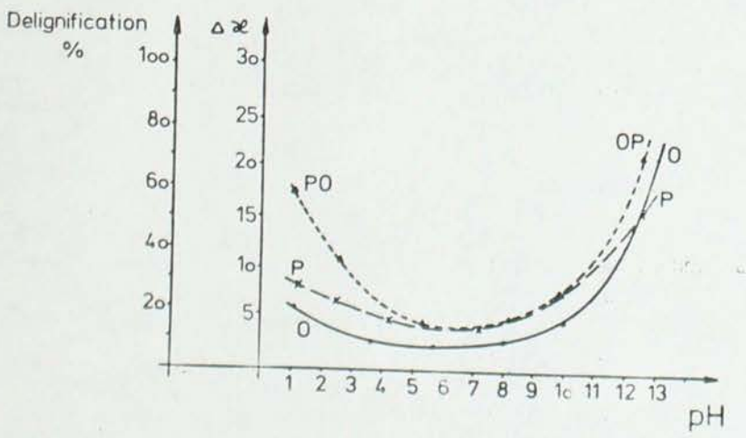

Figure 2. Comparison of the delignification rates achieved with hydrogen peroxide, oxygen and the combination of both as a function of pH-value.

2) Reaction parameters for acidic H_2O_2/O_2-delignification.

Our laboratory-scale trials were made with consistencies between 9 % and 25 %. There is very little change in delignification if the consistency is increased. Very significant, however, is the effect of pH on delignification. To obtain a steep decrease in lignin content, it should be lower than 4.

The oxygen pressure is of less importance. The presence of oxygen is obviously necessary to get a better effect than with hydrogen peroxide alone. There is a synergistic effect if both chemicals are combined. As figure 3 illustrates, in the presence of nitrogen, the delignification rate worsens.

Without pressure, but in the presence of air, results are slightly better than with nitrogen. On the other hand, increasing the oxygen pressure from 0. 2 MPa to 0.7 MPa does not improve results.

The synergistic effect becomes obvious if the pulp is reacted with hydrogen peroxide first, and oxygen is added only after nearly total consumption of the peroxide. The resulting delignification rate is poor compared with the combined addition of both chemicals.

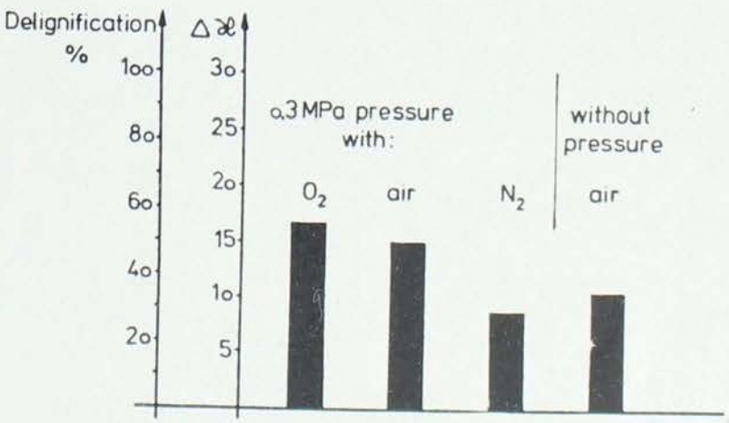

Figure 3. Effect of the addition of oxygen or air to acidic peroxide delignification.

In the presence of oxygen, a relatively small amount of hydrogen peroxide already causes a significant effect on lignin content. This is illustrated in figure 4.

The reaction requires an elevated temperature in order to take place correctly. For example, at 50 °C the peroxide concentration is nearly unchanged after one hour, as is the lignin content. If the reaction time is prolonged, the amount of residual peroxide decreases slowly due to decomposition, but delignification remains poor. If heavy metal ions are added, the peroxide consumption becomes more rapid, but without a change in kappa number of pulp. The addition

of a chelated metal - for example, iron-DTPA-complex - has the same result.

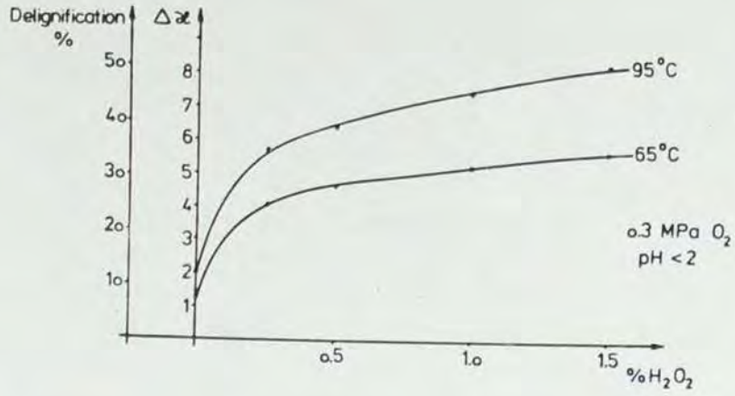

Figure 4. Effect of peroxide concentration in PO_s-delignification.

At 90° C, within one hour of reaction time 1.5 % of the hydrogen peroxide is consumed, and a 50 % reduction of lignin content is the result. On the other hand, the reaction seems to be very rapid if the chemicals and the temperature increase act on the pulp at once. Due to heating up problems on lab scale, we could not reach reaction times below 15 minutes with a fair reproduceability. With the good mixing system of our pilot plant, we achieved main delignification reaction within the first three minutes.

The drastic reaction conditions not only cause delignification. The pulp significantly loses it's viscosity. The steep drop in viscosity surprisingly is not followed by a simultaneous drop in strength. There is a certain loss of breaking length and tearing strength, but by far with lower intensity than the viscosity drop would lead one to expect.

3) The reaction mechanism

The reactions of lignin model compounds with peracetic acid or hydrogen peroxide under acidic conditions are described in the literature (2). According to these results, protonation of the hydrogen peroxide and formation of a hydroxonium ion is the first reaction step.

$$H_2O_2 + H^+ \rightleftharpoons HO^+ + H_2O$$

The hydroxonium ion is a strong electrophilic agent. It attacks the lignin's aromatic nuclei. Ring hydroxylation, oxidative demethylation, displacement of side chains and oxidative ring opening are the main reaction types. Radical reactions are rather unlikely as a main reaction path. The homolytic cleavage of hydrogen peroxide should take place under neutral conditions as well as under acidic ones. As we know from the reaction parameters mentioned earlier, under neutral conditions no delignification occurs.

To prove the similarity of the peracetic acid and the peroxide reactions, we performed trials with both compounds in the absence and presence of oxygen. A delignification with peracetic acid is also intensified if oxygen is present. Calculated on oxidation equivalents, the peracetic acid/oxygen aggregate gives the same result as the peroxide/oxygen combination. Peracetic acid/oxygen delignification takes place at a lower temperature level. Obviously it needs less activation energy. The formation of the hydroxonium ion from protonated peracetic acid takes place more easily.

Reaction products with lignin are the same.

$$CH_3\text{-}COOOH + H^+ \rightleftharpoons CH_3COOH + {}^+OH$$

The formation of polyhydroxylated aromatic ring systems is the first lignin degradation step. The second step is the oxidation of these compounds to quinoid systems. Both chemicals, hydrogen peroxide and oxygen, may react here. Thus, the hydrogen peroxide which makes the important initial reaction step, is not consumed totally in secondary reactions. At least some of these take place with oxygen.
If the degree of substitution with electron-rich substituents of an aromatic system rises, the resonance stabilization decreases. An oxydation reaction becomes easier. Therefore, the polyhydroxylated products of the first reaction step can be oxidized with oxygen, which cannot react with the original lignin.

Some hydroquinones react easily with oxygen under formation of quinones and hydrogen peroxide. This reaction is used technically for the production of hydrogen peroxide, using anthrahydroquinone derivatives. The first lignin degradation step consumes hydrogen peroxide, but some of the subsequent steps may produce peroxide once again. Figure 5 illustrates some of the possible reactions. The possibility for the formation of additional peroxide - which may

react again with the lignin - explains the efficiency of the combination of peroxide and oxygen. Furthermore, it explains the fact that even small amounts of peroxide and oxygen cause significant delignification.

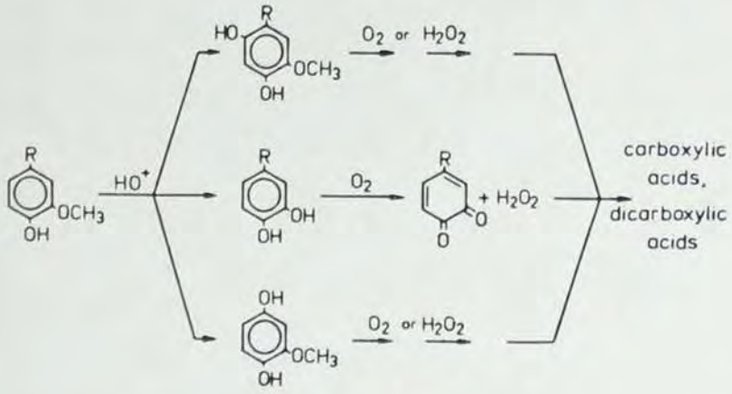

Figure 5. Reactions of lignin with peroxide and oxygen under acidic conditions.

4) Advantages and drawbacks of the process.

There are several regulations governing pollution levels of effluents in Germany. The amount of COD should not exceed 200 kg O_2 per ton of pulp. For each 50 kg of COD a penalty has to be paid to the authorities which now amounts to aproximately U.S. $ 15. For a pulp mill producing 100,000 tons of pulp per year, this means an amount of up to U.S. $ 3,000,000 if the COD level is not decreased. Thus, a delignification process which offers a chance for easy reduction of the COD level - for example, by evaporation and burning of the effluent - is very interesting for the mills.

The acidic peroxide/oxygen process here offers a possibility. The effluent of the PO_s-stage could be evaporated and burnt together with any cooking liquor. Because no kations are present in the PO_s-process, it can be applied to all sulfite pulping types; to the magnesium-based as well as to the calcium-based processes. In the case of counter-current washing, the amount of washing water should not be higher compared with the standard process recovery system. If sulfuric acid is used for acidification, corrosion should be no problem. Small amounts of sulfuric acid are present in every sulfite liquor. Therefore, the bleaching sequence should be started with the PO_s-stage.

The PO_s-reaction causes some degradation of the cellulose, as mentioned earlier. There is a significant viscosity drop, but the breaking length is only slighty decreased. It seems as if the alkaline conditions for the viscosity determination promote degradation of the cellulose. Experiments on a laboratory scale with reductive borohydride treatment after the PO_s-stage yielded better viscosity values. The oxidation of hydroxy groups of the cellulose chain to carbonyl groups in the PO_s-stage is very likely. These carbonyl groups are attacked under alkaline conditions by hydroxy anions and cleavage of the cellulose chain is the result.

Alkali resistance of PO_s-bleached pulps is lower, and the amount of COD in the effluent of a bleaching sequence with an E-stage after intensive PO_s-treatment is higher, compared with standard treatment. Generally, after an intensive PO_s-stage no strong caustic treatment of the pulp can be recommended. This is a significant drawback for the application of PO_s-delignification.

The above-mentioned penalties for COD in the effluent are not the only ones for which manufacturers have to pay in Germany. Heavy metals like cadmium and mercury in the effluent are punishable as well. Another possible hazard to the environment are chlorinated compounds. The authorities plan strict limits on halogenated compounds in effluents, and penalties will be charged on these within the next year.
The amount of chlorinated compounds is determined by an adsorptive method. Nearly all chlorinated watersoluble lignin derivatives are detected with this procedure. Volatile products such as chloroform are detected with a lower efficiency. The limit for the amount of TOX in the effluent will be 2 kg per ton of pulp. For 1 kg of TOX, penalties will be the equivalent of U.S. $ 15, even if the limits are met.

To illustrate this economic threat to pulp mills, it must be mentioned that a standard bleaching sequence like C-E-H-H or C-E-H-D produces up to 7 kg of TOX per ton of pulp. The level depends on kappa number and, naturally, mainly on the amount of chlorine applied.

Therefore, a strong tendency exists in Germany to reduce the kappa number to the lowest possible level. Then also the amounts of COD and TOX are lower. In practice, the kappa numbers currently

range from 12 to 17. Only speciality pulps may have kappa numbers higher than 20. For standard pulps, COD is 60 to 80 kg per ton, and TOX 4 to 5 kg per ton of pulp.

The highest amount of TOX is produced in the chlorination stage. Therefore, the elimination of chlorination gives the best reduction of the TOX-values. Hypochlorite produces less chlorinated compounds compared to chlorine. Even lower levels are achieved if chlorine dioxide is applied. As chlorine dioxide is a very expensive bleaching chemical, the alternative bleaching sequences for the industrial application, so far, try to use as much hypochlorite as possible.

Under the aspect of reducing both levels - the COD's and the TOX's - a three-stage bleaching sequence has produced good results: the PO_s-H-H sequence.

In the PO_s-stage, the kappa number is reduced from 16 to 8. With two carefully buffered hypochlorite stages, a final brightness of 88 is achieved. In the hypochlorite stage, significantly less chlorinated compounds are produced in comparison to the chlorination stage. Therefore, even high amounts of hypochlorite produce less pollution than chlorination. The demand for active chlorine is cut in half by the PO_s-stage. Instead of 6.4 % active chlorine in the C-E-H-H-sequence, 3.2 % active chlorine is distributed in two hypochlorite stages. Figure 6 illustrates the differences between the old C-E-H-H-sequence and the new alternative, in terms of COD and TOX.

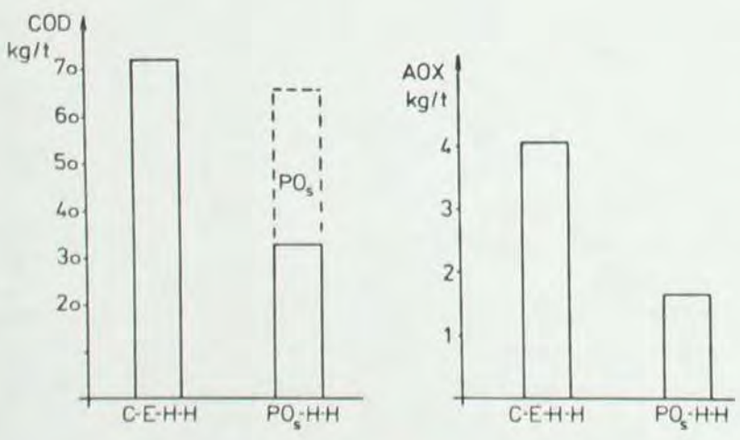

Figure 6. Amounts of COD and TOX produced with different bleaching sequences.

The TOX values are reduced to a level significantly below the limit of 2 kg per ton. The COD is also lower, because some of the hemicelluloses which are extracted normally in the E-stage remain in the pulp. If the effluent of the PO_s-stage is recycled with the waste cooking liquor, residual COD of the two hypochlorite stages is approximately 30 kg per ton of pulp.

For these reasons the PO_s-H-H-sequence was tested in pilot plant trials beginning in February 1985.

Other bleaching sequences with the PO_s-delignification stage were conducted on a laboratory scale. As mentioned above, use of the full delignification power of the PO_s-stage requires a special bleaching sequence. However, there are other application possibilities if the PO_s- stage is used as an activation step only.

The EOP-stage is very efficient in delignification. The kappa numbers of sulfite pulps can easily be reduced to about 50 % - 40 % of their initial levels. Therefore, the EOP-stage is an interesting alternative to reduce the amount of chlorine needed in a bleaching sequence. A sequence like EOP-C-(E)-H-D can cut the chlorine demand by more than half, compared with the standard C-E-H-D-stages. The TOX-level is decreased simultaneously.

For an additional reduction of chlorine demand, chlorine dioxide normally would be required. The new PO_s-stage can do the same job. With a very small amount of hydrogen peroxide and oxygen, the PO_s-stage can be used as an activating tool. Electrophilic attack under acidic conditions prepares the residual lignin for subsequent nucleophilic cleavage reactions in the presence of caustic soda. In practice, this means the combination of alkaline stages with peroxide and oxygen and acidic peroxide/oxygen delignification.

An EOP-PO_s-P-sequence produced a pulp with 85 brightness (Elrepho) in our laboratory. This was without any chlorine applied. So the TOX-level then is zero. Likewise, the kappa number is reduced to a very low level.

Figure 7 gives the data for the amounts of chemicals applied and the reduction of kappa number in the stages. With alkaline stages only, the brightness increase would be limited to about 80 % remission. The PO_s-stage is a very rapid one. Five minutes are absolutely sufficient for the reaction. If the temperature and the amount of peroxide remain low, the strength losses are insignificant.

Stage	Chemicals %	Kappa æ	Brightness R_{457}
unbleached		14.0	54.7
EOP	0.5% H_2O_2, 0.5% O_2, 15% NaOH	6.5	
PO_s	0.15% H_2O_2, 0.5% O_2, 0.7% H_2SO_4	5.1	
P	1.5% H_2O_2, 1% NaOH, 3% Silic.	3.4	84.9
D	0.4% ClO_2	<1	89.3

Figure 7. Bleaching of sulfite pulp with the sequence EOP-PO_s-P.

	Kappa æ	Viscosity dm^3/kg	Breaking length km (600 CSF)
unbleached	32	1330	9.2
Oxygen bl	19	1240	8.7
PO_s-Oxygen bl.	12	1170	8.3

Conditons in O : 1.5 % NaOH, 0.3 MPa O_2, 12% conc., 100 °C, 1.5 h
" " PO_s: 0.75 % H_2O_2, 2% H_2SO_4, 0.3 MPa O_2, 12% conc., 95 °C, 0.5 h

Figure 8. Treatment of kraft pulp with a PO_s-stage prior to oxygen delignification.

As mentioned in a previous paper, an EOP-stage increases the cleanliness of the pulp. Therefore, the EOP-PO_s-P-bleached pulps have the same or a slightly better cleanliness already at a lower brightness level, compared with standard pulps. For an integrated mill, therefore, a lower brightness may suit demands without any problems.

If a higher level of brightness is required, the demand for bleaching chemicals like hypochlorite or chlorine dioxide is low. A final bleaching stage with hypochlorite or chlorine dioxide easily yields a brightness above the 90 % remission level. The amount of TOX produced in such a H- or D-stage normally is less than 200 - 300 g of organically bound chlorine per ton of pulp.

The initial delignification steps EOP-PO_s-EP reduce the demand for active chlorine in the final D-H-stage to a level below 3 % even for magnefite pulps with kappa numbers around 30.

All results so far reported deal with sulfite pulps. The reason for this is simple: there are no kraft pulp mills in Germany. Nevertheless, we also made some promising trials with the PO_s-treatment on kraft pulp. As figure 8 shows, a PO_s-stage can be used as a pretreatment stage prior to an alkaline oxygen-delignification stage. Namely, PO_s-pretreatment increases the overall delignification rate. With the same reaction conditions in the oxygen stage after PO_s-pretreatment, significantly lower kappa numbers are achieved.

Depending on intensity of the PO_s-stage, the strenght of the pulp is somewhat lower than when treated with oxygen alone. The major drawback seems to us the necessity to switch the pH of the pulp from strong alkaline to acidic, and in the oxygen stage to alkaline again.

In principle, the PO_s-pretreatment should be as useful as a nitrogen dioxide - or an ozone-pretreatment for the extended oxygen delignification of kraft pulp.

5) Result of the pilot plant trials.

The pilot plant was designed to show the feasibility of the PO_s-stage in the PO_s-H-H-sequence. If it would fit into the old C-E-H-H-bleach plant installations, only slight changes of the equipment would be necessary. In the bleach plant of the B-line of PWA Waldhof, all stages are run at 10 % consistency in upflow towers with displacement washing systems on top of them. Therefore, the retention times are fixed.

The PO_s-stage should fit within the retention time of either the C-stage or the E-stage. These are 15 and 90 minutes, respectively. The pilot plant's retention tower was a steel tube of approximately 1 m in diameter. Its height was 22 m, which corresponds to the height of the E-tower.

The unbleached pulp was heated with steam and piled in a tower. With a medium-consistency gyro pump the pulp was taken out of the tower. Because of the high capacity of the pump, most of the pulp was recycled back to the

top of the tower, and only a small amount was passed through the oxygen mixer and the upflow tube.

In the oxygen mixer, all the chemicals - oxygen, hydrogen peroxide and sulfuric acid - were added. The pilot reactor tube had a number of sample valves, so the reaction could be followed during the time the pulp needed to flow through the tube.

The initial trials evaluated the effects of temperature and the amount of chemicals used. Here, the results correlated well with the laboratory data. The most important result was the rapidity of the delignification reaction. The main part of the delignification reaction was achieved already after 3 minutes at the first sample valve.

With short reaction times in the PO_s-stage, strength data of the pulps were comparable to those of the standard sequence after the final bleaching stages with hypochlorite.

The reaction is independent from pressure, therefore the height of a towers is of no importance. Important for the delignification is the mixing intensity.
For all pulps tested, the initial kappa numbers of 14 - 20 were reduced to 55 - 52 % of their initial levels.

To achieve an additional decrease of the kappa number, the acidic peroxide/oxygen treatment was combined with an oxygen/peroxide delignification in the presence of magnesium oxide. This two-stage process permited a kappa number reduction of up to 60 % in the pilot plant trials. The resulting PO_s-OP_{MgO}-H-H sequence fits well into the existing bleach plant installation. PWA Waldhof will report about the detailed results in an extra paper.

Conclusions:

Delignification with hydrogen peroxide under acidic conditions is very much improved in the presence of oxygen.

The reaction can be understood as an initial electrophilic attack of the hydroxonium kation and a subsequent oxidation of the hydroxylated lignin by oxygen or hydrogen peroxide.

Acidic peroxide/oxygen delignification further extends the range of chlorine-free bleaching stages.

It can be used as the main delignification step for sulfite pulps. The possibility for evaporation and burning of the PO_s-stage's effluent reduces the COD-level significantly. Because a chlorination stage becomes unnecessary, the TOX-values (organically bound chlorine) are definitely reduce as well.

In combination with alkaline oxygen/peroxide stages, the amount of chlorinated compounds in the effluent can be reduced to a very low level.

It is also useful as a pretreatment stage to decrease the possible kappa level of an oxygen stage in kraft pulp delignification.

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STUDY ON MECHANISMS OF KRAFT AND MAGNESIUM SULFITE DELIGNIFICATION OF BAGASSE WITH SEM-EDXA

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ABSTRACT

The mechanisms of kraft and magnesium sulfite delignification of bagasse were studied. Delignification rates in various morphological regions with SEM-EDXA were also studied. The results showed that it has significant different between kraft and magnesium sulfite delignification processes. 74.9% of total lignin was removed up to 90°C during kraft pulping, and lignin removals in cell cornor (cc), compound middle lamella (CML) and secondary cell wall (S) were taken place rapidly and almost at the same rate. But in magnesium sulfite pulping, only 18.5% of total lignin was removed up to 135°C, and most of which was in S.

KEYWORDS: Mechanism, Delignification.

INTRODUCTION

Bagasse is an important raw material for paper making in South China. In these mills, kraft or soda process is the main process, and only in one mill, the magnesium sulfite process is used. The mechanism of wood kraft pulping had been known in many papers.[1-4] Then the conditions of wood pulping would be correct basically. But the conditions of bagasse pulping, especially the max. cooking temp. and temp.-time curve were not correct. The purpose of this study was to discover the mechanism of kraft and magnesium sulfite pulping of bagasse and to know its main causes with SEM-EDXA[5-6] in order to correct these conditions.

EXPERIMENTAL

Bagasse was depithed about 25% in mill and has the main chemical compositions: Cellulose 48.48%, klason lignin 21.52%, acid-soluble lignin 2.16% and Pentosan 26.02%.

Cooking was carried out in a set of 1-liter pots in glycerol bath. Eighty or seventy grams of bagasse were placed in each one pot. The cooking conditions were listed in Tab. 1.

Pulp yields and klason lignin contents were obtained according to standard methods but without reflux in secondary hydrolysis. Acid-soluble lignin contents were determined by our laberatory's method,[7] in which the absorption determination of acid-soluble lignin of bagasse was run at 202 nm with its absorptivity of 105 l/g•cm. Lignin distribution was established with SEM-EDXA. Bagasse and its pulp were brominated and treated as described by Saka,[6] then examined in a Scanning electron microscope (Hitachi S-550) with an energy dispersive X-ray analyser (EXAC 2000).

RESULTS AND DISCUSSION

The delignification conditions and results during kraft and magnesium sulfite pulping are shown in Tab. 1, Fig. 1 and Fig. 2.

During kraft pulping, the process may be divided into three phases:

1. Bulk delignification phase: This is the period of temp. to 90°C. The total lignin removal is 74.9%. There are almost the same rates of lignin removal in S, CML and cc by SEM-EDXA. This is great different from wood kraft cooking.
2. Complemental delignification phase: This is the period from 90°C. to 140°C. The total lignin removal rises to 92.1%. The delignification rates in CML and cc are higher than that in S. At that time, the raw material has been defibrized completely.
3. Residual lignin removal phase: This is the period from 140°C. to 150°C. or 160°C. The total lignin removal is about 2-3%. Then, it may be seen that the bagasse kraft cooking needs not the time at 140°C. or time to 150°C.

As compared with kraft pulping, magnesium sulfite pulping is quite different. But it is also divided into another three plases:

1. Initial delignification phase: This is the period of temp. to 135°C. The total lignin removal is 18.5%, in which, the lignin removal in S is faster than that in others.
2. Bulk delignification phase: This is the period from 135°C. to 162°C. and 30 min. at 162°C. The total lignin removal rises to 80.2%. The raw material begins to defibrize each other.
3. Residual lignin removal phase: This is the period of 30 min. at 162°C. continuously. The total lignin removal rises to 88.00%. The bagasse had been defibrized completely.

CONCLUSION

1. Kraft cooking of bagasse may be run under 140°C. and the time at max. temp. may be omitted in the batch cooking cycle because of that the delignification rates in CML and cc are as quick as in S.
2. Magnesium sulfite cooking of bagasse must be run at 162°C. for 1hr. because of that the delignification rates in CML and cc are slower than that in S.

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Tab. 1. Conditions and results during kraft and magnesium sulfite delignification of bagasse

No.	Cooking Conditions		yield (%)	acid-soluble lignin content (%)	klason lignin content (%)	total lignin content (%)	Delignification rate of total lignin (%)	Cell Connor		Compound middle lamella		Secondary cell Wall	
	temp. (°C)	time						Br counts	lignin removal (%)	Br counts	lignin removal (%)	Br counts	lignin removal (%)
BA	-	-	100	2.16	21.52	23.68	0	3041	0	2506	0	1537	0
A-1	80	1:00	73.22	0.51	7.33	7.84	66.9						
A-2	90	1:15	68.60	0.39	5.56	5.95	74.9	1137	62.61	828	66.96	448	70.85
A-3	110	1:45	62.30	0.30	4.10	4.40	81.6	772	74.61	551	78.01	389	74.69
A-4	120	2:00	61.42	0.29	3.70	3.99	83.1	540	82.24	330	84.44	303	80.29
A-5	130	2:15	60.25	0.23	2.34	2.57	89.1	300	90.13	255	89.83	231	74.97
A-6	140	2:30	59.03	0.17	1.70	1.87	92.1	134	95.59	117	95.33	202	86.86
A-7	150	2:45	58.39	0.13	1.28	1.41	94.0						
A-8	164	3:06 +0:15	57.80	0.03	1.01	1.04	95.6						
B-1	90	1:20	96.22	2.16	18.54	20.70	12.5	3167	-4.14	2559	-2.11	1432	6.83
B-2	105	1:50	95.61	3.16	17.37	20.53	13.3						
B-3	120	2:20	93.78	4.53	15.43	19.96	15.7	3035	0.02	2507	0.04	1255	18.35
B-4	135	2:50	92.96	6.93	12.35	19.28	18.5	2926	3.78	2372	5.35	1226	20.23
B-5	150	3:20	85.26	10.70	5.06	15.76	33.5	2635	13.35	1771	29.33	1084	29.47
B-6	162	3:44	73.62	5.93	2.61	8.55	63.9	1455	52.15	925	63.09	679	55.82
B-7	162	4:14	66.30	3.06	1.63	4.69	80.2	652	78.56	584	76.70	459	70.14
B-8	162	4:44	60.35	1.97	0.88	2.85	88.0	209	93.13	275	89.03	321	79.12

Note: BA — Bagasse, A — Kraft pulping from 40°C, act. alk. (Na_2O) used 13.58%, sulfidity 12.03%, liq. to bagasse = 6:1; B—Magnesium sulfite pulping from 50°C. FA = 2.5%, CA/FA = 2.33, liq. to bagasse = 7:1

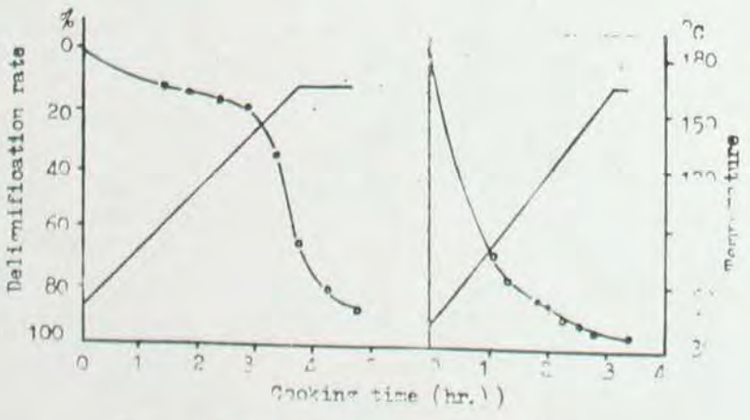

Fig. 1. Delignification rate of total lignin during kraft and magnesium sulfite pulping

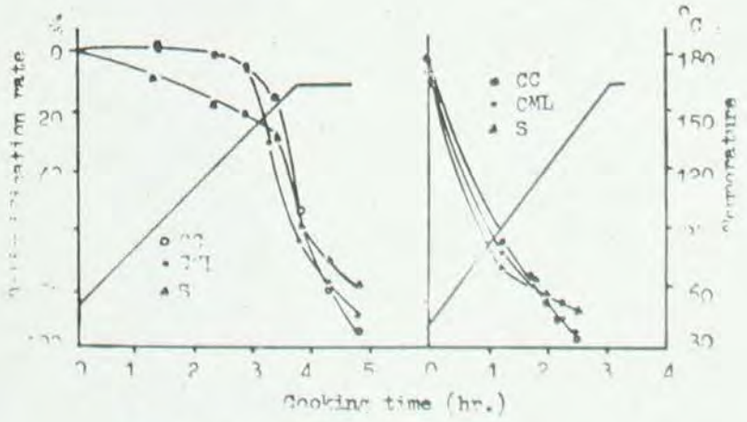

Fig. 2. Delignification rate during magnesium sulfite and kraft pulping

THE MULTIFORM NATURE OF RESIDUAL LIGNIN IN CHEMICAL PULPS

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ABSTRACT

A differentiated model for residual lignin in unbleached chemical pulp is presented. In this model residual lignin has been divided into six hypothetical fragments. The formation of these fragments during kraft cooking as well as their respective significance during bleaching are discussed. Because the amount and chemical properties of various fragments depend on the cooking method, the residual lignin patterns of different types of pulps are different, which means different bleachability, too.

For cooking a pulp of favourable residual lignin pattern, and for bleaching of this pulp without chlorine chemicals, a two-stage method has been developed. It consists of peroxoic acid cooking and one-stage alkaline peroxide bleaching. By this method fully bleached pulps can be made even from softwoods.

KEY WORDS

Delignification, bleaching, residual lignins, organosolv pulping, hydrogen peroxide, formic acid, acetic acid, methane peroxoic acid, ethane peroxoic acid.

INTRODUCTION

Chlorination is usually the first step in conventional multistage bleaching. The purpose of chlorination is to convert the residual lignin of unbleached fibers into water-soluble and alkali-soluble degradation products. Unfortunately, these products cause a number of environmental problems.

However, only part of the residual lignin of pulp really requires chlorination to be converted into soluble products. By modifying or completely changing the cooking process the structure and reactivity of the residual lignin can be made more suitable with respect to bleaching.

In this paper the multiform nature of residual lignins is depicted with the aid of a fragment model (Fig. 1). The fragments in this model differ from each other in the ease with which they can be removed from the pulp.

THE FRAGMENT MODEL OF RESIDUAL LIGNIN

High molar mass crosslinked lignin (Fragment 1 in Fig. 1), lignin chemically bonded to polysaccharides (LC-complexes, Fragment 2) and probably also lignin resorbed onto fibers during cooking (Fragment 3) belong to the category which can be removed only by using bleaching chemicals, in the case of kraft pulp essentially by chlorination.

However, there are also lignin fragments that could, in theory, be removed from the pulp without the use of chlorine. These include the lignin molecules entangled in the microstructure of fiber walls (Fragment 4). The entangled lignin (Goring's lignin) of kraft pulp diffuses extremely slowly from the pulp (1, 2). Soluble lignin, which diffuses faster, is found in macropores and capillaries inside the fibers (Fragment 5) and also between the fibers in the outer liquid of pulp (Fragment 6).

This partly hypothetical model can generally be used to study ways of producing chemical pulps that cause less harm to the environment, for example by trying to render soluble as many of the fragments as possible during the cooking.

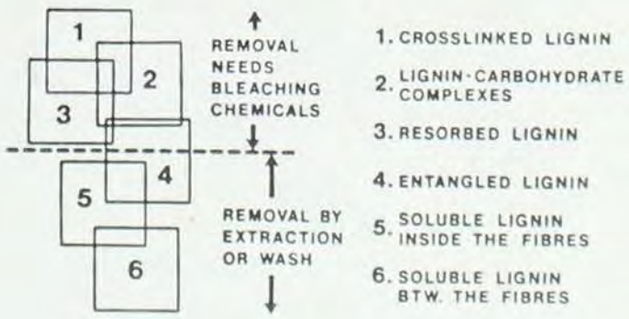

Figure 1. The hypothetical fragment model of residual lignin in unbleached pulp

THE RESIDUAL LIGNIN OF KRAFT PULP

During kraft cooking, some of the lignin in the wood becomes denatured and passive in a way that somewhat resembles the formation of phenol resins. The dark-colored, insoluble and chemically fairly inert substances remain in the fibers. Fragments 1 and 2, i.e. the crosslinked lignin and the lignin chemically bonded to polysaccharides, account for a considerable proportion of the residual lignin.

Flow-through cooking experiments (3) have shown that during kraft cooking dark-colored lignin is resorbed onto the fiber surface (Fragment 3). In experiments at the FPPRI, bleaching of the lignin adsorbed onto the surface of cotton linters during kraft cooking is difficult, even with chlorine, despite the fact that this lignin is present in only very small amounts.

Entangled lignin (Fraction 4) forms an interesting and quantitatively significant part of the residual lignin in unbleached kraft pulp. A correlation has been found between its molar mass and its rate of diffusion (2). Higher molar mass lignin diffuses more slowly. According to our own experiments, the amount of soluble lignin present in the macropores and capillaries inside the fibers and between the fibers in the outer liquid of pulp (Fragments 5 and 6) appears to be rather small, especially if the pulp has been efficiently washed. Measurements made on an industrial kraft pulp (Kappa 35 and consistency 12.3 % in high-consistency storage before bleaching) suggest that residual lignin is distributed among the six fractions as follows: LC-complexes, crosslinked and resorbed lignin (Fragments 1-3) 45-75 %, entangled (Goring's) lignin (Fragment 4) 20-50 % and soluble lignin (Fragments 5 and 6) less than 5 %.

PEROXOIC ACID METHOD FOR PRODUCING BLEACHED PULP

In seeking a chlorine-free pulping method the aim was to find ways of changing the typical fragment distribution of residual lignin described above for kraft pulp in favor of soluble lignin and, if possible, also in favor of low molar mass lignin.

Based partly on observations by Soviet scientists (4-6), a two-stage oxidative delignification method has been developed on the laboratory scale (Fig. 2) (7). The chemicals used in this method contain only carbon, hydrogen, oxygen and sodium, yet the method produces fully-bleached paper-type pulp in good yields from softwood raw material as well as hardwood.

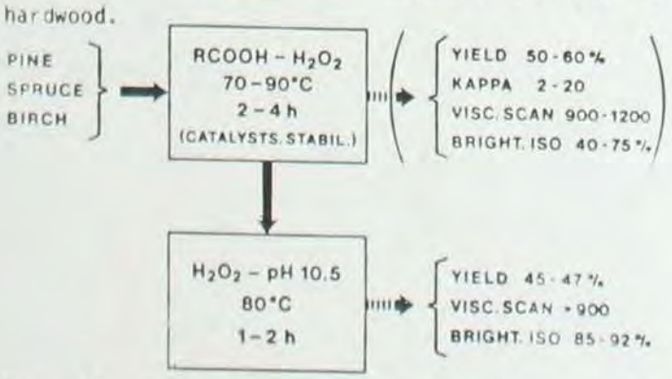

Figure 2. Two-stage oxydative method for preparing fully bleached pulps without chlorine and sulphur

The reaction conditions were chosen so as to maximize lignin cleavage and minimize condensation already from the start of the cook. During the first stage carboxylic acid (formic or acetic acid, conc. between 60 and 80 %) and hydrogen peroxide (20-60 % of the dried chips) produce peroxoic acid, which is a fairly good, selective delignification agent. Depending on the process parameters (70-90 °C, 2-4 h, consistency 15-25 %), the type of wood and the catalysts and stabilizers used, the Kappa number of the pulp is between 2 and 20, the yield after the peroxoic acid stage is 50-60 %, the viscosity is between 1000 and 1300 dm^3/kg (SCAN), and the brightness 50-70 % ISO.

The second stage of this method involves alkaline peroxide bleaching. The dose of hydrogen peroxide is around 0.3-0.6 times the Kappa number in percent, the pH is 10.5, the reaction temperature 80 °C, the time 1-2 hours and the consistency about 10 %. The bleached softwood and hardwood pulps have final brightnesses between 85 and 92 % and viscosities above 900 dm^3/kg.

After the peroxoic acid cook the pulp has far less lignin than after a kraft cook. The rapid cleavage reactions which take place under oxidizing conditions probably prevent condensation and resorption, and also apparently cause the entangled lignin fragment to disappear. This is also suggested by the low molar mass of the lignin found in the cooking liquor (Fig. 3).

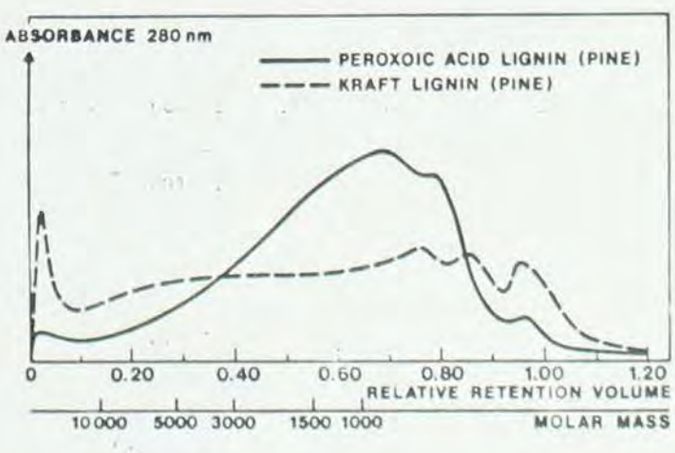

Figure 3. The molecular weight distribution of lignin in peroxoic acid and kraft cooking liquors (8)

The residual lignin from peroxoic acid treatment appears to be much more reactive towards alkaline peroxide than is kraft lignin. This is indicated by the much greater increase in brightness found for peroxoic acid pulp when the two pulps are bleached with equivalent amounts of peroxide in relation to the Kappa number (Fig. 4).

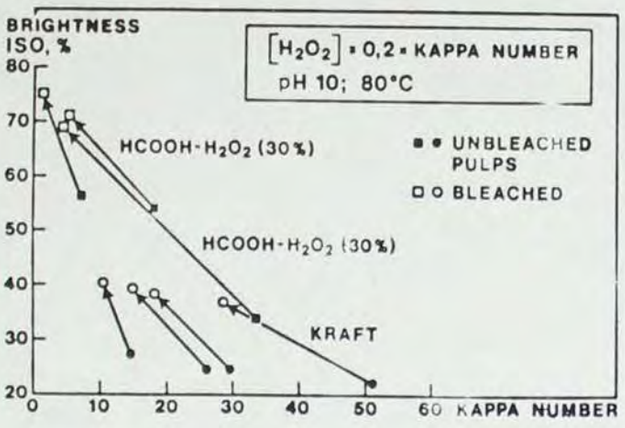

Figure 4. The bleachability of peroxoic acid pulps and kraft pulps with hydrogen peroxide

CONCLUSION

The kraft pulping process and the peroxoic acid-alkaline peroxide delignification method are examples of how the multiform nature of residual lignin can be modified during the actual cooking, and how the residual lignin can be rendered either more passive or more reactive toward the bleaching chemicals.

The two-stage method presented here is probably the only known way of producing fully bleached pine pulp without using either chlorine or sulfur chemicals at any stage. The method works at low temperatures and at atmospheric pressure. Although the process is at present not economically viable in terms of peroxide consumption and although the technology required is only just being developed it is a promising indication that the present industrial pulping methods, which have become almost an institution, can be replaced by new methods that are less detrimental to the environmental.

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ACID-BASE INTERACTIONS BETWEEN CELLULOSE AND ORGANIC MOLECULES

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INTRODUCTION

It is well known that the Lewis acid-base concept and its more modern generalizations give a comprehensive description of a large class of interactions between organic molecules (1). It has been successfully applied to predict solubilities, solvent effects on chemical reactions and many other solvation phenomena. Lately, the acid-base concept has also been introduced in the theory of adhesion (2). Here it has been shown that basic polymers interact strongly with acidic surfaces and vice-versa, giving rise to a high adhesion strength.

METHODS

To study the acid-base properties of a surface, the interactions between the surface and a reference set of acids and bases should be determined. These interactions can conveniently be measured as the extent of adsorption of the reference substances onto the surface. We have in our experiments used a number of small aromatic molecules with known acid-base properties as reference substances. Their sorption by cellulose from hexane solution was measured by immersing dry cellulose in solutions of known concentrations. The extent of sorption was then calculated from the concentrations in the supernatant solutions after 18 h as determined by the UV absorbance. Hexane was chosen as solvent because it is essentially inert from the acid-base point of view and thus gives minimal competition with the sorbate molecules for the sites on the cellulose.

RESULTS

Figure 1 shows the sorption isotherms for the reference substances on a microcrystalline cellulose powder. Obviously one group of substances show very weak sorption or none at all by the cellulose. This group includes anisole, ethyl benzoate and toluene (weak to very weak bases) together with benzonitrile (weakly amphoteric). Pyridine (a moderately strong base) takes an intermediate position whereas benzoic acid and phenol (amphoteric but predominantly acidic) show the highest extent of sorption. Similar results

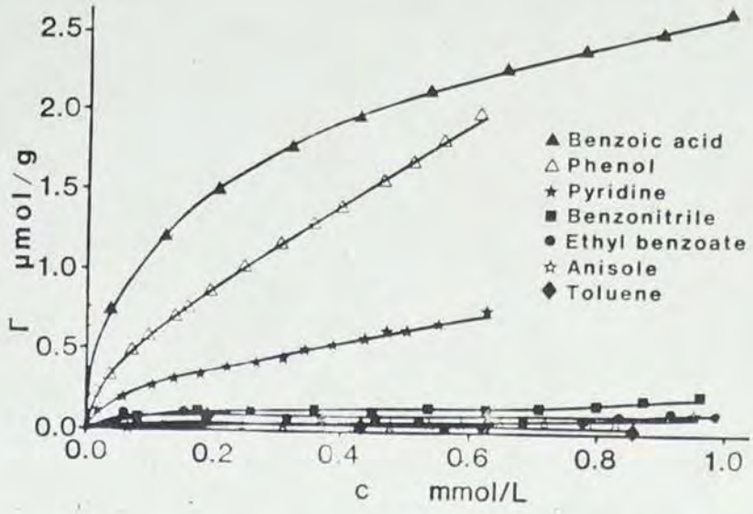

Figure 1. Sorption isotherms for the reference substances on microcrystalline cellulose powder.

were also obtained for a bleached kraft pulp and a sulphite dissolving pulp.

Anisole and ethyl benzoate are analogues of phenol and benzoic acid respectively, where the acidic groups have been blocked by etherification or esterification. This transformation which does not affect the basicity to any greater extent causes a drastic decrease of the sorption. It can thus be concluded that the sorption of phenol and benzoic acid is closely linked to their acidity and consequently occurs on basic sites in the cellulose. Pyridine on the other hand is a pure base and can be expected to sorb at acidic sites.

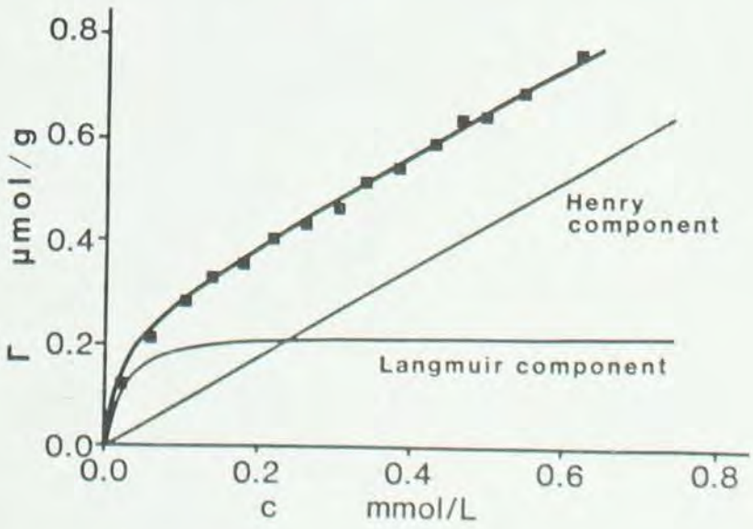

Figure 2. Model isotherm fitted to sorption data for pyridine on microcrystalline cellulose

The isotherms do not follow the Langmuir model. However, they can be fitted to the sum of a Langmuir isotherm and a linear (Henry type)

isotherm according to the following equation:

$$\Gamma = \frac{\Gamma_m \cdot K_L \cdot c}{1 + K_L \cdot c} + K_H \cdot c$$

where Γ is the sorbed amount in µmol/g cellulose, c is the equilibrium concentration in mmol/L, Γ_m and K_L are the constants of the Langmuir model and K_H is the constant of the Henry model. Figure 2 shows the model fit for the sorption of pyridine on microcrystalline cellulose.

Figure 3 illustrates the time dependence of the sorption. A significant amount is sorbed almost instantaneously but the rate rapidly decreases and equilibrium is not completely reached after 24 h.

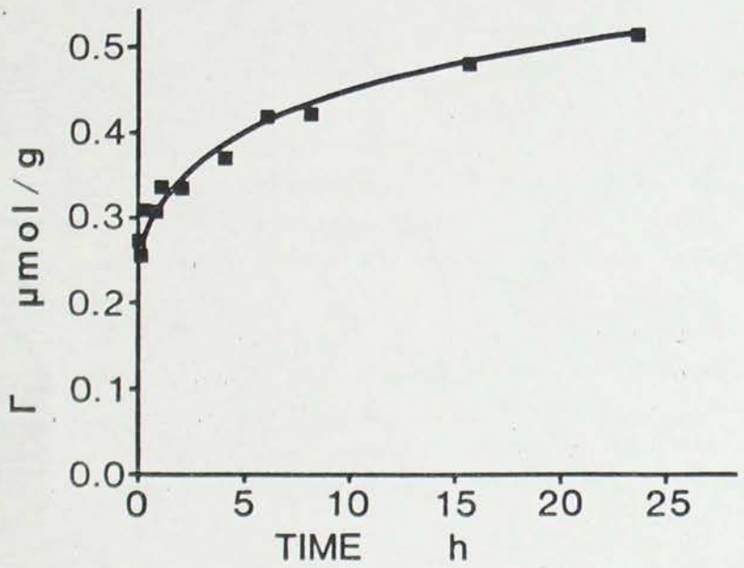

Figure 3. Sorption kinetics for pyridine on microcrystalline cellulose. Start concentration in solution 0.42 mmol/L.

CONCLUSIONS

Cellulose shows an amphoteric behaviour towards the reference substances used. Presumably the active groups are the hydroxyls in the glucose rings.

The complex sorption isotherms and the sorption kinetics might be explained assuming that both surface adsorption and bulk absorption take place. The Langmuir component would then correspond to adsorption on the exposed cellulose surfaces and the linear Henry component to bulk absorption in the amorphous regions of the cellulose. The surface adsorption can be expected to occur rapidly, whereas the bulk absorption is a slow process involving diffusion in the cellulose, which could explain the kinetics observed.

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DISSOLUTION MECHANISM OF CELLULOSE IN THE SO_2-DIETHYLAMINE-DIMETHYLSULFOXIDE SYSTEM

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ABSTRACT

Dissolution mechanism of cellulose in the SO_2-amine-dimethylsulfoxide system was studied by using ^1H- and ^{13}C-NMR spectroscopies. SO_2 and amine were found to form a complex in DMSO, and the SO_2-amine complex, in turn, reacts with an alcoholic hydroxyl group of methanol to produce a new complex. Also in the case of cellulose it was proved that all hydroxyl groups in cellulose form the same complex with the SO_2-amine as that in the case of methanol.

KEYWORDS: Dissolution mechanism, Cellulose, Non-aqueous solvent, Sulfur dioxide, Amine

INTRODUCTION

Recently, many kinds of nonaqueous cellulose solvents have been found, and the finding of these solvents made it possible to modify cellulose in homogeneous and nonaqueous systems. The authors have succeeded in the quantitative preparations of about 30 kinds of tri-O-substituted cellulose ethers by using one of nonaqueous cellulose solvents, the SO_2-diethylamine(DEA)-dimethylsulfoxide(DMSO) system (1-4). These new cellulose derivatives have not only chemically reactive groups such as aromatic rings or double bonds but also unique physical properties such as thermotropic and lyotropic liquid crystals (4,5).

The SO_2-amine solvents for cellulose was firstly found out by Hata and Yokota (6). They reported that DEA, triethylamine(TEA) and piperidine can be used as the amine for the systems. Yamazaki and Nakao (7) reported that DMSO and the other 37 kinds of organic solvents containing small amounts of SO_2 and an amine can dissolve cellulose. As to the dissolution mechanism of cellulose in this system, several papers have been published by Hata and Yokota (6,8,9), Yamazaki and Nakao (7), Philipp et al (10), Turbak (11) and Hudson and Cuculo (12). However, their proposals are somewhat different each other, and the detail of the dissolution mechanism of cellulose in this system has not been clarified.

In the present paper, the dissolution mechanism of cellulose in the SO_2-amine -DMSO system was studied by using ^1H- and ^{13}C-NMR spectroscopies.

RESULTS AND DISCUSSION

1) Reaction of methanol with SO_2 and amine in DMSO

Figure 1 shows chemical shifts of ^1H-NMR spectra of various solutions related to the MeOH/SO_2-DEA-DMSO system. The -OH proton of MeOH and the -NH proton of DEA appeared at 4.1 and 1.3 ppm, respectively, and the -OH proton of MeOH was hardly influenced by the addition of SO_2 into MeOH/DMSO. The -OH proton of MeOH and the -NH proton of DEA are exchangeable each other. Thus, they show only one peak at 3.9 ppm, when they were mixed in DMSO. Noticeably, the chemical shift of -NH proton appeared at 7.1 ppm in SO_2-DMSO. This value indicates the formation of a complex between DEA and SO_2. By the addition of MeOH into the SO_2-DEA-DMSO mixture (MeOH:SO_2-DEA=1:1), a new signal appeared around 7.8 ppm instead of the signal at 7.1 ppm. This indicates that a new complex was formed between the -OH proton and the aforesaid complex. Judging from the chemical shift, the formation of $-OSO_2H$ can be denied.

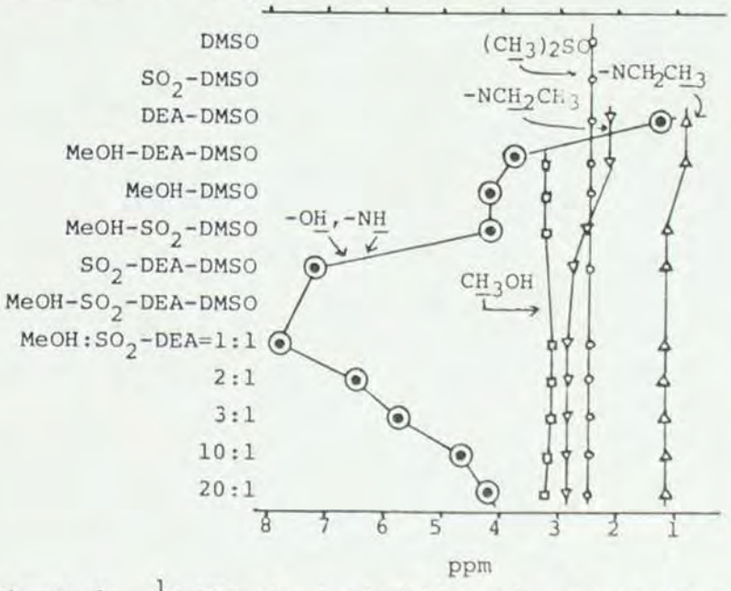

Figure 1. ^1H-NMR chemical shifts of various solutions related to MeOH/SO_2-DEA-DMSO system

When TEA was used as a component of the solvent system in place of DEA, the same results as those shown in Figure 1 were obtained. Namely, the signal of the -OH proton of MeOH moved to locate at 7.8 ppm by the addition of MeOH to the SO_2-TEA-DMSO solution. This value coincides with that in the case of the SO_2-DEA-DMSO system.

On the basis of these results, it is concluded that in the case of the SO_2-DEA-DMSO and SO_2-TEA-DMSO systems the -OH group of methanol reacts with the SO_2-amine complex to form a new complex as shown in Figure 2, and the -NH proton of DEA does not participate directly in the complex formation with the -OH group of methanol.

EFFECT OF EXPLOSION OPERATION FOR EFFECTIVE UTILIZATION OF PLANT MATERIAL

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ABSTRACT

The objective of the present research is to obtain the basic experimental data required for practical system of separation of plant materials into their main components by explosion and its application to production of biomass energy. The effects of operational conditions on properties and amounts of products were examined. It was found that the explosion with high steam pressure and short reaction time was an efficient pretreatment of plant materials for enzymatic hydrolysis and alcohol fermentation.

KEYWORDS: Explosion, Energy.

INTRODUCTION

Many researchers are looking at biomass, particularly woody biomass, as a source of energy. The oil crisis since 1973 has led to the significant development of biological conversions such as enzymatic hydrolysis and alcohol fermentation of wood and grass. However, many technical and economic problems in the pretreatment of biomass have to be overcome, for a practical, efficient utilization of biomass as an industrial low cost energy.

Recently, the autohydrolysis and explosion systems which use steam with high temperature and pressure for degradation of wood materials has attracted attention.[1] In comparison with other treatment systems, this system has the following advantages: (1) The activity of enzymatic hydrolysis of cellulose is high. (2) No chemical is necessary. (3) This system is relatively low in energy consumption.

In this study, the trial constructions of explosion system were attempted for development of the most efficient method of pretreatment for energy utilization of woods such as larix leptolepis.

METHODS AND MATERIALS

The chips (25 x 20 x 4 mm) of Larix leptolepis containing 20 - 30 % moisture to dry weight were used for material in the explosin method. An explosion apparatus is illustrated in the scheme as shown in Figure 1. This apparatus is constructed of a steam generator, a reactor (its volume of 1.2 x 10^{-3} m^3), a receiver for the exploded materials and a condenser equipped with a cyclone to prevent condensed water from going back into the materials collected in the receiver. The apparatus was employed at temperature up to 275°C and maximum steam pressure of 6.0 MPa. The chips (200 g) packed in the reactor were contacted with preheated steam for a desired time and then released into the receiver by opening a ball valve instantly.

Figure 2 illustrates a schematic flow chart in the extraction processes of the exploded samples. The extracts were freeze-dried to give a mixture of hemicellulose and water-soluble lignin, and methanol-soluble lignin, respectively. The residual materials in the extraction were heated in 72 % aqueous sulfuric acid for 4 hr to obtain insoluble lignin (Klason lignin) of wood which was weighed after drying method.

The exploded samples were saccharified with Meicelase at 37°C for 96 hr in 0.5 M phosphate buffer, pH 5.0. The substrate and enzyme concentrations were 2.0% and 0.2%, respectively. The reducing sugars were measured by the Somogyi-Nelson method.

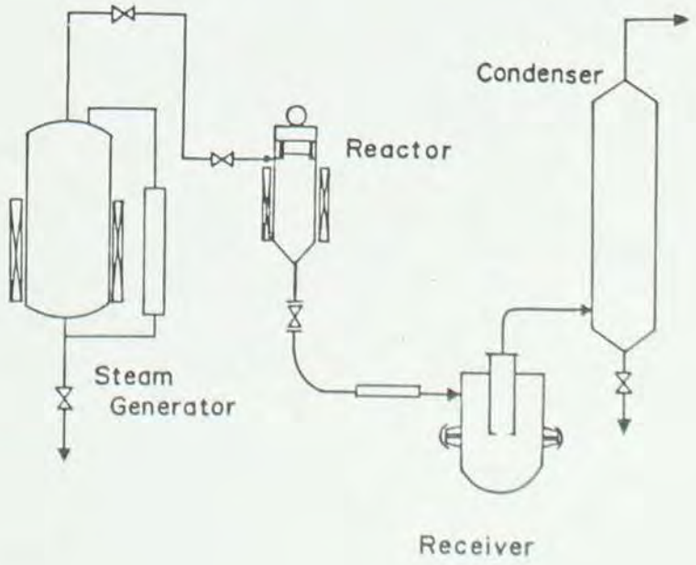

Figure 1. Experimental apparatus.

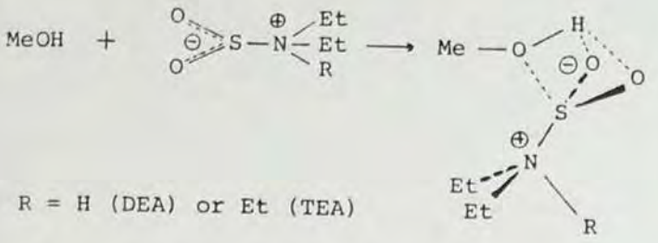

Figure 2. Interaction of methanol and SO_2-amine in DMSO

^{13}C-NMR spectra of various solutions related to the MeOH/SO_2-DEA-DMSO solutions and the MeOH/SO_2-TEA-DMSO solutions also supported the complex formation shown in Figure 2.

2) Reaction of cellulose with SO_2 and amine in DMSO.

Figure 3 and 4 show the ^1H- and ^{13}C-NMR spectra of cellulose solutions, respectively. As shown in Figure 3, the signal of the protons due to the -OH of cellulose and the -NH of DEA in cellulose/SO_2-DEA-DMSO, and due to the -OH of cellulose in cellulose/SO_2-TEA-DMSO appeared around 7.8 ppm as a broad peak. This value coincides well with those observed in the preceeding model experiments.

As shown in Figure 4, there are no difference in the chemical shifts of carbons of cellulose between the two solutions, and the peak of C-6 appeares as one peak at 59 ppm. By comparing chemical shifts of C-2, C-3 and C-6 with those reported by Gagnaire et al (13), it was confirmed that the -OH group of cellulose does not form any derivatives but forms the complex in the solutions.

On the basis of these analyses, it was concluded that cellulose dissolves in the SO_2-amine-DMSO system by forming a complex among the -OH group, SO_2 and amine as shown in Figure 5.

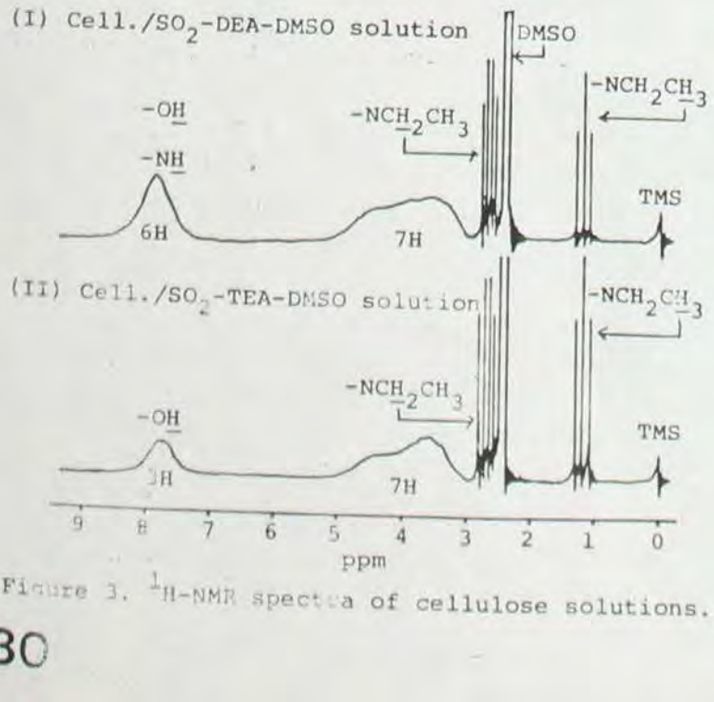

Figure 3. ^1H-NMR spectra of cellulose solutions.

In addition, almost all hydroxyl groups in cellulose were found to form the complex with SO_2 and amine by the NMR analyses and other data reported by Yamazaki and Nakao (7).

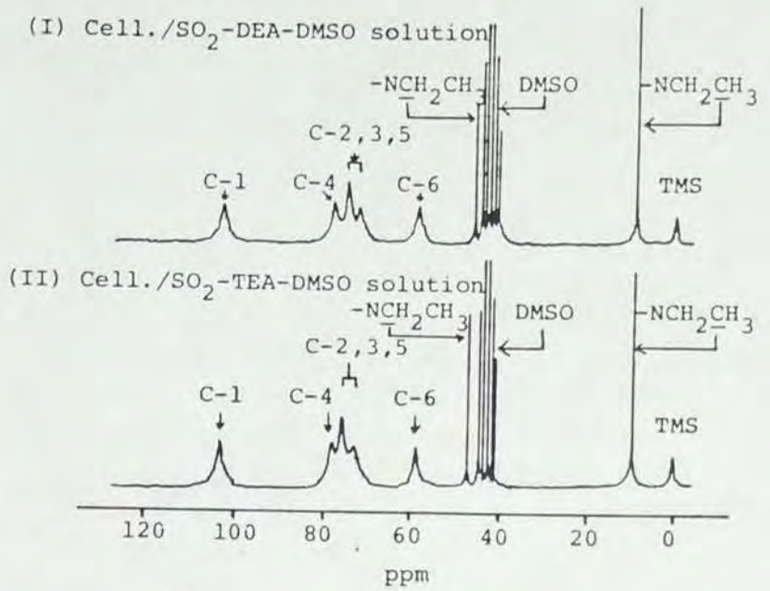

Figure 4. ^{13}C-NMR spectra of cellulose solutions.

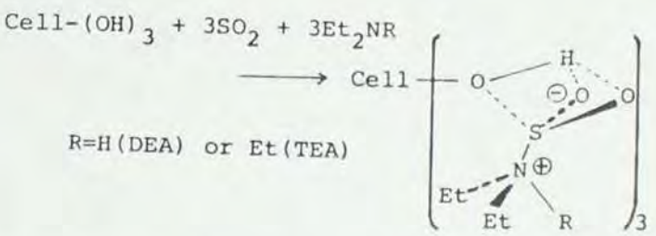

Figure 5. Dissolution mechanism of cellulose in SO_2-amine-DMSO systems.

CONCLUSION

Cellulose dissolves in the SO_2-amine-DMSO system by forming a complex among the -OH group, SO_2 and amine, and all hydroxyl groups in cellulose form the complex in the solutions.

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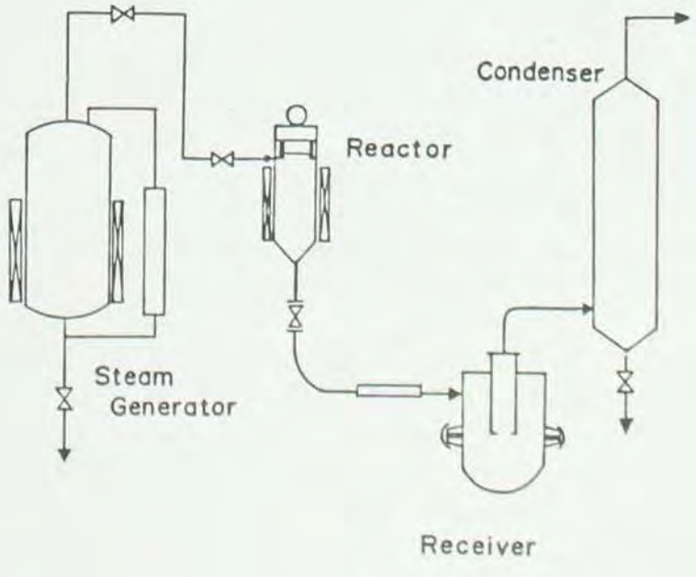

Figure 1. Experimental apparatus.

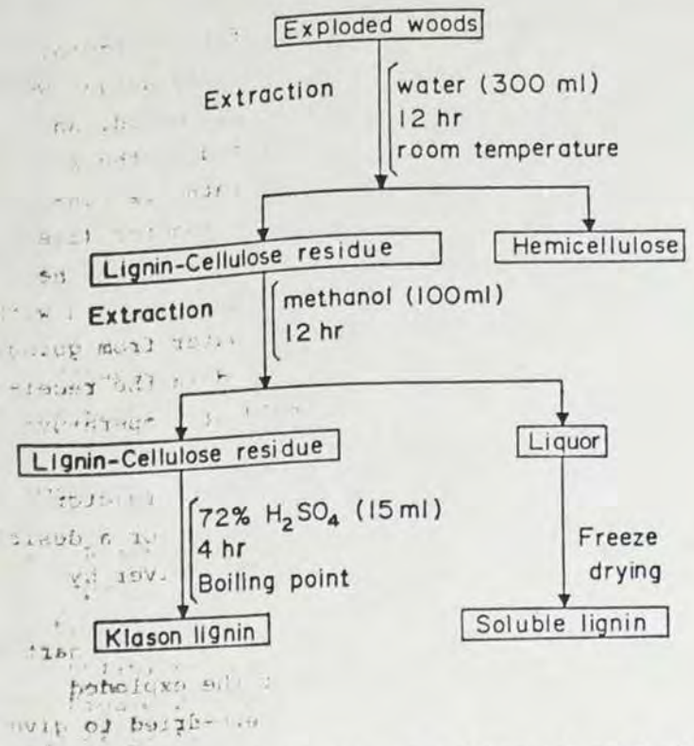

Figure 2. Flow chart on extraction of exploded samples.

RESULTS

The samples produced from wood chips by the hydrolysis with explosion are the materials of multiphase which consist of the fibers broken into pieces and the broken syrupy liquid with a relatively large amount of water condensated from the vapor water. A part of shredded and fluffy solid causes an aromatic odor which is similar to the plant material which was burned by heating of steam. The features in shapes and sizes of broken fibers become very remarkable at a higher steam pressure and a longer reaction time.

Figure 3 shows the micro photographs of wood chips of larix leptolepis exploded under various steam pressures from 1.57 to 4.81 MPa for a period of 5 min in the hydrolysis reaction.

At the steam pressure of 1.57 MPa a part of fiber near the wood chip surface was attacked, but its original form remained. As the pressure rose to 2.55 MPa, the destruction of wood chip rapidly proceeded in the direction of filamental material and much of wood fibers were broken into pieces in just short time. At the high pressure over 3.53 MPa the wood chip is broken into more fibrilliform particles which are destroyed beyond recognition with the syrupy liquid. Particularly, the effect of explosion at the pressure over 4.51 MPa is very remarkable.

As seen from these pictures, the filamental materials made of wood chip by explosin consisted of a great many fibrilliform particles of various sizes. Figure 4 shows the frequency distributions for both sizes of a shorter side (width) and longer side (length) in the filamental flakes from 400 to 500 pieces crushed finely. They were measured by the naked eye or a microscope.

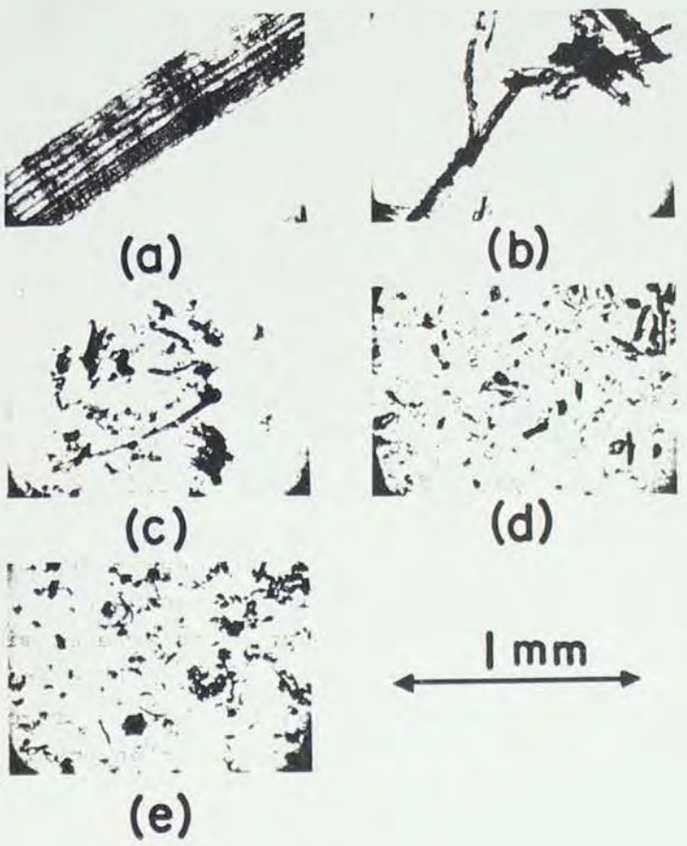

Figure 3. Photograph of exploded wood at reaction time of 5 min: (a) 1.57 MPa, (b) 2.55 MPa, (c) 3.53 MPa, (d) 4.51 MPa, (e) 4.81 MPa

Figure 4 (a) illustrates the distribution of length in the shredded particles of wood chips exploded at a period of hydrolysis of 5 min under various pressure from 1.08 to 4.81 MPa. The raw materials in an almost normal distribution with the mean value at 25 mm and small mean deviation changed to the filamental materials which had the distribution in a wide range from the microscopic size to 20 mm as the steam pressure increases up to 3.53 MPa. The range of distribution in particle lengths by explosin at 4.51 and 4.81 MPa became narrower in comparison with those below 3.53 MPa, and its mean length is below 0.05 mm. From these results, it seemed that the efficiency of explosion on wood chips was very large at pressure over 4.51 MPa. Similarly the distribution of the width is shown in Figure 4 (b). The trends in the changes of distribution curves for the width by pressure were very similar to those for length. The range of width in distribution curve with increasing the pressure became

narrower in spite of the relatively wide range in the raw material. In contrast to the tendency of of width, the range of length with increase in pressure elongated in spite of the narrow range in the raw material. It is clear from this figure that steam pressure is one of the most efficient factors on the fibril of fibers, especially, when the pressure is above 3.53 MPa. When the temperature reaches 243°C, which is inside the range of 231 to 253°C of thermal softening point of cellulose,[2] and saturated pressure of 3.53 MPa, the mechanical strength in the cell wall decreases.

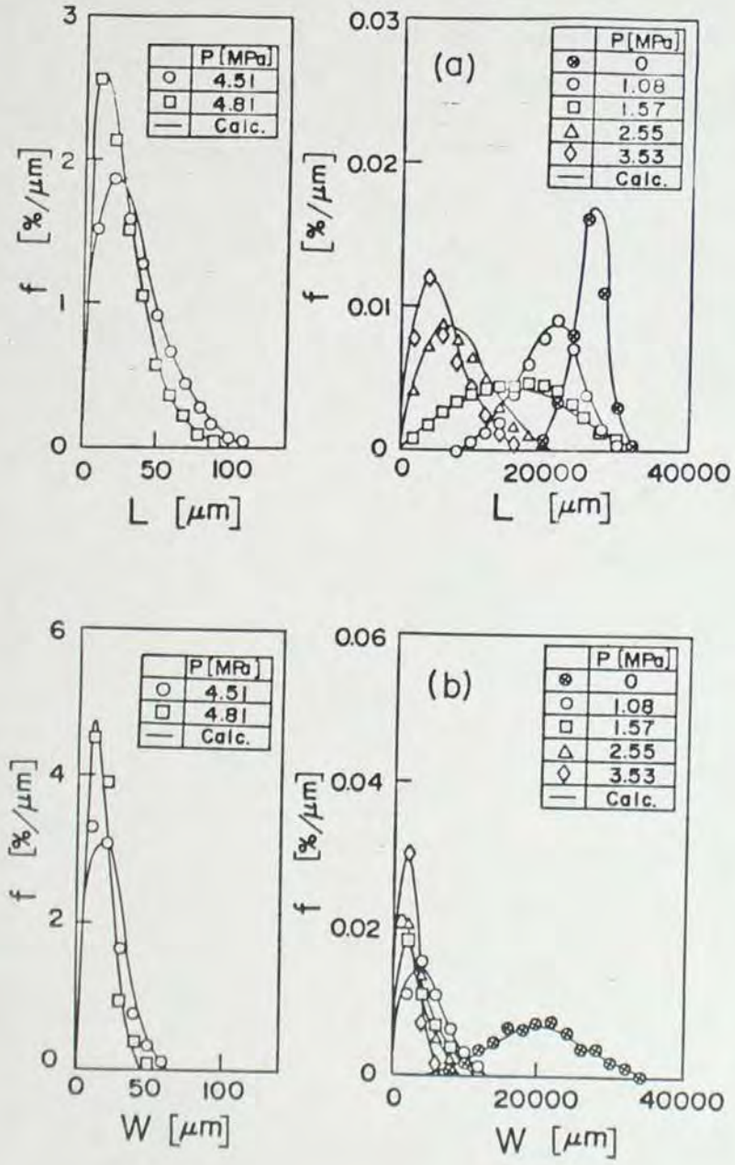

Figure 4. Size distribution of exploded wood fibers: (a) Length, (b) Width.

Figure 5 illustrates a ratio of weight of soluble lignin and that of Klason lignin, ξ_S and ξ_K to weight of exploded dry sample under various reaction times, t, in the steam pressures of 2.55, 3.04, 3.55 and 4.51 MPa. The amounts of soluble lignin increased as the reaction time and pressure were increased. In contrast to the production of soluble lignin amount of Klason lignin decresed sharply, then changed to increase as the reaction time getting longer. The timing when the drastic change from the decrease of amount of Klason lignin product to its increase took place for a pressure was in fair agreement with the timing when the amount of souble lignin became constant regardless of autohydrolysis time. It seemed that the production of souble lignin can not exceed a certain amount by the hydrolysis, however, the production of Klason lignin produceeded progressively as a results of the condensation with compounds of high reactivity except the soluble lignin or the condensation among the lignins of the lower molecular weight which were produced by the explosion.

The changes in the amounts of cellulose and hemicellulose under several operation conditions are plotted in Figure 6. The amount of cellulose decreased sharply in proportion to the reaction time and pressure. On the other hand, the amount of hemicellulose remained almost constant until the reaction time of about 20 min and the steam pressure of about 4.51 MPa.

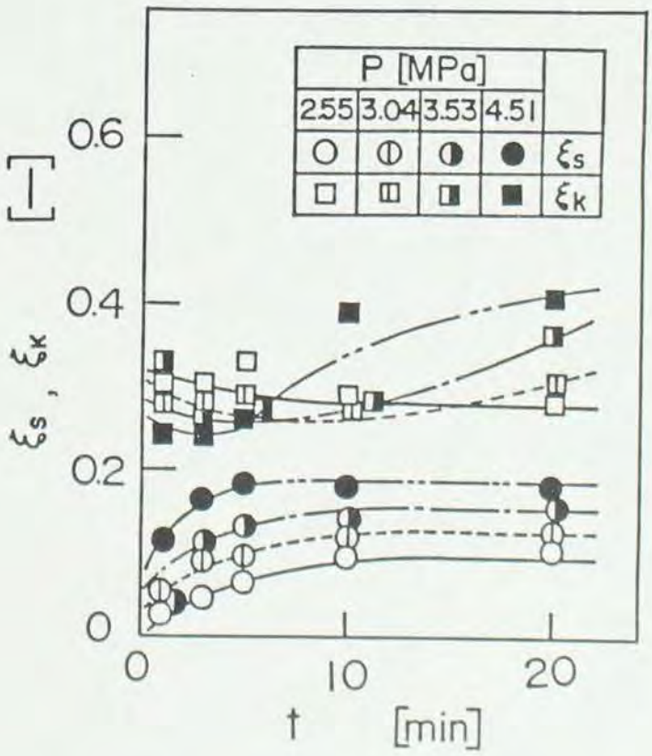

Figure 5. Effects of steam pressure and reaction time on ratics of soluble lignin, ξ_S and Klason lignin, ξ_K to dry weight of exploded wood.

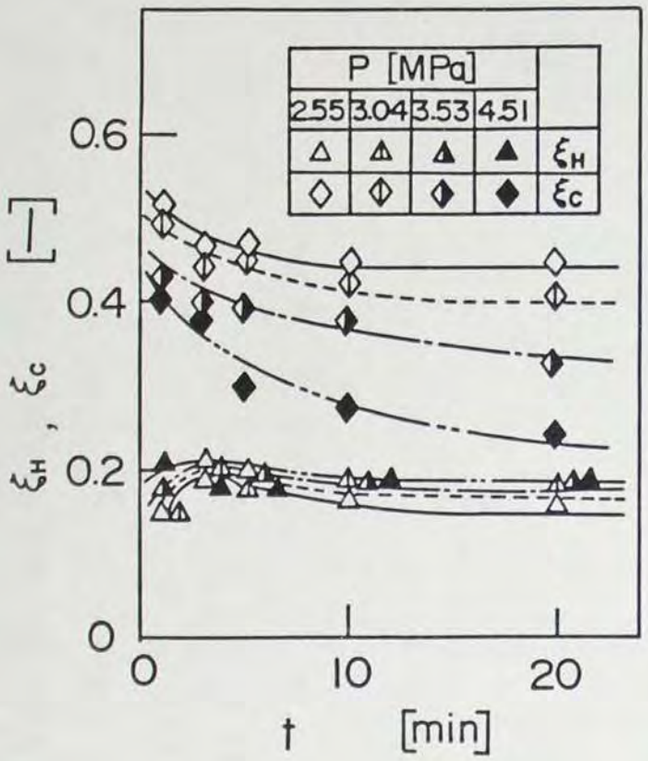

Figure 6. Effects of steam pressure and reaction time on ratios of cellulose, ξ_C and hemicellulose, ξ_H to dry weight of exploded wood.

Figure 7 (a) and (b) show the relationship between enzymatic saccharification, X, and incubation time, θ, at 2.55 and 4.51 MPa, respectively. Enzymatic saccharification was defined as the ratio of weight of reducing sugars produced to that of exploded dry sample. Reducing sugars were measured by Somogyi-Nelson method as glucose. At 2.55 MPa, the small difference in the effects of reaction time on enzymatic saccharification was recongnized and their conversions were about 0.05 after 100 hr of hydrolysis. On the other hand, at 4.51 MPa, enzymatic saccharification increased remarkably with incubation time and the large difference in reducing sugars was recognized. At 5 min of reaction time, enzymatic saccharification increased sharply and reached about 0.35 after 100 hr of hydrolysis. In the range of t ≥ 5, enzymatic saccharification decreased with reaction time.

Several empirical models for the enzymatic hydrolysis of cellulose were proposed. The general form proposed by Walseth[3] is

$$X = k\,\theta^{n} \qquad (1)$$

where k and n are experimental constant. Taking logarithms of both sides of Eq. (1) is

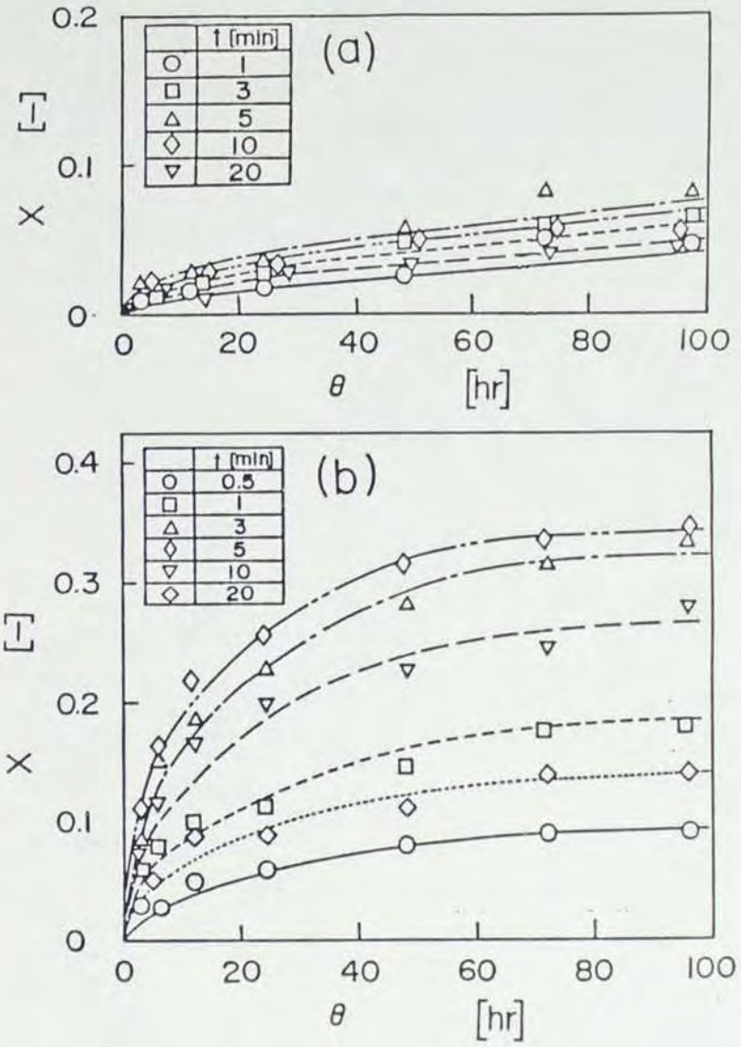

Figure 7. Enzymatic hydrolysis of exploded wood: (a) 2.55 MPa, (b) 4.51 MPa.

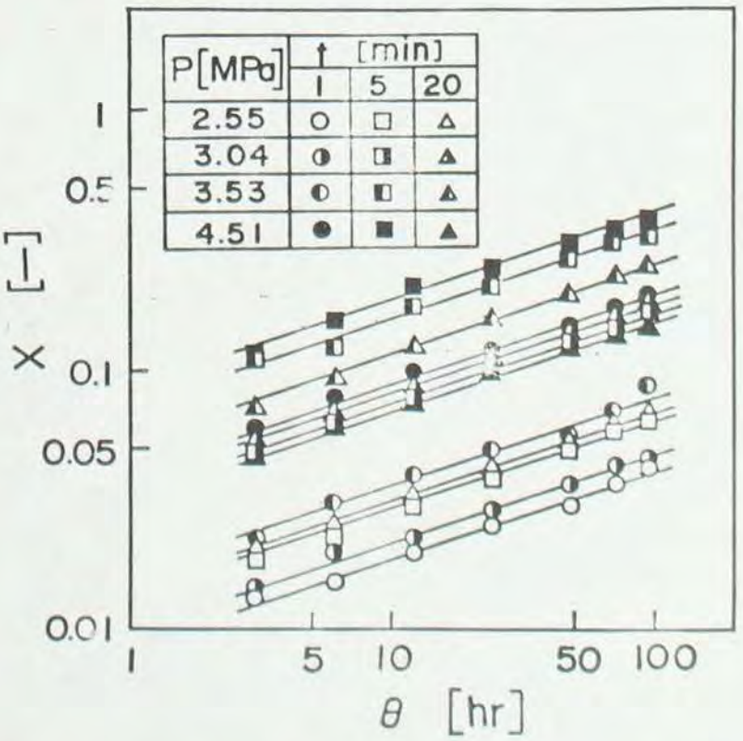

Figure 8. Effects of explosion on saccharification rate constant and reaction time.

$$\log X = \log k + n \log \theta \qquad (2)$$

The relationship between enzymatic saccharification and incubation time gave essentially straight line on a log scale as shown in Figure 8. The slope was proportional to the 0.34 power of X. Then,

$$n = 0.34 \qquad (3)$$

The value of the hydrolysis rate constant, k, was obtained as the value of X at $\theta = 1$. Figure 9 shows the value of k under several operational conditions. In the range of $P < 3.53$, the value of k increased with reaction time. On the other hand, in the range $P \geq 3.53$, the value of k reached a maximum at 5 min and decreased with reaction time. Relationship of k and reaction time, k, was expressed as Eq.(4) using parameters α, β and γ.

$$k = \alpha \,/\, (\beta/t + 1 + t/\gamma) \qquad (4)$$

where α, β and γ are maximum hydrolysis rate constant, hydrolysis rate constant at shorter time and hydrolysis rate constant at higher time.

Figure 10 shows values of α, β and γ in applying Eq.(4) to the experimental data. α and β increased with steam pressure and enzymatic saccharification was high regardless of shorter reaction time. On the other hand, the value of γ decreased with steam pressure and suggested a lower enzymatic saccharification at longer reaction time. From these results, it was found that the operation of explosion for a few minutes at a higher pressure was most effective for enzymatic hydrolysis of exploded wood.

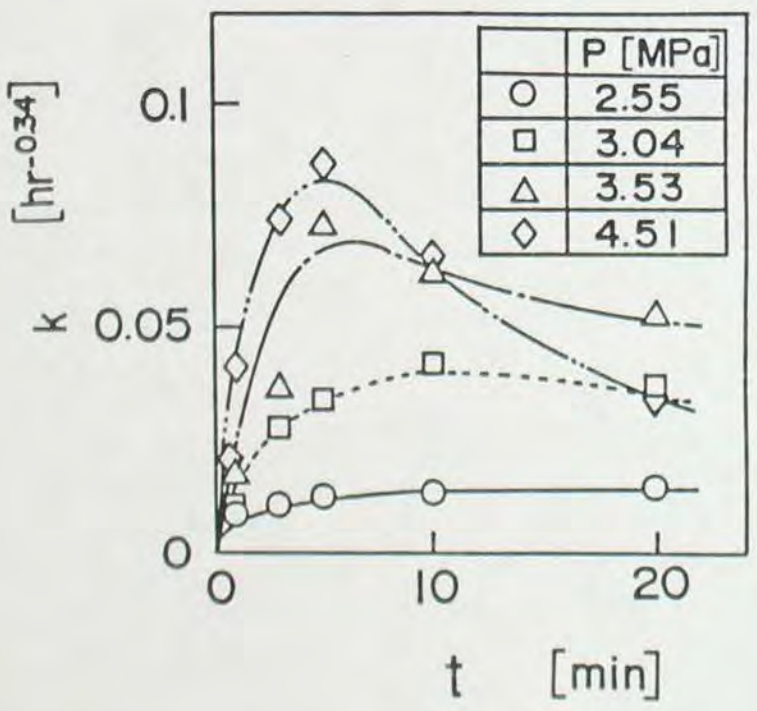

Figure 9. Relationship between saccharification rate constant and reaction time.

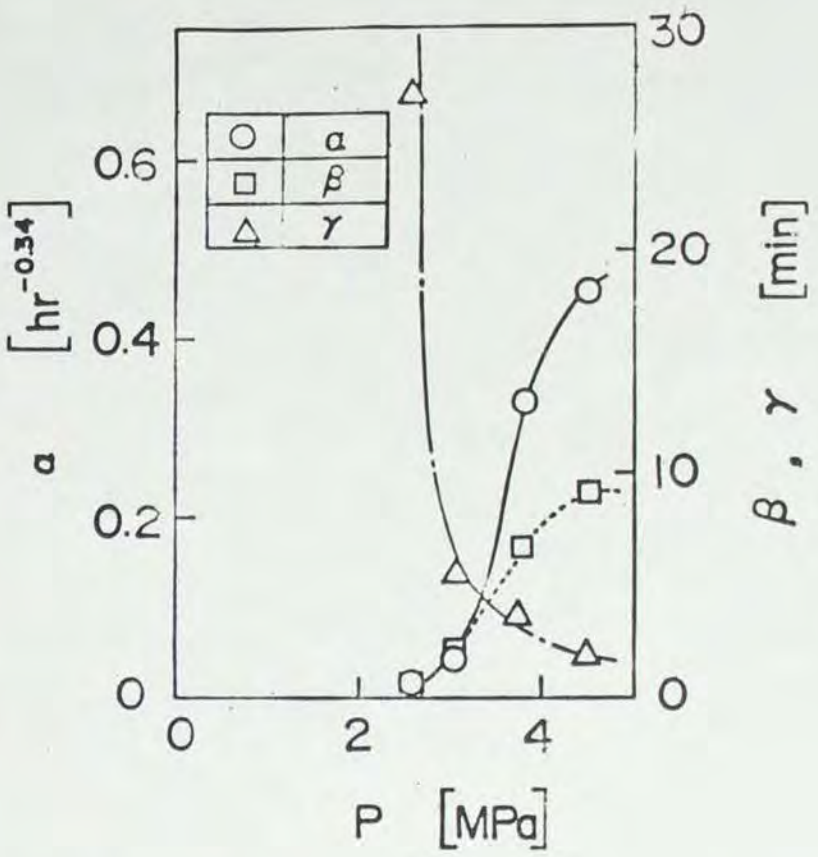

Figure 10. Steam pressure dependence of parameters α, β and γ.

CONCLUSION

The experiments of explosion for the effective utilization of biomass were carried out under various operational conditions. Many of the various macromolecule compounds in wood converted to the lower molecular weight materials in just a short period by the hydrolysis with steam under higher temperature, and their lower molecular weight components were able to be separated relatively easily to the four components such as cellulose, hemicellulose, methanol-soluble lignin and Klason lignin. This investigation will present the basic data required for practical system of separation of wood into main macromolecular components by operations of explosion and extraction, and enzymatic hydrolysis of exploded samples.

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HARMONIZING BLEACHING TECHNOLOGY WITH FUTURE ENVIRONMENTAL REGULATIONS

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Introduction

The following summary is the result of a study of the concession decisions in Sweden during the past 5 - 10 years for all plants manufacturing bleached sulfate pulp. The intention has been to find possible trends in the authorities' view of oxygen bleaching.

The current status of internal and external measures in Swedish bleaching plants

Of the fifteen sulfate mills which manufacture bleached pulp, eight have today oxygen stages for bleaching softwood pulp. Of these mills, one also bleaches hardwood pulp with an initial oxygen stage. One additional sulfate mill is planning to instal an oxygen stage for bleaching softwood pulp.

The portion of chlorine dioxide in the chlorine stage for softwood pulp varies between a few per cent and 20 per cent. The percentage for the bleaching of hardwood pulp varies between a few per cent and 90 per cent.

All fifteen sulfate mills which manufacture bleached pulps have sedimentation ponds. However, at one mill, all or part of the bleach plant waste water is taken directly past the pond. Five of the mills currently have aerated ponds. A decision to construct a biological purification system has been reached at another. In certain cases, all the bleach plant waste water is not led to the aerated pond. One mill uses external purification of bleach plant effluents in the form of adsorption on lime sludge ("the lime sludge method") and another uses ion exchange treatment.

One mill has both an oxygen stage and an aerated pond. At another mill, with oxygen bleaching, a decision has been made to instal biological purification. At the mill planning to instal an oxygen stage, an aerated pond is already in use. At another mill with an aerated pond, permission has been granted to instal extended cooking in combination with improved washing and an increase in the use of chlorine dioxide in the chlorine stage, as an alternative to introducing oxygen bleaching.

Trends in oxygen bleaching in Sweden

During the 1960s and in the early 1970s, the Swedish pulp and paper industry concentrated its environmental protection efforts primarily on the environment in and around the mills. Large resources were invested in an attempt to reduce the discharge of oxygen consuming substances.

The first oxygen stages started operation in the beginning of the 1970s and represented an answer to the demands of authorities to reduce the discharge of BOD_7, lignin and color. Often, conditions were formulated so that companies could choose between an oxygen stage and external purification (1).

During the mid-1970s, the National Swedish Environment Protection Board regarded oxygen bleaching in combination with conventional final bleaching as a "standard requirement" in new mills. In the opinion of the Environment Protection Board, oxygen bleaching was a first step towards a closed bleach plant (2). External purification methods for bleach plant waste liquors and ion-exchange and lime-sludge methods were regarded as an acceptable alternative to oxygen bleaching for existing installations (3).

During the latter half of the 1970s, environmental concerns shifted to an increasing extent towards the long-term effects of discharges in time and space. To an increasing extent, discussions began to be concerned with the reduction of the discharge of chlorinated organic substances. As a result, the Environment Protection Board's demands were increased to encompass oxygen bleaching and measures to reduce these substances. Among the most important of these measures was the exchange of chlorine for chlorine dioxide in the first bleaching stage as well as the external treatment of bleach plant discharges through aerated ponds, and the ion-exchange and fenox methods. Mill closure measures through recycling of portions of the waste liquor from the first alkali extraction stage were also demanded by the Environment Protection Board (4).

A noticeable trend during this period was that the National Swedish Franchise Board for Environment Protection deferred final demands and requirements with respect to bleach plant discharges. At the time, the Franchise Board for Environment Protection decided to await the results of the Swedish Pulp and Paper Association's then ongoing project, "Environmentally safe manufacture of bleached pulp". During the period of deferment, mills were usually ordered to investigate "technical and economical possibilities" to reduce bleach plant discharges through various measures (5).

During recent years, joint research carried out by Swedish industry has shown that the rate of delignification and the transfer or organic substances to bleach plants are two primary factors affecting conventional parameters and toxicity in bleach plant discharges. During the current decade, the Environment Protection Board has also begun to an increasing extent to insist on a reduction in the Kappa number in cooking in conventional bleaching and in oxygen stages, as well as on conditions for washing losses (6).

In addition to demands for oxygen stages and aerated ponds, recent requirements have also been specified for Kappa number reductions, certain proportions of chlorine dioxide in chlorine stages and improved washing (7). It is interesting to note that one mill with an existing aerated pond has received permission to instal extended cooking in combination with better washing and an increase in the level of chlorine dioxide, as an alternative to oxygen bleaching (8).

In summary, it may be said that there was a noticeable trend that mills were either ordered or themselves undertook to instal oxygen stages during the 1970s. During the latter half of the decade, demands increased to encompass oxygen stages in combination with additional internal and external measures.

Concession decisions

1	Vallvik	June 8, 1973
	Skutskär	April 1, 1974
	Korsnäs	April 1, 1974
2	Skutskär	June 10, 1977
	Karlsborg	December 13, 1978
3	Östrand	November 20, 1973
4	Värö	June 25, 1980
	Mörrum	October 28, 1980
	Gruvön	October 2, 1982
	Gruvön	April 6, 1982
	Husum	June 29, 1982
5	Mönsterås	May 26, 1977
	Mönsterås	April 29, 1981
	Skoghall	January 15, 1979
	Östrand	April 10, 1980
	Värö	June 25, 1980
	Mörrum	October 28, 1980
	Norrsundet	October 7, 1981
6	Östrand	April 10, 1980
	Gruvön	October 2, 1980
	Norrsundet	October 7, 1981
	Husum	June 29, 1982
7	Husum	June 29, 1982
8	Karlsborg	December 14, 1982
	Karlsborg	January 12, 1984

FUTURE TRENDS IN BLEACHING TECHNOLOGY

Delignification with an alkaline oxygen stage

A basic precondition for the use of an alkaline oxygen stage in a delignification operation is that the development of the selectivity for the delignification is better than the final phase of the sulfate cooking. The viscosity and Kappa number of the cooked pulp are determining factors for the technical and economic results of the process in the oxygen stage. A high intrinsic viscosity (< 1 200 dm^3/kg) for a Kappa number around 30, with small variations, is a precondition for a good result. The development of cooking technology greatly furthers the possibilities of improving economic and environmental effects by using an oxygen stage as the first stage following cooking. The introduction of high sulfidity, atmospheric steaming and computer control has, generally speaking, increased the possibility of being able to deliver a high-viscosity pulp with stable Kappa number from the digester to the oxygen stage.

Modified cooking processes have been developed and tested on a large scale. It is possible to cook to around Kappa 25 while maintaining viscosity. The total yield will be somewhat lower and the consistent quality of the pulp has not as yet been ensured on a full scale. However, the know-how gained can contribute to the production of a pulp with Kappa numbers of 28 - 30 with consistently better viscosity. Therefore it is very likely that the current cooking-oxygen process can be further developed using improved washing methods now under development so that Kappa numbers of 12 - 14 can be achieved without adversely affecting the quality of the pulp.

This means (contrary to what has been reported in certain contexts) that the improved cooking process should not be regarded as an alternative to oxygen bleaching, but as a complement, which improves the positive effects of the oxygen stage on the production economy and the environment.

In recent years, it has been demonstrated that it is possible to activate the unbleached pulp using certain pretreatments so that the selectivity of a subsequent oxygen stage is greatly improved. Pretreatment with chlorine prior to the oxygen stage considerably improves the selectivity of the oxygen stage. Because of corrosion problems, however, it is hardly possible to recycle the spent liquor to the closed liquid and recovery system of the pulping process. Pretreatment with green liquor, peroxide, ozone or nitric oxides in acid media gives positive results. The best results for sulfate pulps are achieved with

nitric oxides. In Sweden, professor Olle Samuelson, together with MoDo, has carefully studied the treatment of unbleached sulfate pulp with nitric oxides prior to an oxygen stage.

Amazingly good results have been reported in terms of pulp yield and especially for pulp viscosity after the oxygen stage. It appears that pulp quality can be maintained at a high level down to Kappa numbers of about 10. It also appears possible to increase the degree of delignification to 75 per cent from the current average of 50 per cent.

These results have been so promising that a group of Swedish companies - MoDo, Sunds Defibrator, AGA and Kema Nobel - have decided to finance a pilot plant project to facilitate the development of equipment and to evaluate the process from the technical and economic perspective. A thorough analysis and characterization of the effluent from the bleach plant will also be conducted as well as of the health hazards in the environment within the mill.

Hydrostatic oxygen stages

Oxygen-reinforced alkali extraction stages have been shown to be both an effective and economical complement in the bleaching sequence, especially as the first alkali extraction stage. By raising the height of the tower, the effectivity of the delignification process can be increased. This variant may also be introduced as a first stage in special cases such as with hardwood sulfate pulp, sulfite pulp, or other pulps where a lower delignification (around 35 per cent) is acceptable.

A sequence of the (EO)(CD)(EO)D type may be an attractive alternative.

It has also been demonstrated that the replacement of the hypostage with an alkali oxygen stage is favorable for both birch and pine sulfate pulp (for example, a (CD)E(EO)DED sequence).

Ozone

The introduction of ozone into the bleaching process has so far been handicapped by its aggressive character, which reveals itself in difficulties in controlling pulp quality (this applies to the process with high concentration), and its cost, which as a result of the low energy and conversion yield, has remained at a high level. Ozone production technology has developed gradually; important progress has been achieved in recent years. It can therefore be expected that an introduction of ozone in certain positions will be economically feasible within the near future. Low concentration methods (around 3 per cent pulp consistency) appear to be easier to control with regard to the viscosity of the pulp. Ozone may pose an attractive future alternative as a complement to oxygen bleaching, primarily as an activating pre-stage.

Closed systems

The basic idea underlying the increased use of non-chlorine, non-corrosive chemicals in the bleaching plants is to recycle waste liquors to the recovery cycle. It is then possible to burn the organic matter and recover sodium.

A Swedish pulp mill is currently recycling the liquor from the OE stage to the recovery cycle. By using oxidized white liquor in both the O and OE stages, and using the flexibility of the chlorine dioxide production, the plant has succeeded in introducing an economical system with low discharges.

A bleach plant for a brightness of 90 % ISO with two pressurized oxygen stages and satisfactory washing systems may be designed with only chlorine dioxide as a bleaching agent. The bleaching plant is closed to a high degree with a water consumption of only 5 m^3/ton of pulp. A bleed of 0.5 - 1 m^3/ton is assumed. This waste liquor may be treated before it is released to the recipient. If the brightness target is sufficient for the pulp's end use, application of a hydrostatic extraction stage may be a viable alternative to the pressurized oxygen stage.

ON THE REACTION BETWEEN ALKYLKETENE DIMERS (AKD) AND CELLULOSIC FIBERS

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INTRODUCTION

Alkylketene dimer sizing agents have been known for almost 40 years for the sizing of paper under neutral and alkaline conditions. The efficiency of these sizing agents has been ascribed to a chemical reaction with the cellulosic fibers. In papermaking, the alkylketene dimer size is used as a cationic dispersion. In a series of experiments Lindström and coworkers (1) have followed the development of sizing and the extent of reaction as a function of time and solids content of the sheet. In these experiments the reaction between AKD and cellulose in the formed sheets was inferred from changes in the proportions of extractable and unextractable AKD (radioactivity). It is difficult to interpret the data in terms other than those of a covalent reaction, but extraction does not provide uniequivocal evidence for reaction. Therefore a series of investigations was started to obtain direct experimental (eg. spectroscopical) evidence for a reaction. This paper presents some preliminary data related to this issue.

REACTION BETWEEN AKD AND CELLULOSE

During the last year, three different investigations on the reaction between AKD and cellulosic fibers have been reported by Roberts and Garner (2), Rohringer, Bernheim and Werthemann (3) and Merz, Rohringer and Bernheim (4). These authors have investigated the reaction with model substances, radioactive labelling, analysis of extractives, IR-techniques and DSC-techniques. Without discussing these investigations, the authors conclude that they find no evidence of a reaction, although the experimental data presented are suggestive rather than conclusive at the present stage.

It must be realized that the amount of AKD that can be expected to react is very small. According to our experiments at STFI, only 0.01-0.04 % of a fully sized sheet consists of reacted AKD. This amount gives 5 % monolayer coverage of the BET-area, and this surface coverage has in our studies been shown to give hydrophobicity to a paper surface.

IR-STUDIES

Since very weak signals were anticipated, a modern FT-IR spectrometer (Bruker IFS-113 v) was used, operating in the internal reflexion mode using a KRS-5 crystal. The absorption bands of the AKD, which we have examined closely are those of the lactone ring at 1720 cm^{-1} (C = C bond) and 1850 cm^{-1} (C = O bond) and the CH stretching vibrations at 2917 cm^{-1} and 2849 cm^{-1}.

To avoid possible complications from dispersants etc., the AKD was dissolved in THF. A 80 g/m^2 sheet made from decrilled bleached softwood kraft was impregnated with this solution to give various percentages of AKD. After drying in air, the sheets were cured at 110°C for 30 min. After the curing, the sheets were extracted by first swelling the sheets in H_2O and then extracting them with THF (1). IR-spectra of samples were run after impregnation, after curing and after curing + extraction. If the reaction occurs, a β-keto ester is formed and one expects carbonyl bands to appear at 1745 cm^{-1} and 1720 cm^{-1} and the lactone bands to disappear.

The observation that could be most easily made was that the intensity of the lactone ring vibrations relative to the CH vibration of the alkyl chain changed. As an example, I_{1850}(C = O, lactone)/I_{2916} (C-H) was 0.35 in the impregnated sheet. When the sheet was cured, the ratio was 0.27 and after extraction it was 0.20. The easiest explanation is of course that the relative intensities have changed due to reaction with the lactone ring. This effect will of course be greater when most of the unreacted AKD has been extracted from the sheet. That all the AKD cannot be extracted from the sheet in this case is most probably due to the fact that the AKD was not added as a dispersion but as a THF-solution (internal trapping in the cell wall).

The most direct indication of a reaction between the cellulose and the AKD is, however, the appearance of a weak IR-bond at approximately 1745 cm^{-1}. This band is most clearly seen in the sample that has been both cured and extracted (see fig.). The intensity of this small band gives a concentration of reacted AKD in the sheet of 0.047 %, a figure which is of course very approximate. The extinction

coefficient for the carbonyl band has been estimated from the case where the AKD had reacted with CH_3OH.

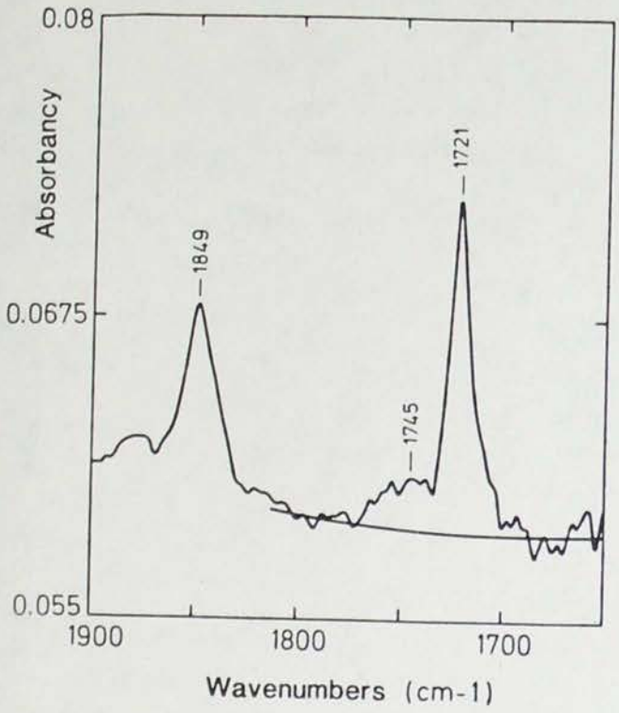

Figure 1. IR spectrum for a cured and extracted sheet. The baseline used in the calculations is also shown.

CALORIMETRIC INVESTIGATIONS

Another way that could be used to trace the reaction is to follow it calorimetrically. If the value 0.047 % obtained in the IR-study is taken and we estimate an enthalpy of 100 kJ, we can expect a total evolution of heat of the order of 100 mJ per gram of pulp. A sensitive calorimeter needs at least an hour to come to equilibrium after the sample has been placed in t, which means that the temperature must be lowered to ensure that the reaction has a half life of at least a couple of hours. This also means that the calorimeter must be able to detect a couple of μW. It was therefore decided to work at 40°C and with the LKB-Biological Activity Monitar Calorimeter, which has this level of sensitivity.

A pulp sample impregnated with dichloromethane and a pulp sample impregnated with a 1 % solution of AKD in dichloromethane were placed in the calorimeter. In the sample with AKD there was an excess of generated heat. When this excess heat was plotted logarithmically against time a straight line was obtained that gave a half life of the reaction of 8.6 h. If the activation energy and the reaction rates determined at higher temperatures (1) are used, a half life of 5.2 h would be expected. This is as close an agreement as can be expected for this type of experiment.

ACKNOWLEDGEMENTS

We should like to thank Drs Bo Liedberg and Jaak Suurkuusk for valuable contributions to this work.

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DELIGNIFICATION OF HIGH-YIELD SULFITE PULP WITH ALKALI

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ABSTRACT

Sodium bisulfite and sodium sulfite cooking of beech wood meal to a high residual lignin content followed by a further delignification with alkali was investigated. Comparisons between the single-stage cooking and the oxygen-alkali cooking were also made.

Two-stage cooking gives a high delignification rate and acceptable pulp yield as compared to the single-stage cooking. It is, therefore, concluded that sulfonic acid groups introduced into a lignin molecule by sulfite pretreatment contribute to the acceleration of the delignification reaction because of their electron-withdrawing property.

KEY WORDS: Delignification, Two-stage Cooking, Single-stage Cooking, Sulfite Pretreatment

INTRODUCTION

Pulping with sodium sulfite would appear to be the most promising approach because the pH of these chemicals in aqueous media lies in the preferred range and sulfite ions have the ability to stabilize carbonydrates against the peeling reaction. However, sodium sulfite is very slow in its pulping action as compared to sodium bisulfite or kraft cooking liquor. Therefore, a two-stage pulping method using sodium sulfite or sodium bisulfite in the first stage and another mild sulfide-free pulping in the second stage seems to be a promising process.

In the present paper, sodium bisulfite and sodium sulfite cooking of beech wood meal to a high residual lignin content followed by a further delignification with sodium hydroxide has been investigated.

EXPERIMENTAL

Extractive-free beech wood meal was treated by sodium bisulfite and sodium sulfite cooking liquors to be about 80% pretreated yield. Sodium bisulfite cooking liquor was composed of 52 g/L $NaHSO_3$ and 31.2 g/L Na_2CO_3, and sodium sulfite cooking liquor consisted of 30 g/L of Na_2SO_3.

Alkali cooking (second-stage cooking) was carried out with 1 N NaOH. Wood to liquor ratio was 1:15. Oxygen-alkali cooking also was performed at same conditions as the above.

RESULTS AND DISCUSSION

In the case of 120°C cooking temperature, pulp yield decreased with increased cooking time, considerably during the initial 60 minutes, and then levelled off. After the sulfite pretreatment, there was evidently a decrease in pulp yield as compared to the single-stage cooking. As the cooking temperature was increased to 160°C, pulp yield decreased significantly as compared to the former. Also, pulp yield differences between the two-stage and the single-stage cookings were getting closer at the final stage of cooking than at 120°C.

As can be seen in Fig. 1 and 2, the delignification rate is dependent on the cooking temprature and cooking time. Single-stage alkali cooking shows 23.5-27.6% of low delignification rates. Two-stage cooking resulted in delignification rate 2 times higher than that of single-stage cooking, and differences of delignification between two different cooking methods are seen to be maintained even after 120 min. cooking time. As the temperature is raised to 160°C, the delignification rate at the initial stage showed relatively large differences (12-18%), but these differences gradually became smaller with increasing cooking time. In the case of single-stage cooking, on the other hand, a continuous increase in the delignification rate was observed even after 180 min. cooking.

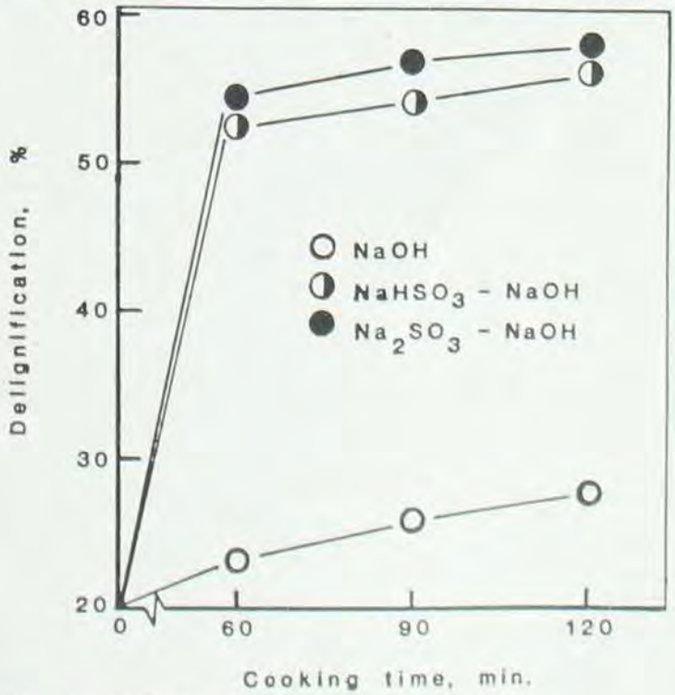

Fig. 1 Effect of two-stage cooking on delignification of pulp (120°C).

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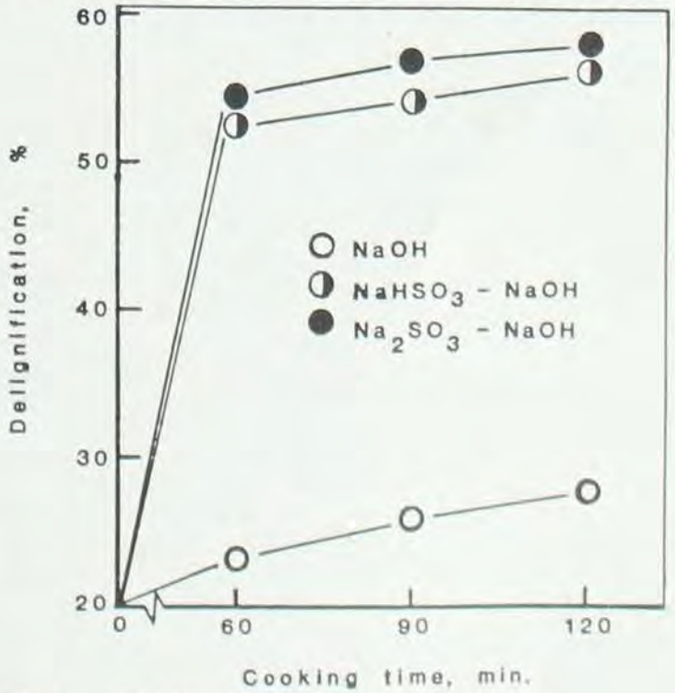

Fig. 1 Effect of two-stage cooking on delignification of pulp (120°C).

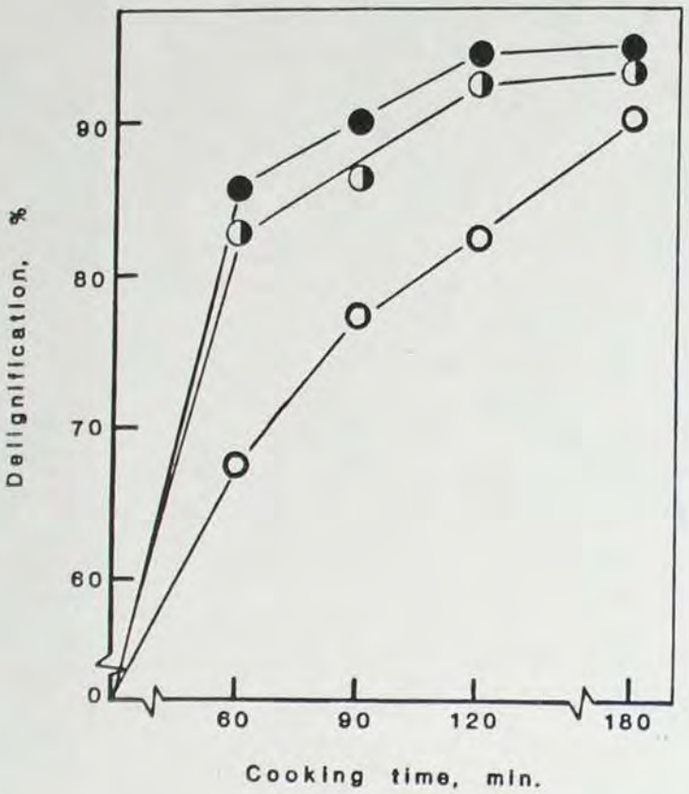

Fig. 2 Effect of two-stage cooking on delignification of pulp (at 160°C). The symbols correspond to those in Fig. 1.

A comparison of the data described above with those listed in Table 1 shows clearly that the single-stage cooking results in a relatively low and continuous increase in delignification rate, while the two-stage cooking shows a lower lignin content within a shorter cooking time.

The authors (1) have proposed that sulfonic acid groups on the side chain of the lignin molecule activate the alkaline degradation of aryl glycerol-β-aryl ether linkages. Relative to the alkaline cleavage of β-aryl ether linkages with an α-sulfonate substituent, two alternative ways of the cleavage of β-aryl ether structure (1-5) have been proposed: elimination of the α-hydrogen, or elimination of the γ-hydrogen. The elimination of an α-hydrogen is more possible than that of a γ-hydrogen because of an increase in the acidity of the α-hydrogen according to the α-sulfonate electron-withdrawing property.

From the results of this experiment, the effect of sulfite pretreatment in oxygen-alkali cooking is acknowledged to some extent on the stabilization of carbohydrates rather than on the acceleration of lignin dissolution.

CONCLUSION

Two-stage cooking results in a rapid delignification rate within a comparatively shorter time than single-stage cooking. Also, sodium sulfite-alkali cooking shows a higher pulp yield with a lower lignin content than sodium bisulfite-alkali cooking because the former has many more sulfonic acid groups in pulp than in the latter.

It is, therefore, concluded that sulfonic acid groups introduced into a lignin molecule by sulfite pretreatment contribute to the acceleration of the delignification reaction because of their electron-withdrawing property.

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Table 1. Cooking Results of Beech Wood Meal by Single-stage and Two-stage Cookings.

Cooking Method	Compound	Temp. (°C)	Time (min.)	Yield (%)	Lignin (% on wood)	Dissolved Lignin (%)
Single-stage cooking	NaOH	120	120	68.3	18.69	27.64
		160	120	51.3	4.65	82.00
	O_2 - NaOH with $MgCO_3$	120	90	55.3	7.58	70.65
		160	120	42.1	2.93	88.66
Two-stage cooking	$NaHSO_3$ - NaOH	120	90	62.6	11.88	54.01
		160	90	49.6	3.60	86.06
	Na_2SO_3 - NaOH	120	90	61.3	11.19	56.68
		160	90	48.0	2.65	89.74
	Na_2SO_3 - O_2 - NaOH with $MgCO_3$	120	90	65.4	7.15	72.32

NOTE: Total lignin content in original wood meal is 25.83%.

DEGRADATION OF CHLORINATED LIGNIN AND CHLORINATED ORGANICS BY A WHITE-ROT FUNGUS

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ABSTRACT

Rotating Biological Contactor (RBC) treatment of E_1 effluent from a kraft bleach plant with a white-rot fungus (Phanerochaete chrysosporium) is shown to be effective for the removal of organically bound chlorine as well as color. Analysis of the change in the amount of total organic chlorine and inorganic chloride revealed that the conversion of organic chlorine into inorganic chloride results from the degradation of organic chlorine compounds in E_1 effluent.

INTRODUCTION

Since the late 1970's, North Carolina State University and the U.S.D.A.'s Forest Products Laboratory (Madison) have jointly studied the application of the lignin degrading ability of white-rot fungi to the removal of color from E_1 effluent. During this study, Huynh and co-workers (1) showed that chlorinated phenolic compounds can be modified or degraded by the fungus in the same manner as lignin or lignin model compounds. The similarity of lignin degradation mechanisms to the dehalogenation reactions known to be used by some other microorganisms (2) created an interest to learn more of the ability of white-rot fungi to degrade chlorinated organic compounds. The present report deals with the conversion of organically bound chlorine by fungal treatment of E_1 stage effluent.

EXPERIMENTAL

Measurement of the Concentration of Chlorine Species

The Schoniger combustion method was used for the measurement of total chlorine (TCl) according to the procedure developed by Sjostrom (3). Inorganic chloride (IOCl) was measured by employing a chloride specific electrode. Total organic chlorine (TOCl) was calculated by subtracting IOCl from TCl: (TOCl = TCl - IOCl).

Fungal Treatment of E_1 Effluent

Phanerochaete chrysosporium Burds (Me-446) was obtained from the U.S. Forest Products Laboratory and was cultured in Roux bottles to obtain the conidial inoculum. Fungal treatment of E_1 by the RBC was performed according to previously published procedures (4). During the decolorization (and dechlorination) stage, E_1 effluent was renewed every day. Treatment of E_1 in flask cultures was also performed according to previously published procedures (4). Every two days, the contents of three flasks were analysed.

RESULTS AND DISCUSSION

The removal of organically bound chlorine from the E_1 effluent results in a decrease in the amount of TOCl. If the removal of organically bound chlorine is based on the conversion of organic chlorine into inorganic chloride, an increase in inorganic chloride as well as a decrease in organic chlorine should be observed.

To evaluate the ability of white-rot fungi to remove organically bound chlorine from chlorinated organic compounds, the low molecular weight fraction of E_1 (MW < 1000), high molecular weight fraction of E_1 (MW > 1000), and unfractionated E_1 were subjected to fungal treatment using the RBC. Figure 1 shows the results for one day treatment using the RBC over three successive days. The removal of organic chlorine is clearly shown with an average removal rate of 62%, 43%, and 45% for low molecular weight E_1, high molecular weight E_1, and unfractionated E_1, respectively. Inorganic chloride as well as low molecular weight chlorinated compounds are thought to penetrate into the fungal cell; a portion of them may be excreted, while some may remain inside the cell. This will cause a change in the measured amount of total chlorine. Actually, in these experiments, the amount of total chlorine (TCl) was occasionally observed to change significantly before and after RBC-treatment. Although the removal of organically bound chloride from E_1 by RBC treatment was observed, the mechanism for the removal of organic chlorine remained uncertain.

To clarify the mechanism for the removal of organic chlorine, the penetration and excretion of chlorine species into the fungal cell had to be evaluated. To this end, fungal treatment of E_1 was performed in an Erlenmeyer flask without changing effluent throughout the fungal growth

and dechlorination stages (Figure 2). Thus, it is clearly shown that a decrease in the total organic chlorine is accompanied by an increase inorganic chloride. Because of the penetration of inorganic chloride into the fungal cell, the amount of total chlorine decreased in the first six days. After six days, however, when a rapid increase in the amount of inorganic chloride was observed, the amount of total chlorine gradually increased almost to the original level. The possibility still can not be excluded, however, that the accumulation of chlorinated organic compounds in the fungal body also contributes, to some extent, to the removal of organically bound chlorine. It can be concluded, though, that a major portion of the organically bound chlorine is converted into inorganic chloride by fungal treatment.

It is still unknown whether or not the conversion of organic chlorine into inorganic chloride is completely an enzymatically catalyzed process. It should be noted, however, that the lignin degradation reactions known for this fungus -- oxidation of side chains and oxidative cleavage of the aromatic moiety -- would assist in chlorine elimination as chloride. Some examples are known for the chlorine elimination reaction combined with oxidation reactions. Shimada (5) showed that a photo-oxidative treatment can effectively remove organic chlorine from E_1 effluent. As an example for biological oxidation, oxidative ring opening of 2,4-D (2,4-dichlorophenoxy acetic acid) catalyzed by some enzyme system (2) is known to be followed by a dechlorination reaction.

The formation of volatile chlorinated compounds by fungal treatment was not evaluated in this experiment.

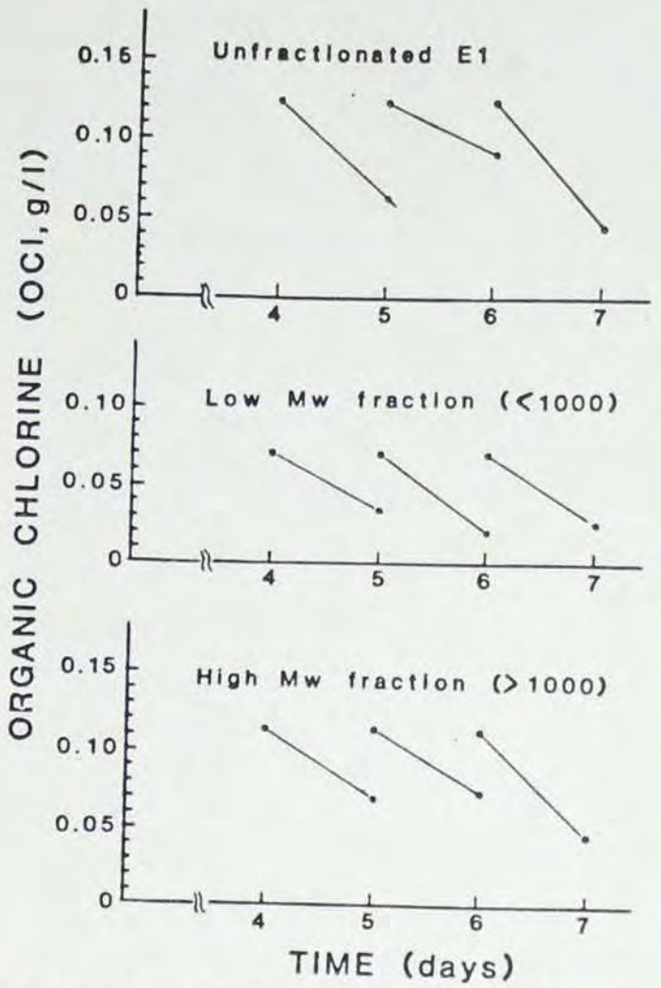

Fig. 1 Removal of organic chlorine from E_1 effluent by RBC treatment.

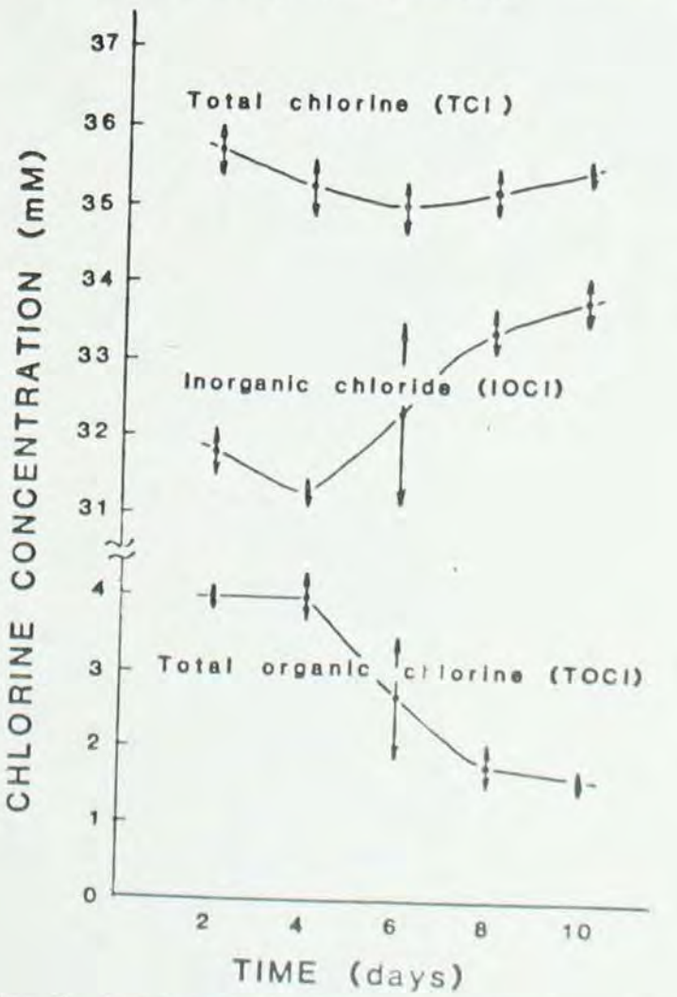

Fig. 2 Formation of inorganic chloride during fungal treatment.

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CATABOLIC SYSTEM OF LIGNIN-RELATED MODEL COMPOUNDS BY PSEUDOMONAS SP. TMY1009 STRAIN

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ABSTRACT

A bacterial strain TMY1009, which was able to degrade many types of lignin model compounds, were isolated. From the results of catabolic experiments by mutants of TMY1009, it was suggested that three different types of O-demethylating system and two different types of ring-cleaving system are related to the catabolism of lignin model compounds by TMY1009.

KEYWORDS: Pseudomonas, Lignin model compounds, Mutant, Biodegradation

INTRODUCTION

Recently, it have been confirmed that some bacterial strains are able to degrade lignin related polymers such as DHP and MWL (Crawford, 1981; Kern, 1984). However, the mechansim of bacterail degradation of lignin related compound have never been investigated in detail.

We have isolated a new bacterial strain TMY 1009, from FK-2 culture (Fukuzumi, 1977), which is able to degrade completely many types of lignin model compounds with major interlinkages of the C_6-C_3 unit in lignin. This bacterium is confirmed to be a closely similar strain to Pseudomonas paucimobilis by the cell form and physiological characteristics. We have started to investigate on detailed catabolic mechanism of lignin related compounds by TMY1009, and to determine the catabolic systems and pathways of monomeric and dimeric lignin model compounds, catabolic experiments by deficient mutnats of TMY1009 on a part of the catabolic systems have been undertaken.

PREPARATION OF MUTANTS

Mutant strains of Pseudomonas sp. TMY1009, which are unable to grow on the M9-agar plate containing 0.2 % of dehydrodivanillic acid (DDVA:I) as a sole source of carbon, were prepared by N-methyl-N'-nitro-nitrosoguanidine mutagenesis followed by penicillin-cycloserine screening in the M9 medium containing 0.2% of DDVA(I).

Four different types of mutants on dissimilating abilities were obtained.

Table 1 Dissimilating abilities of TMY1009 and derived mutants

Strain	Substrate			
	DDVA	VerA	VA	PA
TMY1009(wild)	++	++	++	++
TMY1014	-	++	++	++
TMY1015	+	++	++	++
TMY1017	-	+	+	-
TMY1018	-	+	-	++

++:completely dissimilated +: partialy dissimilated, -: not dissimilated

DISSIMILATION OF DERIVERTIVES OF BENZOIC ACID

TMY1009 is able to dissimilate completely all of DDVA(I), VerA(II), VA(III), and PA(IV), whereas mutant strains are unable to degrade a part of these compounds.

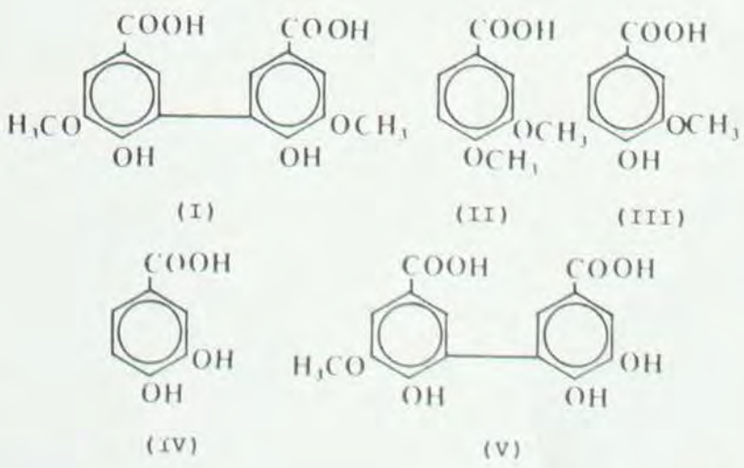
TMY1014 is unable to degrade entirely DDVA (I). However, this mutant can dissimilate completely VerA(II), VA(III), and PA(IV).

TMY1015 is also able to dissimilate completely VerA(II), VA(III), and PA(IV). Furthermore, this mutant converts DDVA(I) to 5-(2'-hydroxy-3'-methoxy-5'-carboxyl-phenyl)-vanillic acid(V).

Therefore, TMY1015 might be deficient on the ring-cleaving system of compound(V). On the other hand, TMY1014 might be deficient on O-demethylating system of DDVA(I) to compound(V).

TMY1017 can't degrade entirely PA(IV). However, this mutant is able to convert both VerA (II) and VA(III) to PA(IV). Therefore, this mutant lacks ring-cleaving system of PA(IV).

TMY1018 can't degrade entirely VA(III). However, this mutant dissimilates completely PA(IV) and converts VerA(II) to VA(III). Therefore, this mutant is deficient O-demethylating system



to VA(III).

RELATIONSHIP OF CATABOLISM BETWEEN DDVA(I) AND VA(III)

TMY1014 and TMY1015 are deficient on earier catabolic steps of DDVA(I). However, these deficiency dose not affect on the catabolism of VA(III), which is dissimilated completely in these mutants as same in the case of the wild strain(TMY1009). Therefore, the catabolism of VA (III) is considered to be independant from the catabolism of DDVA(I).

On the other hand, the catabolic deficiency of VA(III) in either TMY1017 or TMY1018 cause to repress the initiation of catabolism of DDVA(I). Although it is difficult to explain the reason of this phenomenon, the catabolic system of VA (III) might be related to the latter catabolic steps of DDVA(I) and affect the initiation of catabolism of DDVA(I).

These idea were further supported from the results of induction experiments by TMY1009 as shown in Table 2.

Table 2 Results of induction experiments in TMY1009

Inducer	Catabolism of DDVA	Catabolism of VA
DDVA	+	+
VA	-	+
None	-	-

+: induced, -: not induced

DDVA(I) induced both of catabolisms of DDVA (I) and VA(III). However, VA(III) dose not induce the catabolism of DDVA(I). These observation also suggested that the catabolism of VA (III) is independant from the catabolism of DDVA (I). On the other hand, the catabolism of DDVA (I) is closely related to the catabolism of VA (III).

O-DEMETHYLATING SYSTEM

Three different types of O-demethylating system might be related to the catabolism of lignin model compounds by TMY1009.

The first one is O-demethylating system of DDVA(I) to convert to compound(V). This system might be distinguished from both 4-O-demethylating system of VerA(II) and 3-O-demethylating system of VA(III), because TMY1014, which is deficient on O-demethylating system of DDVA(I), is able to degrade completely both of VerA(II) and VA(III).

The second system is 4-O-demethylating system of VerA(II). It is quite different system from the third system, 3-O-demethylating system of VA (III), because TMY 1018, which is deficient 3-O-demethylating system, can still convert VerA(II) to VA(III).

RING-CLEAVING SYSTEM

Two different types of ring-cleaving system are related to the catabolism of lignin model compounds by TMY1009.

The first one is the ring-cleaving system of compound(V). This system is clearly distinguished from the another ring-cleaving system of PA(IV) because TMY1015, which is deficient in the ring-cleaving system of compound(V), can degrade PA(IV) as same as the wild strain (TMY 1009).

CONCLUDING REMARKS

From the catabolic experiment by mutant strains derived from TMY1009, it is suggested that TMY1009 has three different types of O-demethylating system and two different types of ring-cleaving system on the catabolism of lignin model compounds. However, further investigations on enzymic levels will be required for final determination of these systems.

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^{13}C NMR of Lignocellulosics

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High resolution ^{13}C NMR of crystalline celluloses is both complementary and supplementary to x-ray diffraction analysis because it is effective for both crystalline and non-crystalline materials. Good spectral quality has been achieved for a range of cellulose samples and spectral elements related to lateral order are observed but interpretational details are still evolving.

The spectrum of a complex material such as wood, shows morphological and conformational features for each chemical component. The resolution achieved is sufficient to allow identification of carbohydrate resonances, methoxyl and aromatic resonances and carbonyl resonances of hemicellulose acetyls as shown below in Figure 1.

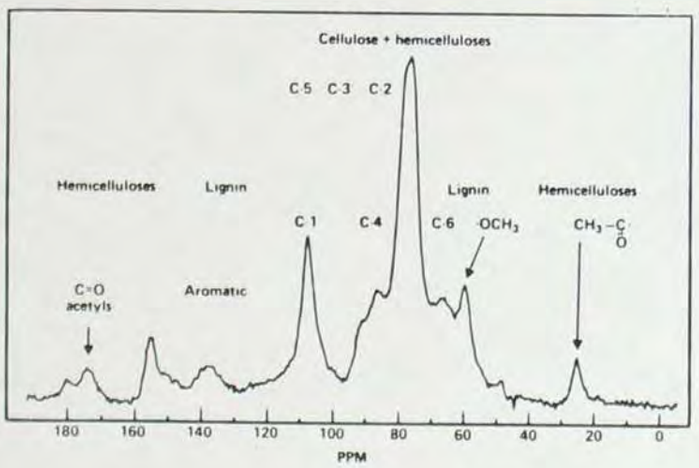

Figure 1. ^{13}C NMR of solid ash wood

The effect of solid state chemical treatments such as acetylation and prehydrolysis are readily detected. The use of interrupted decoupling allows one to separate some of the lignin and carbohydrate components in the spectra. This technique is illustrated in Figure 2.

The potential of the technique for rapid ^{13}C analysis of paper and other composites is now becoming well-established. More complex biosubstances such as grasses, bark and plant cell wall are being molecularly examined in their true nascent state for the first time. In this paper, a series of spectra are presented covering various physical states of Esparto grass: native, holocellulose, alkali extracted and pulp. These spectra are shown in Figure 3.

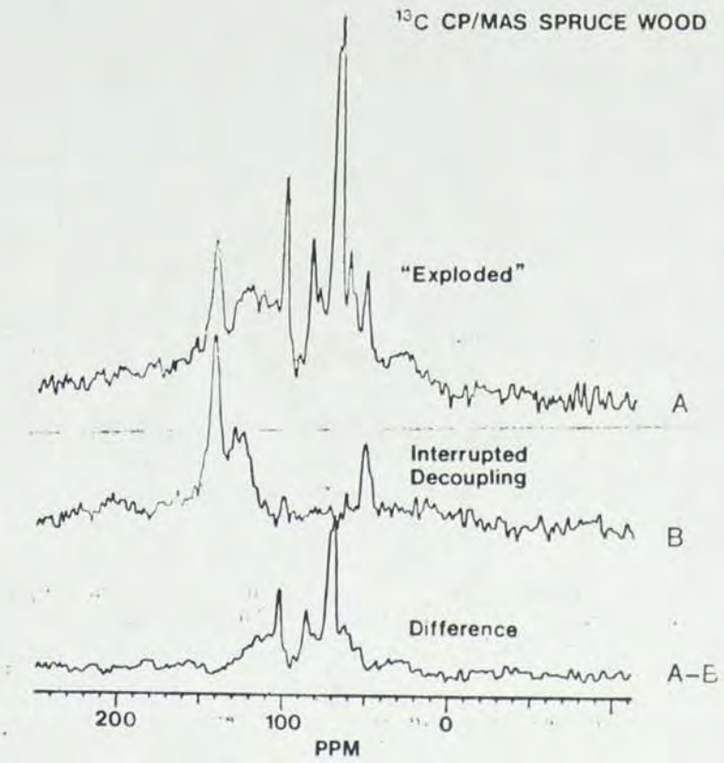

Figure 2. ^{13}C CP/MAS NMR spectra of 'exploded' spruce wood. Spectrum A is the normal spectrum, while spectrum B was obtained using the interrupted decoupling technique.

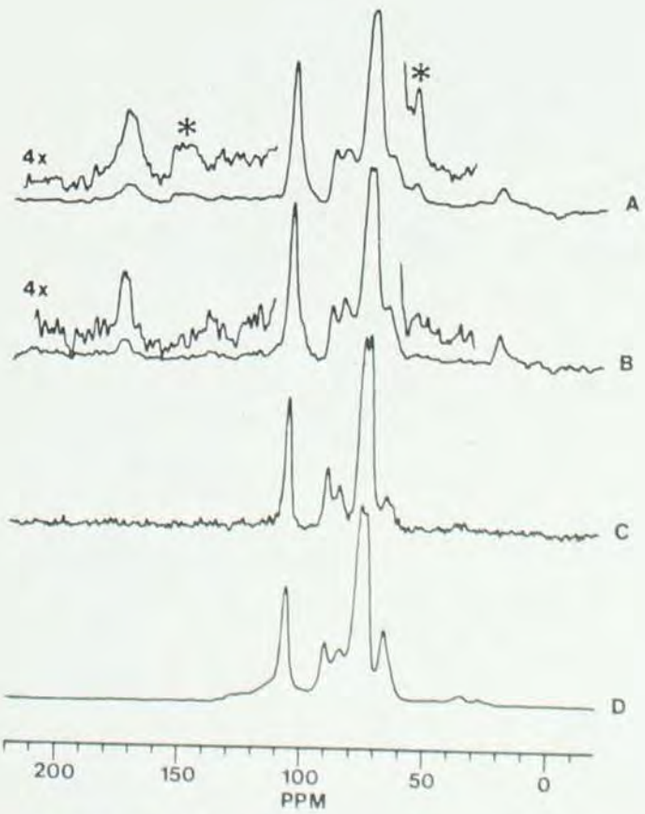

Figure 3. ^{13}C CP/MAS NMR spectra of Esparto grass derived samples. Spectrum A corresponds to the native material after ethanol/benzene washing. Spectrum B is chlorite holocellulose. Spectrum C is holocellulose extracted with 1% NaOH. Spectrum D is a commercial Esparto grass pulp.

The xylan component extracted form the grass is also examined in dry and hydrated states (cf. Figure 4.).

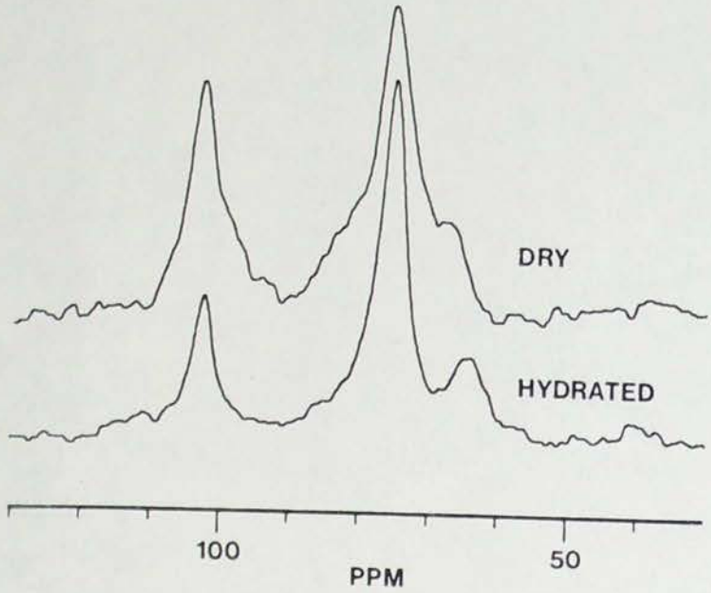

Figure 4. ^{13}C CP/MAS NMR spectra of Esparto grass xylan corresponding to the "dry" and "hydrated" polymorphs.

The line broadening effect of the latter on the C-1 resonance of the cellulose, as illustrated in Figure 5, demonstrates the difficulty in interpreting the effects of fine structure vs. heterocomposition

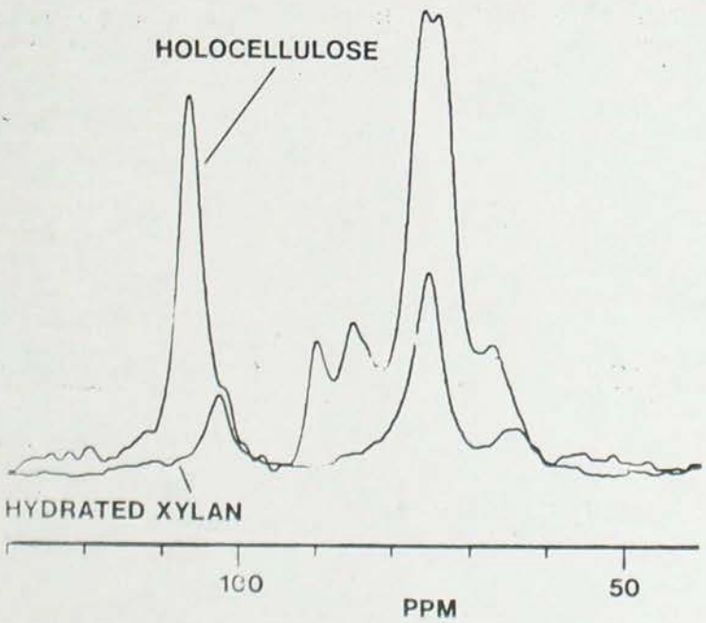

Figure 5. ^{13}C CP/MAS NMR spectra of Esparto grass holocellulose and hydrated xylan.

ULTRASTRUCTURAL MODIFICATIONS OF WOOD AFTER DEGRADATION BY SPOROTRICHUM PULVERULENTUM AND ITS MUTANTS

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KEYWORDS : Wood ultrastructure, white rot fungus cellulose-hemicellulose-lignin associations.

Modifications of the ultrastructure of samples of spruce wood which had been submitted to the action of the white rot Sporotrichum pulverulentum and two of its mutants were studied by electron microscopy. Comparison of the images observed on the undegraded wood, the wild type and the cellulase less-mutant degraded wood provided information on the mode of action of the fungus but also on the distribution and association of cellulose, hemicellulose and lignin at the microfibrillar level.

Wood degradation by white rot fungi involves the combined action of lignin degrading enzymes and polysaccharide degrading enzymes. The enzymic equipment of Sporotrichum pulverulentum and of some of its mutants has been studied by Eriksson et al (1). The ultrastructural modifications resulting from the fungus action has been shown to be mainly located in the S_2 layer (2). In order to study the proper action of each of the different enzymes acting on the main polysaccharide constituents of the wood, we used two genetic mutant strains lacking cellulase activity, and a catabolically repressed strain having lost its cellulase and hemicellulase activities. In order to visualize the removal or degradation of the different cell wall polymers, specific markers were used. Lignin was stained by permanganate and the hemicelluloses were identified by two newly developed techniques. Both techniques involve the use of a purified enzyme corresponding to the polysaccharide to be identified. In the first one, enzyme-gold complexes were prepared (3) and were applied to the ultra-thin sections. In the second, a slight enzymic hydrolysis of the polysaccharide-substrate was performed directly on the ultra-thin section followed by silver st aining of the newly created reducing ends (4).

From the images obtained with the wild-type strain, it appears that the fungal degradation starts from the lumen by lysing the transition zone between S_2 and S_3 without any degradation of S_3. As a result S_3 is detached from S_2. Then S_2 undergoes important damages (bore holes) before being split from S_1 which is degraded later. The most resistant parts are the cell corners.

The pattern of propagation observed with the mutants which lack cellulase activity differs in that no large holes are visible in the wall. Instead a loose "treillis" is apparent in S_2. In order to characterize the exact nature of this undegraded material the specific markers were applied. It could then be demonstrated that even at the level of the thinnest fibrillar elements, glucomannans and xylans were still present. As shown by shadowing and by "low dose" observation the fibrillar network was identified as primarily constituted of cellulose. Although the modified fungus strain was reported to be cellulase-less, it is clear from the electron diffraction diagram that the fibrillar material lost most of its characteristic crystallinity. These images are interpreted in terms of ultrastructural relationship between cellulose-hemicellulose and lignin at the microfibrillar level.

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CHARACTERISATION OF LIGNIN STRUCTURES IN WHOLE WOOD BY CARBON-13 CP/MAS NUCLEAR MAGNETIC RESONANCE

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ABSTRACT

A spin-locking pulse sequence has been combined with digital resolution enhancement to improve details in solid-state NMR spectra of wood. The procedure has provided estimates of syringyl/guaiacyl ratios, the extent of β-O-4 etherification and lignin/tannin ratios for several hardwoods and softwoods.

KEYWORDS: Nuclear magnetic resonance, lignin, tannin.

INTRODUCTION

Carbon-13 CP/MAS NMR spectroscopy allows characterisation of lignin in solid wood, avoiding the risk of chemical modification that accompanies extraction. Lignin signals form an almost continuous band from the cellulose signals to about 155 ppm. We have tried to resolve this continuity by using a spin-locking pulse sequence to extract specific signals from the band. This involves insertion of a delay (τ) between cross polarisation and data acquisition. The carbon transmitter power is adjusted to spin-lock magnetisation from non-protonated carbon, methyl and methoxyl groups. Signals from rigid CH and CH_2 groups do not survive this treatment, because of strong C-H dipole-dipole interactions.

EXPERIMENTAL

Wood chips were packed in a Kel-F rotor and spun at 2.5 kHz in the magic-angle spinning probe of a Varian XL-200 spectrometer, for NMR at 50.3 MHz. Each 1 ms contact time was followed by the delay τ, 20 ms of data acquisition, and a delay of at least 0.2 s to allow for recovery of the proton magnetisation. Between $3x10^4$ and $2x10^5$ transients were averaged. A nominal value of τ=1 ms was used for routine spectra. Lorentzian-to-Gaussian transformations were used for resolution enhancement (1).

RESULTS

The broken line in Fig. 1 marks a common baseline for both curves.

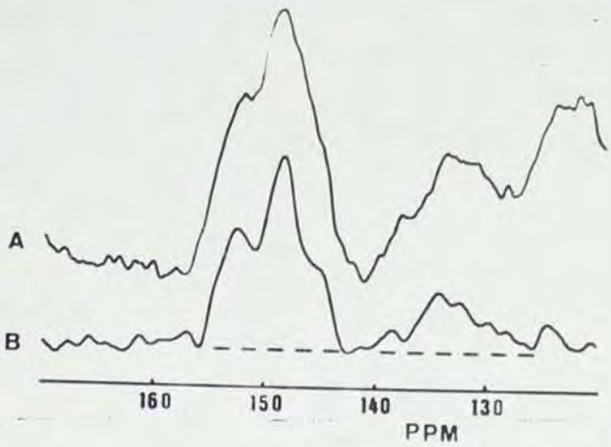

Figure 1. Carbon-13 CP/MAS NMR spectra of Pinus radiata wood: (A) normal spectrum, (B) with spin locking and resolution enhancement.

unit	C-1	C-3	C-4	C-5
S^e	134	153.4	137	153.4
S^f	133	147.8	138	147.8
G^e	134	148.4	152.7	-
G^f	133	148	145.5	-
H^e	?	-	163	-
H^f	?	-	158	-

Table 1. Chemical shifts (ppm from TMS) averaged over several samples.

S,G and H units

Relative contributions from syringyl (S), guaiacyl (G) and p-hydroxyphenyl (H) units can be estimated from the spectra by: (a) measuring the ratio of signal areas assigned to methoxyl and aromatic carbon, or (b) computer simulation of the region from 125 to 165 ppm. The results from method (a) show a strong dependence on τ, and must be extrapolated back to τ=0. Both methods must include corrections for intensity lost in spinning sidebands.

Methods (a) and (b) gave S/G=5 and S/G=4 (respectively) for wood from Eucalyptus regnans. Bland (2) found S/G=3.7-4.4 for wood from the same species, based on nitrobenzene oxidation.

Method (b) gave S/G=0.5 for wood from Pseudowintera colorata (fig. 2). This is unusually low for a hardwood, but consistent with published values of 0.53 (by acidolysis) and 0.56 (by permanganate oxidation) for wood from the same species (3).

Our results therefore support the reliability of chemical procedures for estimation of S/G.

A spectrum of a softwood showed a weak signal assigned to H units (Fig. 3B). Spectra of two monocotyledons (bamboo and Cordyline australis) showed only signals from G and S units.

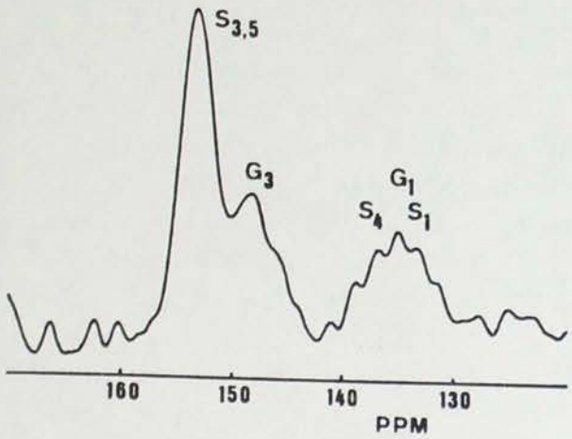

Figure 2. Carbon-13 CP/MAS NMR spectra of Pseudowintera colorata wood.

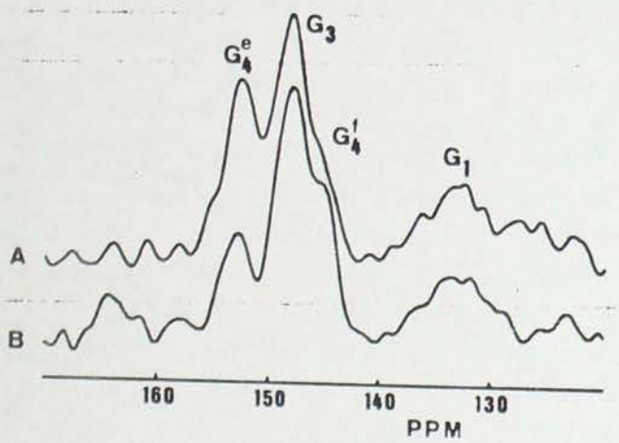

Figure 3. Carbon-13 CP/MAS NMR spectrum of wood from two rimu (Dacrydium cupressinum) trees.

Etherification

Structures with ß-0-4 ether linkages are labelled S^e, G^e and H^e in Table 1. Structures lacking this linkage are labelled S^f, G^f and H^f. Fig. 3 shows that the extent of etherification can vary from sample to sample, even within a species.

Lignin/tannin ratios

Condensed tannins contribute signals at 145 and 155 ppm. In the case of pohutukawa wood (fig. 4), simulation of the NMR spectrum gave a lignin-tannin ratio of 2.5 (by weight). Some of the tannin was extracted by refluxing ethanol, but most ended up in Klason "lignin". In our surveys of Eucalyptus and Nothofagus species we found particularly low lignin/tannin ratios for E. botryoides and N. fusca.

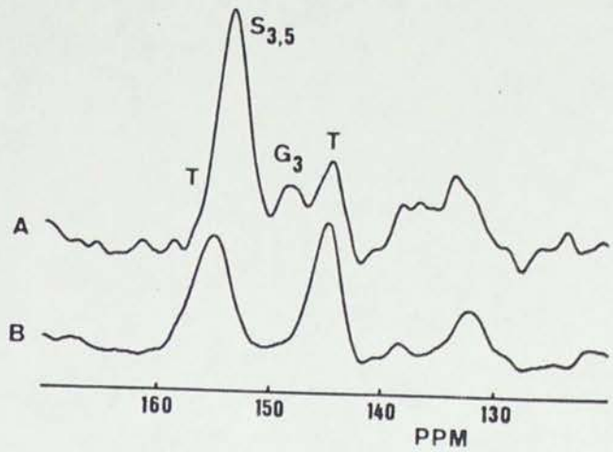

Figure 4. Carbon-13 CP/MAS NMR spectra of (A) pohutukawa wood (Metrosideros excelsa), (B) tannin extracted with acetone/water at 20°C.

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ENZYMATIC HYDROLYSIS OF PRETREATED WOOD TO FERMENTABLE SUGARS USING CELLULASES FROM TRICHODERMA HARZIANUM

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ABSTRACT

During the last six years the Biotechnology and Chemistry program at Forintek has looked at the overall process of converting wood residues into higher value products. Initially a variety of chemical methods of hydrolysis including hydrofluoric acid and organosolv were compared with various enzymatic hydrolysis methods associated with different pretreatment procedures. A preliminary economic study indicated that all of the three major wood components, i.e. lignin, hemicellulose and cellulose have to be used if the conversion of wood to fermentable sugars is to become a commercially viable process. Steam pretreatment proved to be an excellent method for fractionating wood into its three components as well as considerably enhancing the efficiency of enzymatic hydrolysis.

In all of the processes which hope to produce ethanol and other liquid fuels from wood residues using enzymatic hydrolysis the most expensive step has been shown to be the production of the cellulase enzymes. It is this requirement for an active cellulase complex acting at optimum conditions on a wide range of cellulosic substrates which has severely curtailed the application of bio-conversion processes based on enzymatic hydrolysis. The wood decay fungi have proven to be among the most cellulolytic organisms with relatively few cellulolytic bacteria so far identified. A comparison of cellulolytic fungi and bacteria isolated on field trips and available from culture collections indicated that fungi were generally 100-1000 times more hydrolytic than the most active cellulolytic bacteria. This higher activity was mostly due to the greater amount of extracellular protein secreted by the fungi. Most of the bacteria secreted an incomplete cellulase complex which could only hydrolyse highly modified substrates such as filter paper and carboxymethyl cellulose. When the overall hydrolytic activity of the fungal and bacterial systems were compared it was found that the majority of the complexes were deficient in one or more of the endoglucanase, exoglucanase or ß-glucosidase components. Apart from the deficiencies that were apparent in the methods for assaying for individual and collective cellulase activities, other factors such as the half-life of the enzymes, enzyme regulation, growth of the organism, etc., all significantly affect the way in which the hydrolytic potential of the various microorganisms could be measured.

A screening of isolates from various culture collections indicated that there were some naturally occurring strains of cellulolytic fungi which appeared to be as hydrolytic as the various Trichoderma reesei mutants used by other groups. We compared the various enzyme activities of T. reesei C30 with one of the strains from our culture collection, T. harzianum E58, which was known to be highly hydrolytic. T. reesei C30 produced considerably more extracellular protein indicating that the high hydrolytic activity of the culture filtrates was probably due to more enzyme being present. When the culture filtrates from the two fungi were used to hydrolyze a range of pretreated wood substrates comparable reducing sugar values were obtained. There was a major difference however in the proportion of glucose that was obtained. The higher ß-glucosidase activity of T. harzianum culture filtrates was reflected by the fact that the majority of the sugar was detected at glucose.

Although we were able to increase the efficiency of hydrolysis compared to that achieved with some of the earlier T. reesei mutants we have not been able to substantially increase the specific activity of the cellulases. The term specific activity is used here to mean the amount of extracellular protein required to hydrolyse a stated amount of cellulose. Previous attempts at increasing the efficiency of cellulose hydrolysis have primarily concerned themselves with increasing the productivity of the strains or at increasing the amount of extracellular protein. Although these higher values have significantly increased the efficiency of hydrolysis it is unlikely that these very high levels of extracellular protein can be increased much more than the levels of approximately 40 mg/mL reported by some workers. It is apparent that before enzymatic hydrolysis of cellulose to glucose can be expected to be competitive with other sources of sugar it is important that we fully understand the nature of the synergistic action of cellulase hydrolysis and, more importantly, substantially increase the specific activity of the cellulase enzymes.

STUDIES OF THE IMPREGNATION OF BIRCH USING SCANNING ELECTRON MICROSCOPY AND ENERGY DISPERSIVE X-RAY ANALYSIS

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ABSTRACT

A method of determining the amount of sodium sulphite at any given position in a wood sample has been developed. Birch wood was impregnated with sodium sulphite under varying conditions. The amount of sodium and sulphur that enters the wood longitudinally was measured at different distances from the ends of the samples with a scanning electron microscope equipped for energy dispersive x-ray analysis. The sulphur content was determined as a function of the distance from the ends for the various morphological regions.

The distribution of sodium and sulphur obtained by this method of analysis showed good correlation to those obtained for sulphur by ion chromatography and for sodium by atomic absorption spectroscopy.

INTRODUCTION

Chemithermomechanical pulps, CTMP produced from chips that have been given a mild treatment with sodium sulphite are being used in fluff, tissue and paperboard products [1], whereas chemimechanical pulps, CMP produced from chips treated with sodium sulphite to high sulphonate content are used as a reinforcement component in newsprint [2]. The development of desirable strength and optical properties of CTMP and CMP requires good impregnation and distribution of sodium sulphite solution in the wood chips prior to sulphonation and subsequent disc refining. Poorly impregnated chips will contain a significant amount of untreated wood which can produce a pulp containing large proportion of stiff, shortened fibres that form weak interfibre bonds. Since sodium sulphite is a mild bleaching agent, poor impregnation can also cause low pulp brightness.

Tracer techniques with radioactive isotopes have been used in laboratory studies to evaluate the impregnation of pulping chemicals during chemical pulping [3-5] and chemimechanical pulping [6]. In addition, x-ray fluorescence has been used to study chip impregnation with sodium sulphite in the production of CMP [7]. Although these methods can be used to study chip impregnation on a macroscopic scale, they cannot be used to determine the distribution of chemicals in the various morphological regions of wood.

Scanning and transmission electron microscopy have been used to study the anatomy and morphology of wood [8,9], and in combination with energy dispersive x-ray analysis have been used to determine the distribution of chemicals in the different morphological regions of wood [10,11]. The aim of this study has been to develop a method of determining the distribution of chemicals such as sodium sulphite in wood chips as a function of distance of penetration, as well as the relative distribution of chemicals in the various types of cells in wood.

EXPERIMENTAL

The impregnation experiments were carried out on sawn samples of white birch, Betula papyrifera with dimensions 30 x 10 x 7 mm in the axial, tangential and radial directions respectively, as shown in Figure 1. The samples were steamed at 100°C for either 10 or 15 minutes and immediately immersed into 126 g/L sodium sulphite solution for 15 minutes at room tempera-

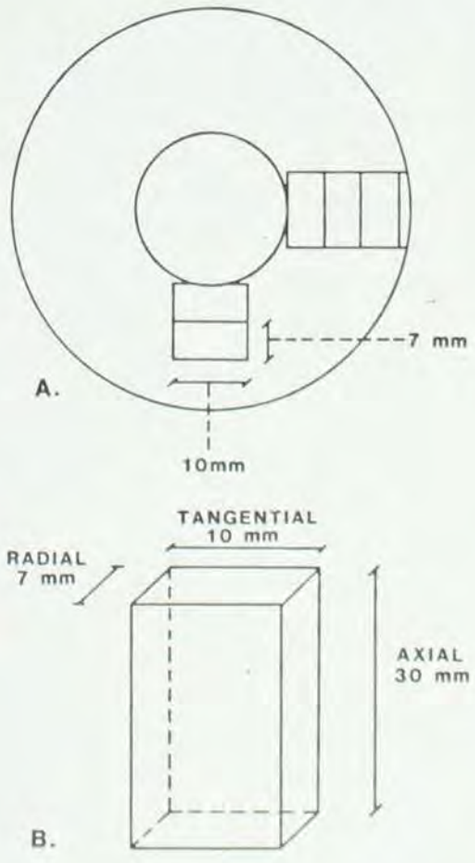

Figure 1. A. Position of samples for impregnation in transverse projection of birch log.
B. Dimensions of sample for impregnation studies.

ture. Excess solution was drained and free solution on the outside of the sample was removed by wiping. Thermal post-treatments were carried out by on some samples by heating the impregnated samples at 80°C or in saturated steam in an autoclave at 120°C for 25 minutes.

The radial and tangential sides of the wood block were cut with a Reichert "Om E" sledge microtome to give a sample from the centre of the impregnated block with dimensions of 30 x 2.5 x 2.5 mm in the axial, radial and tangential directions respectively, as shown in Figure 2. Thus, the effects of diffusion of sodium sulphite from the tangential and radial directions were excluded and the transport of sodium sulphite into the wood primarily through the cavities in the wood structure in the longitudinal direction was observed. Immediately after cutting, the samples were frozen in liquid nitrogen to avoid further changes in chemical distribution. The samples were then freeze dried, mounted on carbon stubs and coated with carbon for examination by scanning electron microscopy and energy dispersive x-ray analysis of sulphur and sodium.

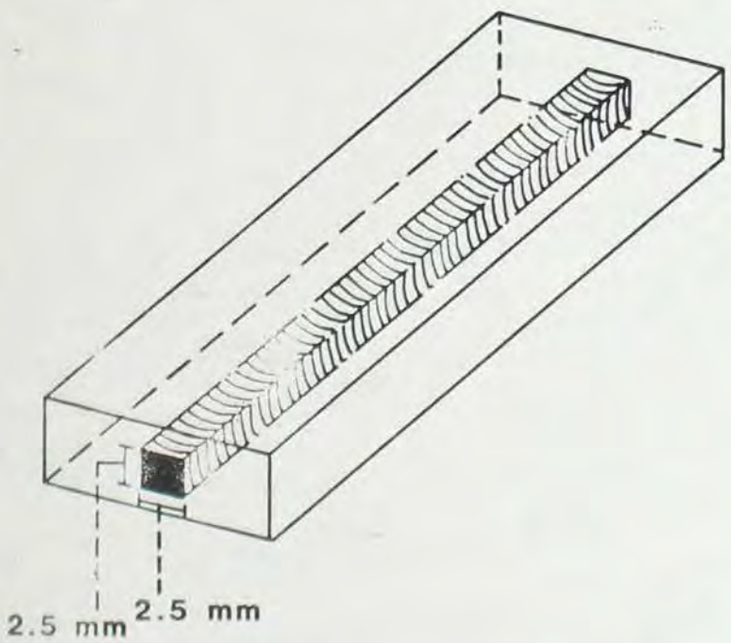

Figure 2. The centre of the sample examined by SEM-EDXA.

Sulphur and sodium distributions were determined with a Princeton Gamma Tech. System III x-ray analyzer together with an Akashi DS 130 scanning electron microscope. When the sample was bombarded with electrons in the sample chamber of the microscope, x-rays at energies characteristic of sulphur and sodium were emitted, collected and displayed as an energy dispersive x-ray spectrum as shown in Figure 3. The x-ray counts in the spectral windows corresponding to sodium and sulphur were divided by x-ray counts arising from background radiation in the window corresponding to chromium. In this manner, a sodium and sulphur content of the wood independent of the surface roughness and microsope magnification was obtained.

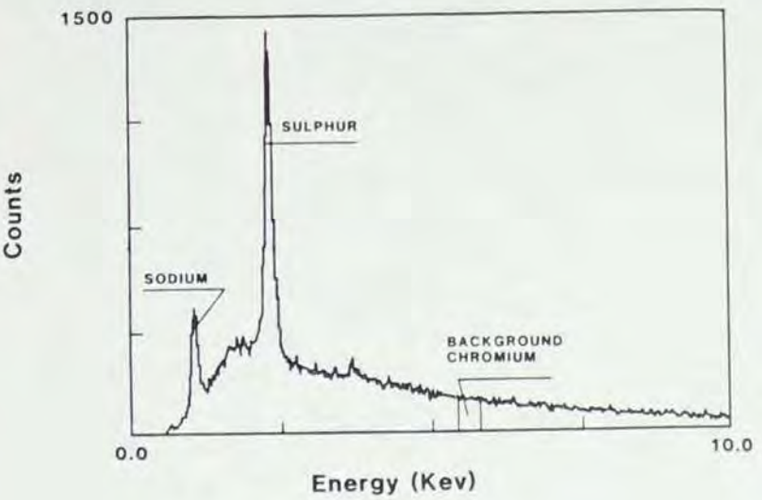

Figure 3. EDXA spectra of birch wood impregnated with sodium sulphite.

The distribution of sulphur and sodium as a function of sample penetration was determined by collecting x-ray counts for 100 seconds every 5 mm along the sample using a microscope magnification of 40 times. A magnification of about 230 times was used to determine the degree of impregnation in different types of cells using a "selected area system" in the equipment that made it possible to choose fully opened cells with clean surfaces. The readings from different morphological parts are mean values of readings of several cells of the same type at the same distance from the end of the sample. As seen in Figures 4 and 5, all measurements of

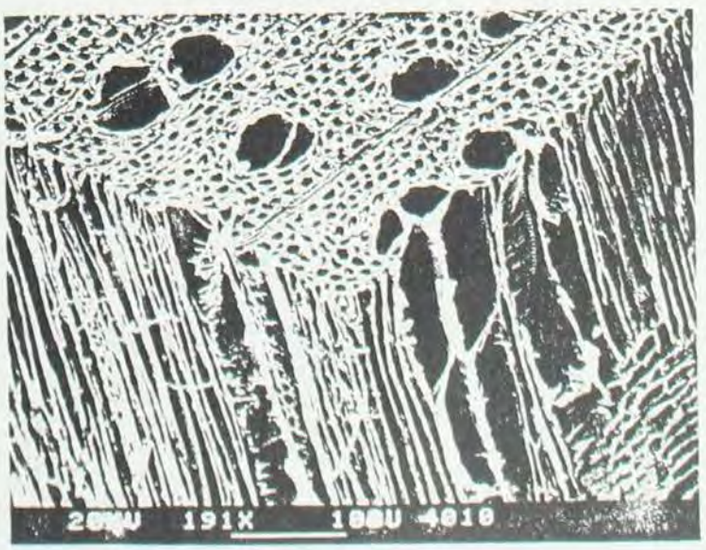

Figure 4. Three dimensional view of birch sample.

different cells were made from the radial side of the sample to expose all different cell-types in one plane.

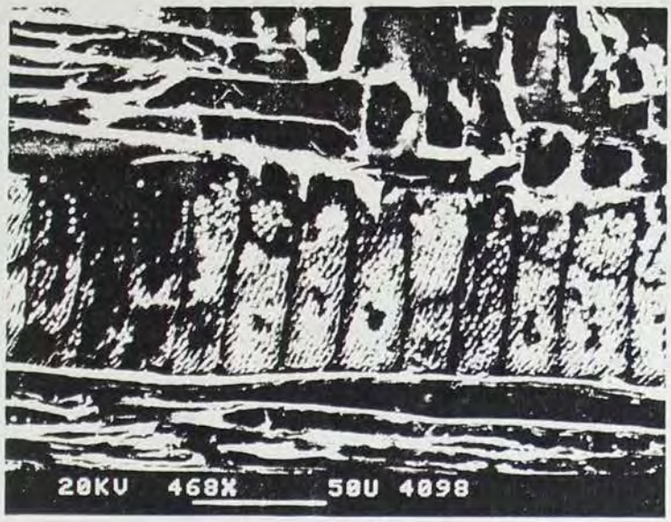

Figure 5. Radial side of birch sample showing vessel, ray and libriform cells in one plane.

RESULTS AND DISCUSSION

As seen in Figure 6, sodium sulphite is distributed throughout the length of the sample. A fairly even distribution of both sulphur and sodium is seen; the amount of sulphur in the middle of the sample being about 80 per cent of that found at the ends.

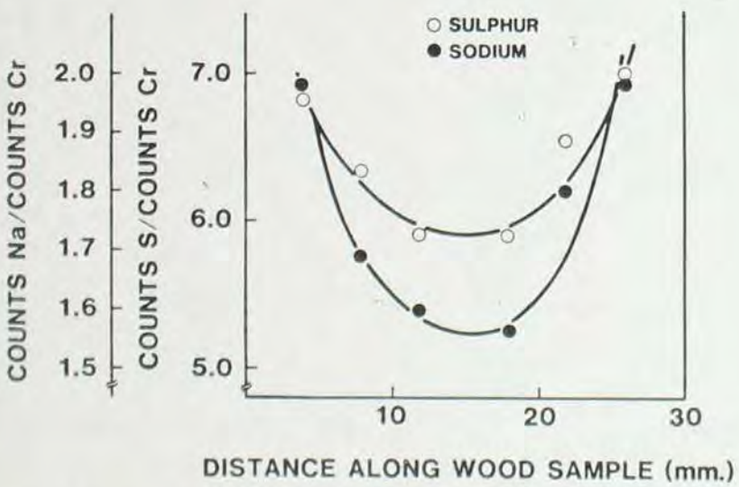

Figure 6. The content of sulphur and sodium in birch impregnated with sodium sulphite decreases toward the middle of the sample.

Sulphur and sodium distribution in wood samples previously analyzed by SEM-EDXA were determined by ion chromatography and atomic absorption spectroscopy respectively. The sample was divided into 5 pieces for analysis of sulphur by ion chromatography and into 9 pieces for analysis of sodium by atomic absorption spectroscopy. Figures 7 and 8 show that there is excellent correlation between values obtained by SEM-EDXA and those from ion chromatography and atomic absorption spectroscopy.

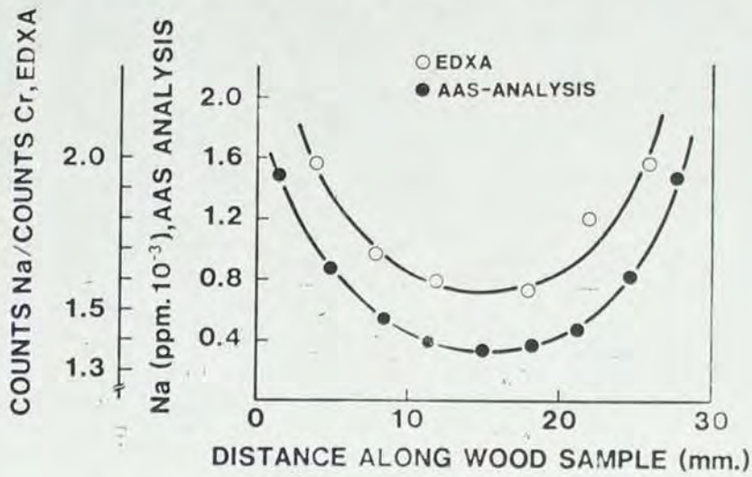

Figure 7. The distribution of sodium determined by SEM-EDXA is the same as that determined by atomic absorption spectroscopy.

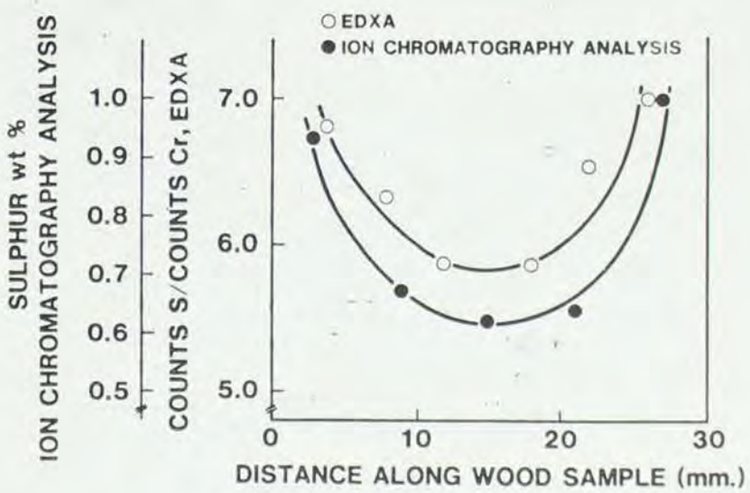

Figure 8. Relative sulphur distribution determined by SEM-EDXA is the same as that determined by combustion followed by ion chromatography.

In order to determine whether the mechanical action of the microtome knife changed the distribution of chemicals in the sample, a wood block twice as long as normal (60 mm) was impregnated and then divided into two 30 mm samples each with one end from the middle of the original sample. These samples were cut with a microtome each in different directions; one from the middle to the end and the other from the end to the middle of the original 60 mm sample. Figure 9 shows that sectioning impregnated wood samples with a microtome does not significantly change the distribution of sodium sulphite.

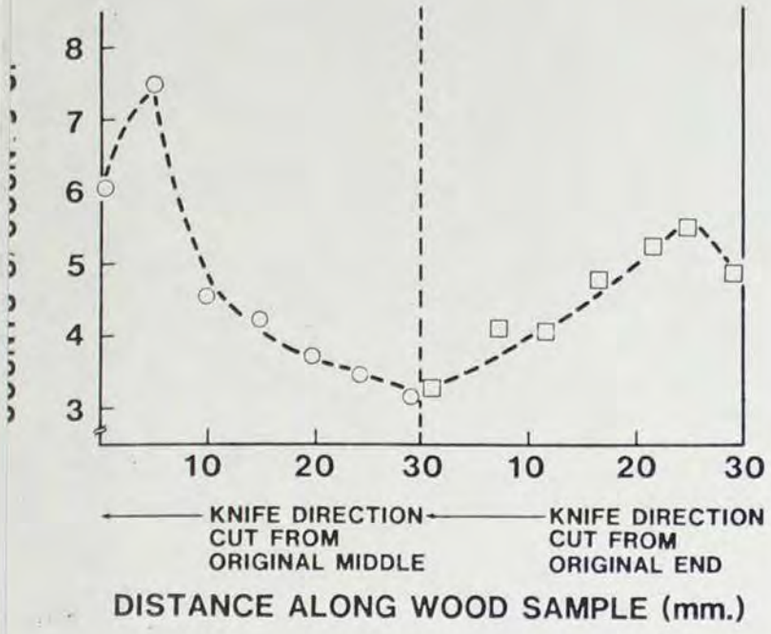

Figure 9. Microtome knife direction has no effect on the distribution of sodium sulphite.

Energy dispersive x-ray analysis was used to study the effect of moisture content of wood, steaming time, pH of sodium sulphite solution and thermal treatment of impregnated samples on the distribution of chemical in the wood samples. The initial moisture content and steaming time determine both the extent of impregnation and the distribution of sodium sulphite in the wood, as seen in Figure 10.

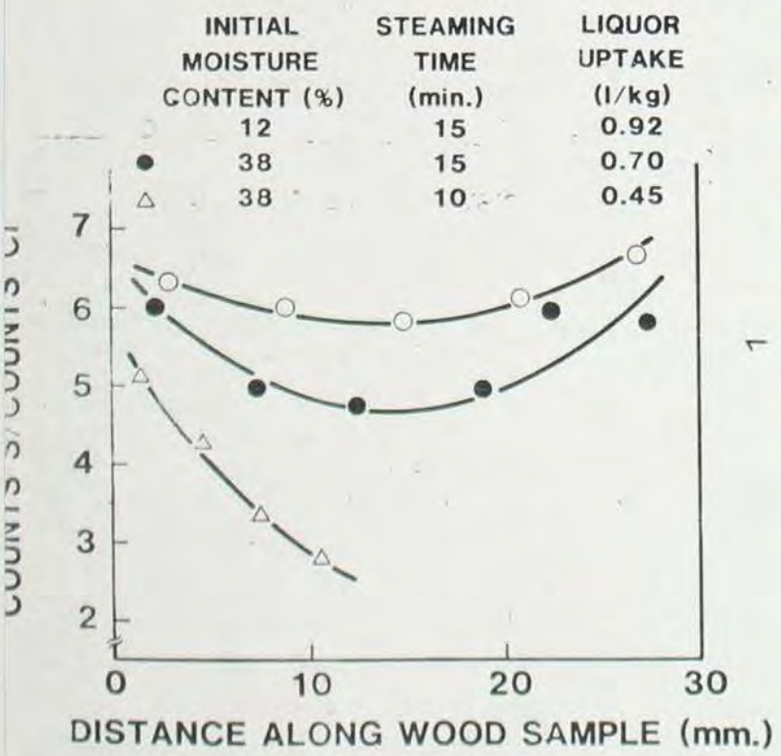

Figure 10. Decreasing the moisture content of wood and increasing the time of steaming from 10 to 15 minutes increases the amount of chemical penetration into the wood.

Decreasing the moisture content from 38 to 12 per cent increases the amount of sodium sulphite transported into the chips from 0.70 to 0.92 L/od kg of wood and also increases the uniformity of chemical distribution in the wood. Steaming time appears to have a greater affect on the degree of uniformity of impregnation of wood with sodium sulphite solution. Decreasing the steaming time from 15 to 10 minutes decreases the amount of sodium sulphite solution transported into the wood from 0.70 to 0.45 L/od kg of wood. This decrease is accompanied by a large decrease in sodium sulphite in the centre of the sample.

Heating impregnated wood above water at 80°C for 25 minutes has only a small effect on the distribution of sodium sulphite, as seen in Figure 11. When the thermal treatment of impregnated wood was carried out at 120°C, the distribution of sulphite, as shown in Figure 12 was the same throughout the length of the sample. Therefore, the uneven distribution of sodium sulphite can be equalized after impregnation by steaming at 120°C.

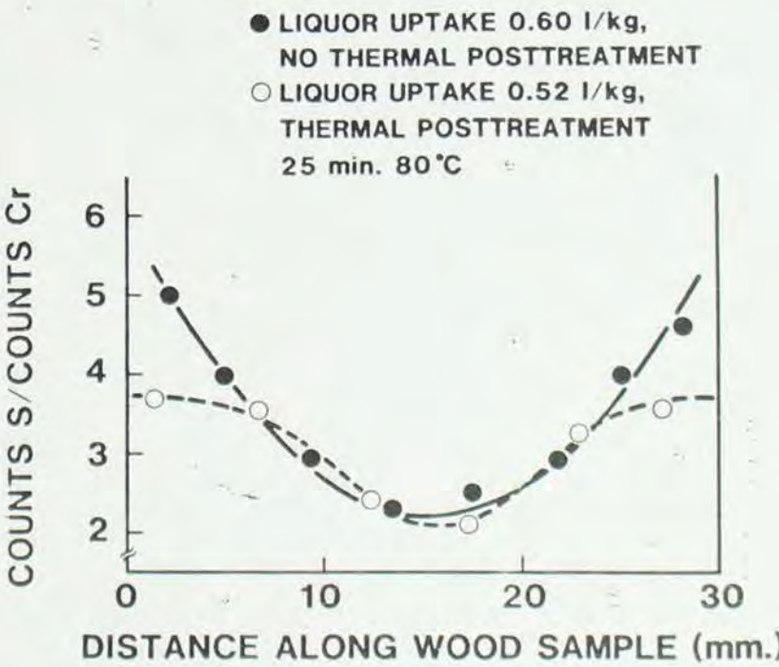

Figure 11. Heating to 80°C after impregnation has little effect on the sulphite distribution in birch.

As seen in Figure 13, changing the pH of the sodium sulphite solution in the range 4 to 12 has no significant effect on the distribution of sulphur in the longitudinal direction of wood.

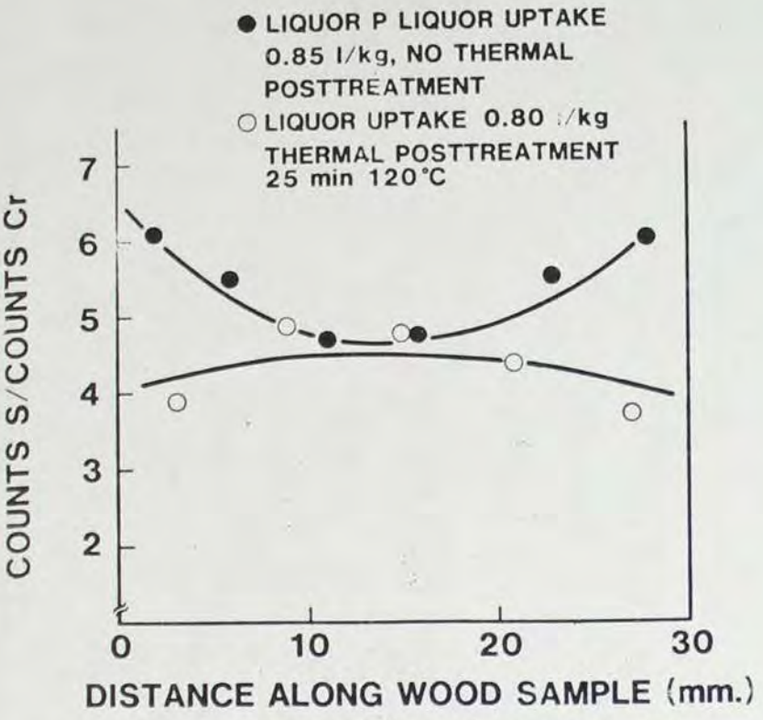

Figure 12. Heating birch impregnated with sodium sulphite to 120°C increases the sulphite content in the centre of the wood sample to the same level as the ends.

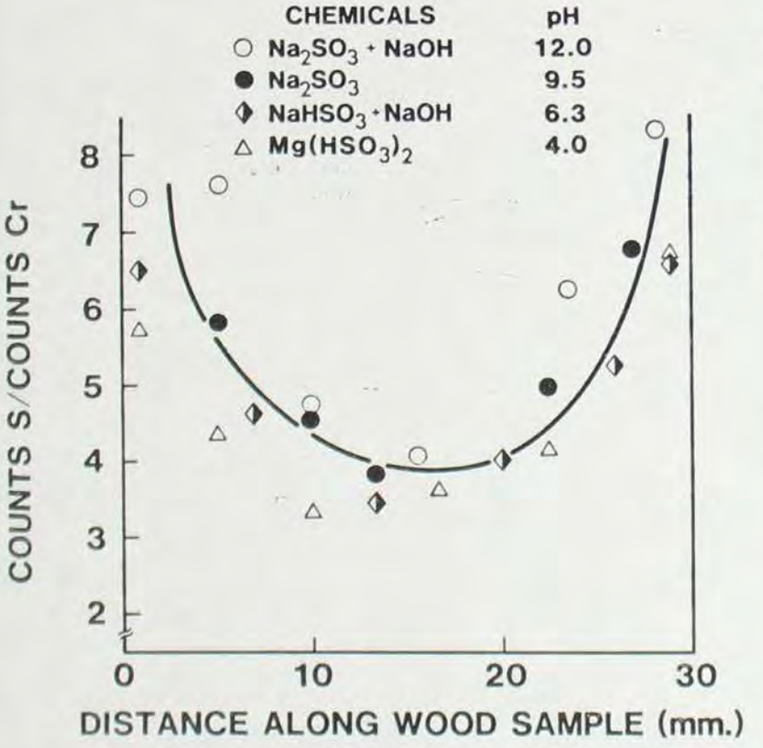

Figure 13. The pH of the sodium sulphite solution has no significant effect on sulphite distribution.

Stone and Green [13] have shown that the penetration of chemical solutions into hardwood samples occurs via the vessels. They have postulated that transport of chemical from the vessels into the surrounding libriform cells occurs by diffusion. As shown in Figure 14, analysis of EDXA at high magnification, of the different types of cells in the impregnated samples indicates a uniform distribution of sodium sulphite in the ray and libriform cells and a slightly higher sodium sulphite content in the vessels at a constant distance from the end of the sample.

It should be noted that small differences in the sulphur content may be masked by limitations in the resolution of this technique. Although one cell type was exposed to the electron beam on the sample surface, electrons scatter as they penetrate the sample. For example, under the experimental conditions used, x-rays are likely to be generated from regions more than 30 μm from the surface being examined. Since the average diameter of birch fibres is about 18 μm, the sulphur content determined for one morphological region will include a contribution from an adjacent morphological region.

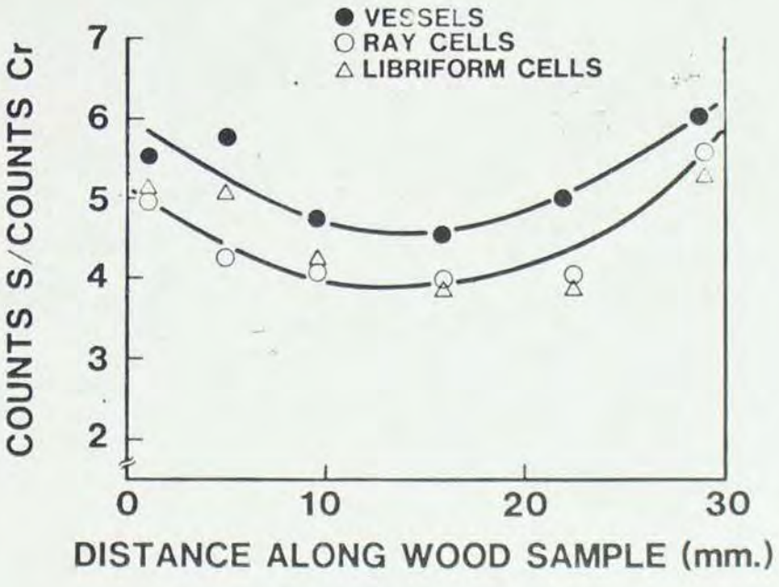

Figure 14. For a given set of impregnation conditions the relative distribution of sulphite ion as a function of distance from the sample end is about the same for ray and libriform cells. The sulphite content of the vessel cells is slightly higher than those of the ray and libriform cells.

There are extensive pit regions in the vessel ray cell contact areas shown in Figure 15 and a considerable number of pits connecting the ray cells to each other as seen in Figure 16 [9]. Figure 17 shows that although the libriform cells have less pits, most of them are concentrated in the tapered ends of the cells that are adjacent to the ray cells. Therefore, it is likely that much of the initial impregnation of birch wood occurs via liquid flow of sulphite solution from the vessels through the ray cells into the libriform cells by means of the pits.

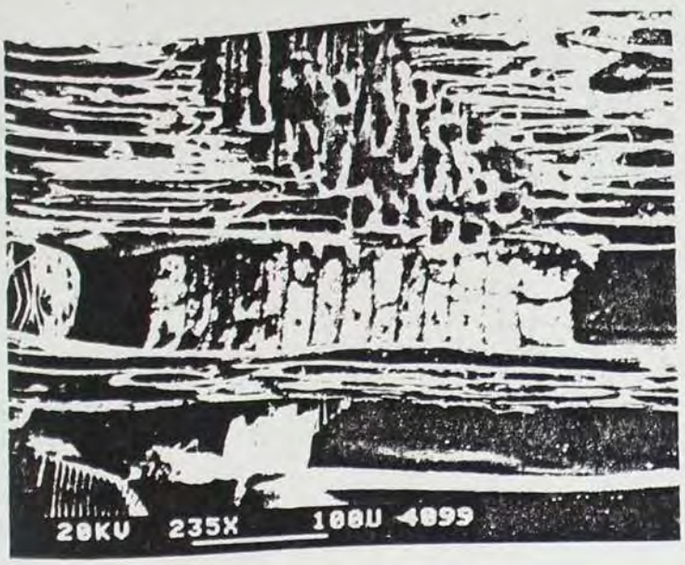

Figure 15. The pit region in vessel cell connecting to ray cells.

Figure 16. Ray cells cut open to show the pit system.

There is an indication of chemical transport into the wood structure occurs not only by the penetration mechanism which depends on pressure gradient but also by a diffusion controlled mechanism dependent on capillary cross-sectional area [14]. As shown in Figure 18, the sulphur to sodium ratio is increased with increased distance from the end of the sample when the impregnating liquor has a pH of 6 or higher. When sodium sulphite solution which is basic contacts the wood, acidic hydrogen (mainly from carboxylic groups with pK of about 5) is exchanged for sodium ions producing sodium bisulphite. This ion exchange would occur when sodium sulphite transversely diffuses into the cell wall where these acidic groups are located. Some ion exchange is also possible with the acidic extractives in the lumens. Therefore, more sodium bisulphite is produced as the chemicals move towards the centre of the sample. When a bisulphite solution at pH 4 is used, the ratio of sulphur to cation remains the same as the solution penetrates the wood block, as seen in Figure 18. No ion exchange between the cation and the acidic constituents of wood occurs due to the low basicity of the bisulphite anion. A constant S/Mg ratio does not mean that diffusion is not operative at pH 4.

Figure 17. Tapered ends of birch libriform cells with pits connecting to the ray cells.

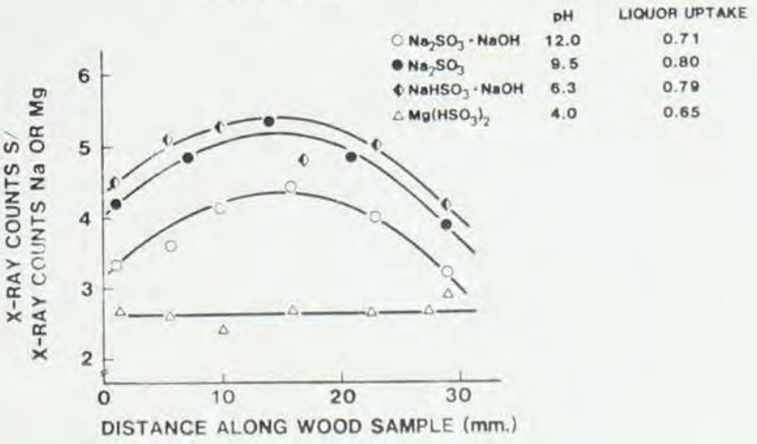

Figure 18. The ratio of sodium to sulphur is higher in the centre of the sample after impregnation with sodium sulphite solutions with pH in the range 6.3 to .2.0. However, there is no such difference in the magnesium to sulphur ratio when birch is impregnated with magnesium bisulphite at pH 4.0.

CONCLUSIONS

Scanning electron microscopy coupled with energy dispersive x-ray analysis can be used to determine the distribution of sodium and sulphite ions in wood impregnated with sodium sulphite. The results obtained with energy dispersive x-ray analysis are comparable to those obtained by ion chromatography for sulphur and atomic absorption for sodium.

The degree of impregnation of sodium sulphite into birch wood increases with decreasing initial moisture content which in turn promotes a more uniform distribution of sulphite ions into the centre of the wood. Initial impregnation of birch wood occurs by liquid flow of sodium sulphite solution from the vessels through the ray cells into the libriform cells via the connecting pit membranes. However, since sodium ions were partially exchanged for hydrogen ions as sodium sulphite proceeded toward the middle of the sample, a diffusion controlled component is also operative.

ACKNOWLEDGEMENTS

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MACROMOLECULAR CHARACTERISTICS OF ALKALI AND ORGANOSOLV LIGNINS FROM BLACK COTTONWOOD [1a]

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ABSTRACT

Black Cottonwood platelets have been delignified in a flow through reactor using both an alkaline aqueous solution and an acidic methanol-water solution. $\bar{M}_n$ and $\bar{M}_w$ and other macromolecular parameters have been evaluated for incremental fractions dissolved. Results are compared with prior findings concerning the delignification of Western Hemlock wood with a 1.0 N aqueous NaOH solution. All lignins studied appear to show effectively tetrafunctional branch points. The degrees of crosslinking now found for an alkali Cottonwood lignin and for acidic organosolv Cottonwood lignin are very similar and both are significantly lower than our estimate of the degree of crosslinking in alkali Hemlock lignin. This difference may explain in part the greater difficulty experienced in bringing about delignification of Hemlock wood versus Cottonwood and perhaps all gymnosperms versus angiosperms.

KEYWORDS: LIGNIN, COTTONWOOD, MACROMOLECULE, ALKALI, ORGANOSOLV, CROSSLINKING, FUNCTIONALITY

INTRODUCTION

In recently published papers we have developed the concept of lignin in wood as a crosslinked gel[2,3] and have viewed the delignification process as one of degelation[3-6]. Hydrolysis of chemical bonds in the lignin polymer is thought to give rise to lignin fragments which thereupon dissolve in the ambient solvent[3,6] and are removed from the zone of reaction by use of the flow-through reactor (FTR) in which the experiment has been conducted.[7]

Prior studies have included the FTR delignification of Western Hemlock[8] with 1.0 N NaOH aqueous solutions. The weight and number average molecular weights and other related parameters associated with dissolved lignin fractions have been evaluated. Application of degelation theory[6] has led to the conclusion that the gymnosperm lignin studied under alkaline conditions of delignification seems to be crosslinked in a tetrafunctional manner.

Softwood lignins, in native or dissolved state, can be thought of as branched polymers which initially were composed of "primary" linear chains. The "C6-C3" structural units seem to be linked mainly in a head-to-tail fashion although tail-to-tail and head-to-head linkages are also possible, as for example in pinoresinol and in diaryl ethers. Softwood structural units, in addition to the highly reactive head and tail sites, also provide a seemingly less reactive site or "arm" located usually in the C-5 position of the ring, although other positions are also plausible. These arms are responsible for subsequent branching. When branching occurs, the involved structural units may assume trifunctionality. Moreover two trifunctional units may pair up to form, in effect, a tetrafunctional branch point[4]. The syringyl units known to be present may be expected to have some effect on the branching properties because the C-5 position is blocked by the presence of an additional methoxyl group in some structural units.

Thus the present study has been conducted to provide evidence relative to the functionality and the crosslinking density calculated for the lignins isolated from a hardwood, Black Cottonwood, by use of an alkaline aqueous solution and an acidic methanol-water solution at elevated temperature.

Preparation of Wood Platelets

Small blocks of Black Cottonwood (Populus trichocarpa) were swollen under vacuum for 48 hours with an ethanol-water mixture (1/1: v/v), and then cut into platelets (65 x 21 x 0.4 mm) with the aid of a microtome. Secondary components of wood were removed by two successive Soxhlet extractions for 72 hours each, one with deionized water to remove tannins, and then another with an ethanol-benzene mixture (1/2: v/v) to remove resins, fats and waxes. Between extractions, the platelets were washed with ethanol to eliminate residual water.

Delignification and Procedures for Alkali Lignins

Our 150 mL flow-through reactor ("FTR") system and a procedure for its use have already been described[7,8]. Treatment was carried out using about 15 g of the extracted wood platelets at the desired temperature and time with 1.0 N NaOH flowing at about 17.5 mL min-1. The resultant solutions were cooled immediately after exiting

from the reactor. After termination of the reaction, the liquid in the reactor was filtered off. The remaining platelets were broken up by of an electrically driven mixer (Braun Mini-[illegible]er). The pulps were exhaustively washed on a filter with deionized water. The wash waters were collected and combined with the reaction liquid. The cellulosic residue was dried in air at ambient temperature for about 48 hours: the yield was found to be about 44% and the Kappa Number about 9.

During the delignification run, the effluent liquid was collected as ten sucessive samples (Table 1). Each of these lignin fractions was first precipitated by addition of HCl to provide pH 2. The two phase system was then directly freeze-dried whereby the volatile HCl was removed. The residue from the freeze-drying was extracted with dry dioxane to accomplish elimination of ash and other dioxane-insoluble substances, and the dioxane solution of lignin was again freeze-dried and weighed. The lignin powders obtained were soluble in several organic solvents: dioxane, tetrahydrofurane, methoxyethanol, dimethyl formamide and dimethyl sulfoxide.

Analyses and Calculations for Alkali Lignins

The values of $\bar{M}_n'$ and $\bar{M}_w'$ were determined by use of previously described procedures[2-5] using a vapor pressure osmometer (VPO) and a low angle laser light scattering (LALLS) apparatus, respectively and are presented in Table 1 and Figure 1. The carbon, hydrogen and methoxyl contents of three alkali lignin fractions were determined by quantitative microanalysis in Galbraith Laboratories (Knoxville, Tennessee) and oxygen was calculated by difference (Table 2). The calculation procedures used were the same as those previously described[6].

Delignifications and Procedures for Organosolv Lignins

Conditions of delignification for Run 29 were chosen similar to those used in batch experimentation conducted by S. Tirtowidjojo[9] with K.V. Sarkanen and were as follows: solvent methanol/water (70/30:v/v); catalyst - 0.01 M H_2SO_4; flow rate, = 17 mL min^{-1} and temperature 252°C. The delignification was carried out substantially as previously described for the alkaline reaction except that here the residual tissue was washed exhaustively on a filter [illegible] the methanol-water solution (free of catalyst), then with acetone and finally with distilled water. The effluent liquid was collected as fourteen separate increments. The dissolved lignins were recovered and characterized.

The dissolved solids were almost completely soluble at ambient temperature in the solvent mixture utilized. After filtration, the liquid phase was vacuum evaporated at 40°C whereby the methanol was removed. After most methanol had been eliminated, an abundant light brown precipitate of water insoluble lignin, "L-1", was formed. This was separated from the solution, "S", by centrifugation for 15 minutes at 10,000 rpm, and then washed several times with distilled water until the acidity of the washings, W, reached nearly that of the water. Between each washing, the precipitate was settled and recovered by centrifugation for 15 min at 10,000 rpm. The final aqueous suspension was then freeze-dried.

The acidic solution, S, mixed with the washings, W, contained a non-negligible fraction of water soluble lignin, "L-2", and also soluble carbohydrates. The recovery and purification of L-2 was accomplished as follows: neutralization to pH 4.5 by addition of a filtered aqueous solution of $Ba(OH)_2$, elimination of barium sulfate by filtration, vacuum evaporation in part at 40°C, and then freeze drying. The solid material obtained was extracted with dry acetone to dissolve the lignins and to leave behind a residue of impure carbohydrates which was separated by filtration. The acetone was evaporated from the solution at ambient temperature under a stream of nitrogen. Finally, L-2 was completely dried under vacuum in a desiccator.

Each pair of the several fractions was combined and characterized. Fractions L-1 and L-2 were soluble in dioxane, 2-methoxyethanol, dimethyl formamide and dimethyl sulfoxide. L-2 was also soluble in acetone.

Analyses and Calculations for Organosolv Lignin

Estimation of weight and number average molecular weights ($\bar{M}_w'$,$\bar{M}_n'$) and related parameters were conducted by low angle laser light scattering (LALLS) and vapor pressure osmometry (VPO) as previously described.[7,8] and results are presented graphically in Figure 2.

Carbon, hydrogen and methoxyl analyses were carried out (Galbraith Laboratories, Knoxville, TN.) on three organosolv lignin fractions and the mean molecular weight for a C6-C3 structural unit was found to be $\bar{M}_o$ = 207.

RESULTS AND DISCUSSION

For each alkali lignin fraction, the number and weight average molecular weights, $\bar{M}'_{n,i}$ and $\bar{M}'_{w,i}$, and the polydispersity index, $r = \bar{M}'_{w,i}/\bar{M}'_{n,i}$, were determined by previously described procedures.[2,3] (Table 1 and Figure 1). As delignification proceeded, $\bar{M}'_{n,i}$ increased, and $\bar{M}'_{w,i}$ increased markedly so that the polydispersity rose from about 1.8 to nearly 10. The second virial coefficient A_2, fluctuated around a slightly positive value and then declined significantly during the latter stages of the delignification. The anisotropy parameter, δ, declined monotonically from 0.16 to 0.01 over the course of the delignification reaction, while the refractive index remained nearly constant at about 0.16. These trends are in general agreement with those which we observed with FTR delignification of Western Hemlock using an aqueous 1.0 N NaOH solutions.[8] For the organosolv fractions, similar results were obtained as shown in Figure 2.

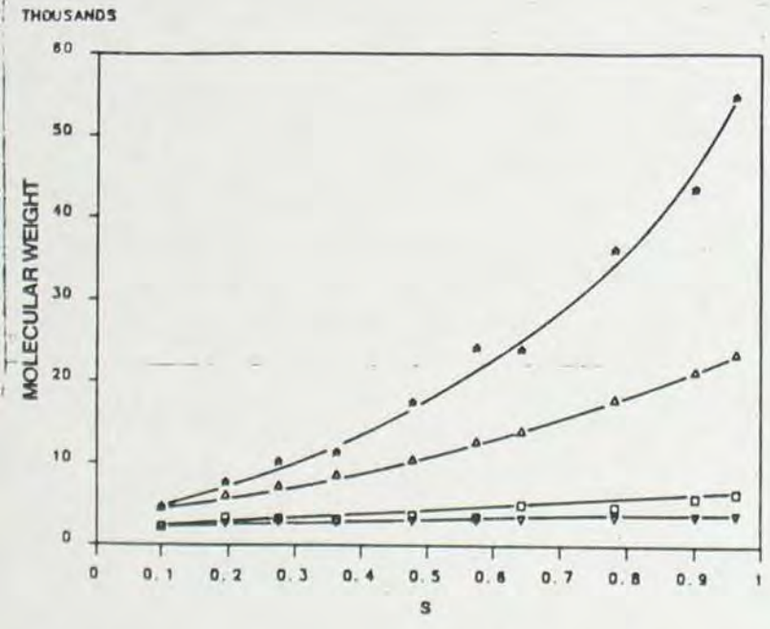

Figure 1. Weight and number average molecular weights of individual (✡ $=\bar{M}_w'$, □ $=\bar{M}_n'$) and cumulative (△ $=\bar{M}_w'$, ▽ $=\bar{M}_n'$) fractions of alkali lignin, versus weight fraction of lignin in the solution.

From the $\bar{M}'_{n,i}$ and $\bar{M}'_{w,i}$ results obtained for each fraction, the cumulative mean values of each molecular weight type, $\bar{M}'_{w,j}$ and $\bar{M}'_{n,j}$, were calculated for the alkali lignin and also the fractions and results are shown in Figures 1 and 2.

Shown in Table 2 are analytical results which indicate that the mean molecular weight of a structural unit in alkali lignin was $\bar{M}_o = 204$. Similar analyses showed $\bar{M}_o = 207$ for the organosolv preparation. The proportion of the total

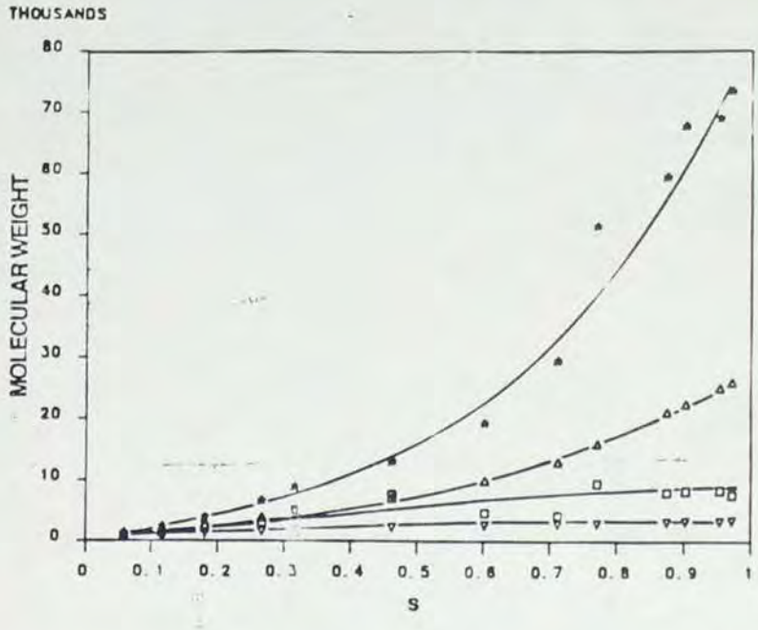

Figure 2. Weight and number average molecular weights of individual (✡ $=\bar{M}_w'$, □ $=\bar{M}_n'$) and cumulative (△ $=\bar{M}_w'$, ▽ $=\bar{M}_n'$) fractions of organosolv lignin, versus weight fraction of lignin in the solution.

lignin found in the sol phase, $s = 1-g'$, at several intervals as the alkali delignification proceeded are shown in Table 3.

Using these molecular weight and sol phase data, several parameters associated with the model which we are studying for the sol phase lignin fractions were calculated by use of previously described definitions and procedures.[6]

Results for the alkali lignin are shown in Table 3 from which it may be seen that the cumulative weight and number average degree of polymerization, $\bar{x}'_w$ and $\bar{x}'_n$, the polydispersity indicies, $r' = \bar{x}'_w/\bar{x}'_n$, and the weight average degree of polymerization of the primary chains, $\bar{y}'_w$, all increase steadily as delignification proceeds. As the sol phase proportion increases, the extent of reaction of primary chains, p', (Figure 3) the weight average degree of polymerization of the primary chains, $\bar{y}'_w$ (Figure 4) and the crosslinking density, r', (Figure 5) also are found to grow steadily larger.

From the now-estimated values of p' and ρ' for each sol alkali lignin phase fraction (Table 3), the chain branching probabilities, α_f, have been calculated by use of previously described relationships[6] and results are shown in Figure 6.

According to Flory[11], α_f reaches a critical value, α_c, at the gel point where

$\alpha_c = (f-1)^{-1}$, where f = functionality

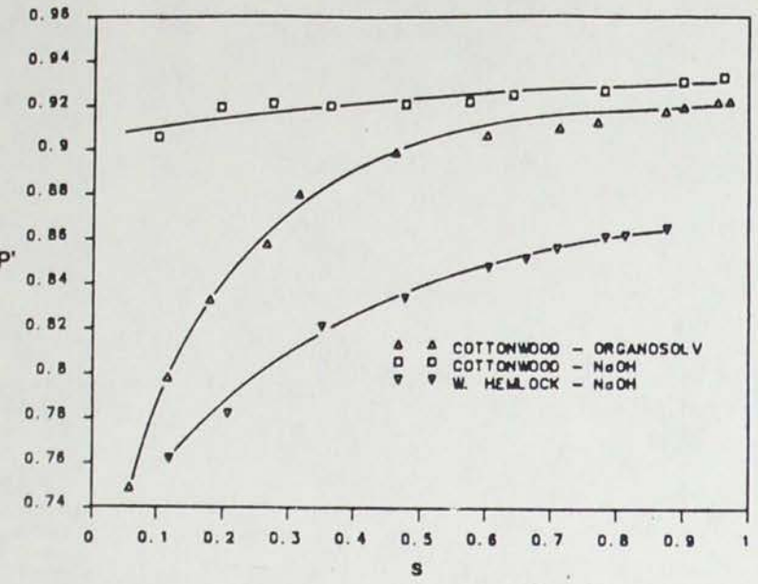

Figure 4. Weight average degree of polymerization of primary chains as a function of s, (Symbols as in Figure 3.).

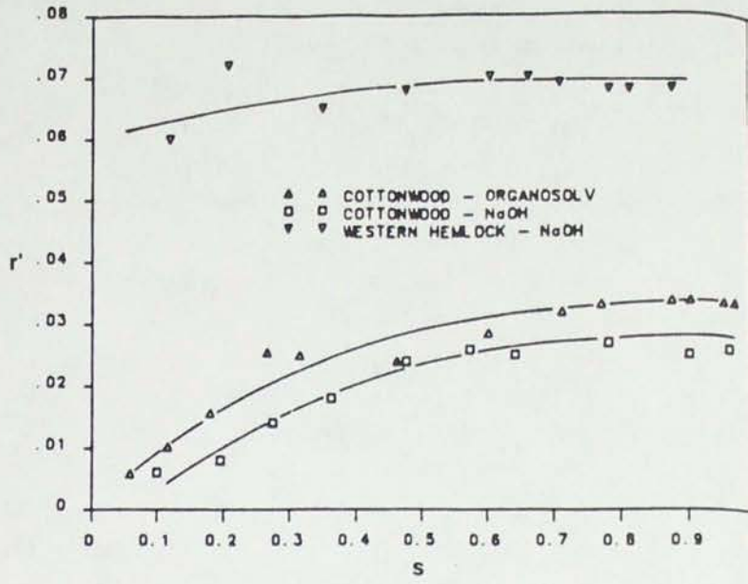

Figure 5. Crosslinking density as a function of s, (Symbols as in Figure 3.)

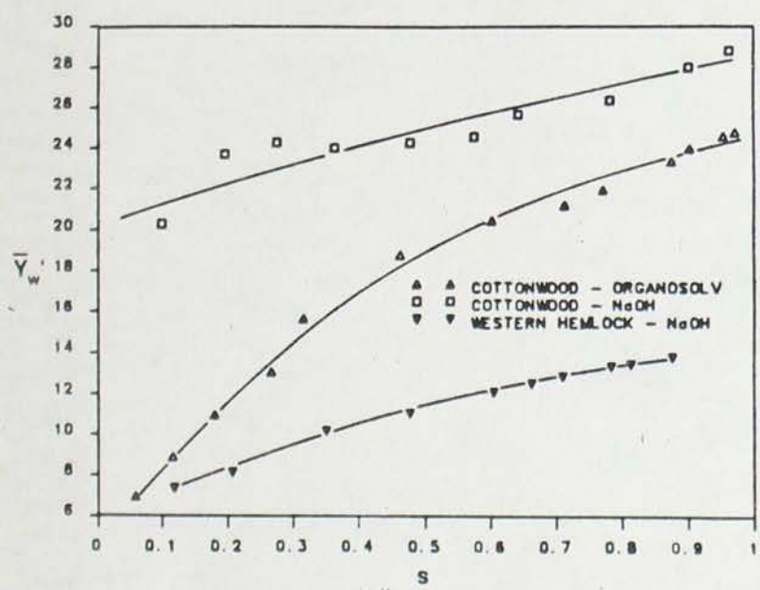

Figure 3. Extent of reaction of primary chains as a function of weight fraction of lignin in solution.
△ =organosolv lignin from Black Cottonwood.
□ =alkali lignin from Black Cottonwood.
▽ =alkali lignin from Western Hemlock.

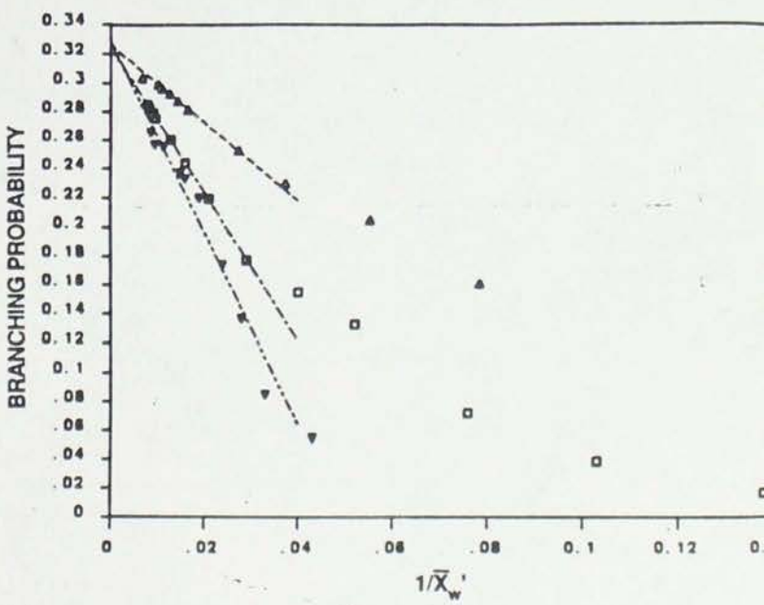

Figure 6. Branching probability as a function of s.
△ =alkali lignin from Western Hemlock.
▽ =alkali lignin from Black Cottonwood.
□ =organosolv lignin from Black Cottonwood.

Thus the gel point and α_c are approached as $\bar{x}_w'$ approaches infinity, or else as $1/\bar{x}_w'$ approaches zero.

In Figure 6, the values now found for α_f are plotted against $1/\bar{x}_w'$. Although the curve is not linear, it has been extrapolated to $1/\bar{x}_w' = 0$ by use of a fitted polynomial. The limiting value found is 0.33 which is in agreement with the theoretical value of 0.33 expected for a tetrafunctional branch point system, and is substantially distant from the value of 0.50 which should be associated with a trifunctional branch point assembly.

Similar calculations have been made for the organosolv Cottonwood lignin fractions. These results, along with those previously reported for an alkali Hemlock lignin are shown in Figures 3 through 6.

For Black cottonwood the results derived from the now-reported delignification experiments, conducted with both an alkaline aqueous solution and an acidic organosolv solution, along with those previously obtained with Western Hemlock wood lignin, seem to confirm at least the permissibility of application of the degelation model to lignins from both a gymnosperm and an angiosperm isolated under both acidic and alkaline conditions. Also it appears that the lignins in at least one gymnosperm (Western Hemlock) and one angiosperm (Black Cottonwood) are comprized of cross-linked polymer chains which manifest tetra-functional branch points.

A substantially lower crosslinking density appears to exist in Cottonwood lignin as compared with the Hemlock lignin, and perhaps this difference is characteristic of all angiosperm versus gymnosperm lignins. Investigations in this field are continuing.

ACKNOWLEDGMENTS

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Table 1
Some Characteristics of R-15 Lignin Fractions: Purification Method Two

Fraction	Time (min)	m_i (g)	s	$\bar{M}_{n,i}$ (g)	$\bar{M}_{w,i}$	$A_2 \times 10^3$ (mole $cm^{+3} g^{-2}$)	δ	dn/dc ($cm^3 g^{-1}$)	$\bar{M}_{w,i}/\bar{M}_{n,i}$
F-0[a]	2.5	0.107	0.031	-	-	-	-	-	-
F-1[a]	7.7	0.235	0.100	2250	4725	0	0.14	0.187	2.1
F-2	13	0.324	0.195	3375	7760	0	0.12	0.192	2.3
F-3	21	0.274	0.275	3280	10280	-1.2	0.10	0.184	3.1
F-4	30	0.301	0.363	3170	11430	-2.1	0.11	0.188	3.6
F-5	40	0.394	0.478	3715	17575	1.4	0.09	0.190	4.7
F-6	52	0.329	0.574	3540	24200	1.3	0.10	0.192	6.8
F-7	70	0.234	0.642	5010	24050	-0.6	0.11	0.195	4.8
F-8	95	0.479	0.782	4770	36200	0.9	0.06	0.191	7.6
F-9	135	0.405	0.901	5900	43600	1.7	0.04	0.189	7.4
F-10	240	0.213	0.963	6450	54900	1.1	0.01	0.193	8.5

(a) Determinations were made for the mixtures of F-0 plus F-1 which is identified as F-1* in Table 3.

Table 2
Analytical Characteristics of Certain Lignin Fractions[a]

Fraction	C (%)	H (%)	O (%)	$-OCH_3$ (%)	Unit Weight	Calculated $C_6 - C_3$ Unit[b]
F-1	56.79	6.02	37.19	13.91	210.1	$C_9H_{9.82}O_{3.94}(OCH_3)_{0.94}$
F-5	59.44	6.22	34.34	15.43	202.1	$C_9H_{9.55}O_{3.33}(OCH_3)_{1.01}$
F-10	58.85	6.17	34.98	13.14	200.8	$C_9H_{9.84}O_{3.54}(OCH_3)_{0.85}$

(a) Fractions from R-15 using purification Method Two; (b) Mean molecular weight of C_6-C_3 structural unit = $\bar{M}_o$ = 204.5.

Table 3
Properties of Lignin Fractions[a]

Fraction / Parameter	F-1*	F-2	F-3	F-4	F-5	F-6	F-7	F-8	F-9	F-10
s	0.100	0.195	0.275	0.363	0.478	0.574	0.642	0.782	0.901	0.963
$\bar{M}'_{w,j}$	4725	6200	7390	8370	10580	12860	14050	18020	21380	23540
$\bar{M}'_{n,j}$	2250	2685	2835	2910	3070	3140	3270	3465	3665	3770
$\bar{M}'_{w,j}/\bar{M}'_{n,j}$	2.1	2.3	2.6	2.9	3.5	4.1	4.3	5.2	5.8	6.2
$\bar{x}'_w$	23.1	30.3	36.1	40.9	51.7	62.9	68.7	88.1	105	115
$1/\bar{x}'_w$	0.0433	0.0330	0.0277	0.0244	0.0193	0.0158	0.0146	0.0114	0.0095	0.0087
$\bar{x}'_n$	11.0	13.1	13.9	14.2	15.0	15.4	16.0	16.9	17.9	18.4
p'	0.906	0.919	0.921	0.920	0.921	0.922	0.925	0.927	0.931	0.933
ρ'	0.006	0.008	0.014	0.018	0.024	0.026	0.025	0.027	0.025	0.026
α_f	0.055	0.085	0.137	0.174	0.220	0.233	0.237	0.255	0.257	0.265
$\bar{y}'_w$	20.3	23.7	24.3	24.0	24.3	24.6	25.7	26.4	28.0	28.8

(a) Fractions from R-15. (b) F-1* = F-0 plus F-1.

WHY DOES CHLORINATION AND EXTRACTION FAIL TO DELIGNIFY UNBLEACHED KRAFT PULP COMPLETELY?

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ABSTRACT

A new hypothesis has been developed to explain the qualitative features of the kinetics of chlorination. It is postulated that alkali-labile 'blocking groups' are formed during chlorination and that these allow residual lignins to react only very slowly with chlorine. Hitherto, the failure of chlorination and extraction to remove all the lignin has been ascribed to incomplete reaction caused by the failure of chlorine to diffuse to all parts of the fibre wall. Evidence is given to show that the present diffusion theories are inadequate, and that the new hypothesis, invoking chemical rather than physical restraints, is more suitable.

KEYWORDS: Chlorination, Extraction, Delignification, Kraft Pulps, Kraft Pulping, Unbleached Pulps, Kappa Number, Time, Reaction Time, Diffusion, Cell Walls, Lignins, Pseudotsuga, Abies Balsamea, Softwoods.

INTRODUCTION

The complexity of lignin is well illustrated by the difficulty that exists in relating kinetics to chemistry at any stage of delignification. The standard first stage of bleaching – chlorination – provides no exception.

The chemistry of chlorination seems to have been well studied, with much of our understanding stemming from the work of Dence and Sarkanen [1]. Yet no relationships, even qualitative, between the deduced chemistry and the observed kinetics have been forthcoming. Some authors have concluded that chlorination is best represented by two simultaneous first-order reactions (undefined) between chlorine and lignin [2,3] but the prevailing view is that chlorination chemistry and kinetics are not closely related and that the rate-controlling step is not a chemical reaction [4].

The kinetics of chlorination of a softwood kraft pulp, illustrated in Figure 1 as a plot of CE Kappa number versus time, have two features that need to be explained. First, a sharp transition from a rapid to a slow rate of delignification and second, a limiting CE Kappa number. The literature contains many references to the fact that chlorination is 60-80% complete in 2 minutes or less [3-7] and that many of the chlorination reactions take place before the pulp reaches the chlorination tower. It is also known that more retention time, often 45 minutes, is necessary in the tower to complete the chlorination, during which time pulp viscosity can be lost [8]. The literature also describes the concept of a limiting CE Kappa number [2,3, 6,9]. There have been fewer attempts, however, to explain why it takes 40 minutes (at temperatures below 35°C) to get rid of only 0.5 wt % of lignin and why some lignin always remains.

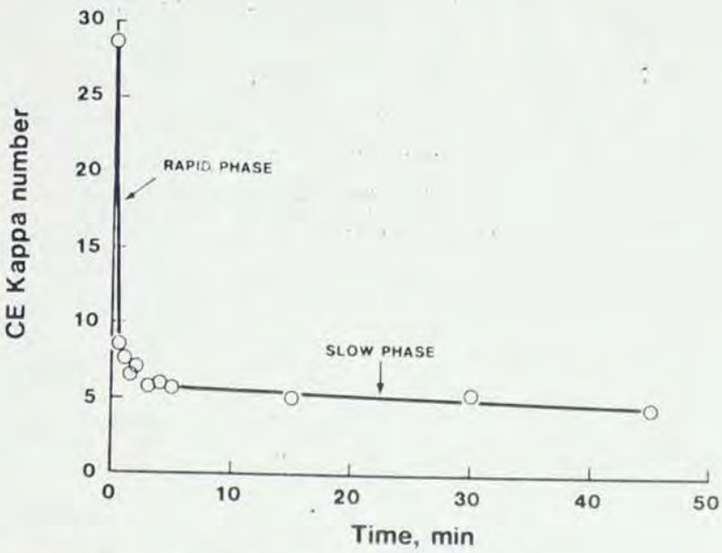

Figure 1. The rate of delignification, as measured by CE Kappa No., makes a sharp transition from a rapid to a slow phase during the chlorination stage.

Unbleached pulp: black spruce kraft pulp; Kappa No., 28.8.
C-stage: 5.7% Cl_2 on o.d. pulp; 25°C, 3.5% consistency.
E-stage: 3.2% NaOH on o.d. pulp; 90 min at 70°C; 10% consistency.

Only one hypothesis has been proposed that explains all these observations. It relates to the restricted diffusion of chlorine to the residual (unchlorinated) lignin: Karter and Bobalek [6], following the idea of Giertz [10], postulated that a chloro-lignin layer forms in the fibre walls, and that this layer constitutes a barrier to further chlorination, by limiting the motion of the chlorine front through the fibre matrix.

There is another hypothesis, put forward by Rapson and Anderson [11] who found that in dynamic bleaching (wherein the chemical solution flowed through the pulp suspension), reaction rates were higher than in normal static bleach-

ing. The observation was explained by postulating that bleaching is controlled by diffusion of oxidant through a thick "water layer surrounding each fibre". The hypothesis can be used to explain rate changes particularly in the rapid phase of a bleaching reaction. It does not, however, explain either a limiting CE Kappa number, or the transition from a rapid to a slow phase of chlorination.

RESULTS AND DISCUSSION

We first questioned the diffusion theories when we studied a sequence consisting of repeated rapid chlorination (C^R) and extraction stages. We observed that if chlorination is terminated after the initial rapid phase, and the pulp is extracted with alkali, the residual lignin appears to be reactivated to chlorine (Figure 2). Treating C^RE pulp with chlorine produces delignification at the original fast rate, as would be expected from the diffusion theories. However, prolonging the second chlorination beyond 2 minutes leads, once again, to slow lignin removal. Again an alkali treatment restores the rapid rate. It is significant that each chlorination stage is capable of fast reaction with only a portion of the remaining lignin and after that the slow phase sets in. The diffusion theories cannot effectively account for this observation; complete removal of lignin would be expected after the second extraction stage.

We were able to think of only one explanation for the observations illustrated in Figure 2 – that a chemical rather than a physical mechanism is operating. However, before abandoning the diffusion theories, we decided to carry out several experiments designed to reveal a diffusion-controlled mechanism for chlorination, should it exist.

If Karter and Bobalek are correct and chlorolignin in the fibre wall presents a barrier to further chlorination, then the lignin which is behind the barrier (i.e., what remains

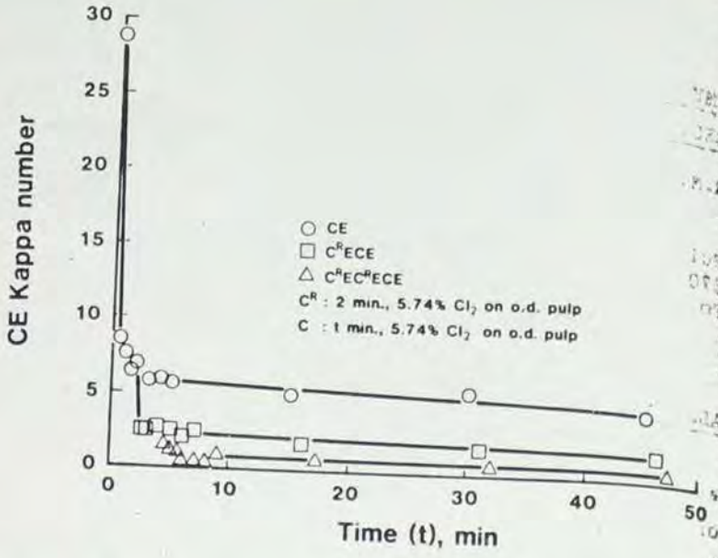

Figure 2. The same sharp transition from a rapid to a slow phase of delignification is found when the chlorination is repeated after extraction. When multiple chlorinations were used (○, △) the initial chlorinationa were done for 2 minutes only. Bleaching conditions were the same as for Figure 1.

after the barrier is removed) must not have been chlorinated. To test this idea we measured the Kappa numbers and chlorine contents of pulps which had been chlorinated and extracted. As shown in Table I, the CE pulp contained a significant amount of chlorine, which is presumably bound to the residual lignin. The conclusion is that chlorine has managed to penetrate throughout the lignin matrix.

Kuang's results [12] are also pertinent. He found that when kraft pulp was chlorinated, the chlorine penetrated to all morphological regions and "the topochemical distribution of the chlorine in chlorinated kraft pulp is similar to that of the lignin." Moreover the photomicrographs of the CE pulp [12] did not show a band of unreacted lignin in the middle of the fibre wall, as one might expect from the theory of Karter and Bobalek; the residual lignin was evenly dispersed throughout the fibre wall.

Table I. Changes in Chlorine Content of CE Pulp with Time of Alkaline Extraction

Extraction Stage Time, min.	Temp., °C	CE Kappa No.,	Organic Chlorine, % on o.d. pulp	Calculated Cl atoms/C_9
2	25	6.4	0.33	1.9
15	70	5.4	0.31	2.1
30	70	5.4	0.24	1.6
45	70	4.9	0.21	1.6
60	70	4.8	0.24	1.8

Unbleached Pulp: black spruce kraft pulp; Kappa No., 30.8.
C-stage: 6.2% Cl_2 on o.d. pulp; 45 min at 25°C; 3.5% consistency.
E-stage: 3.4% NaOH on o.d. pulp; 10% consistency.

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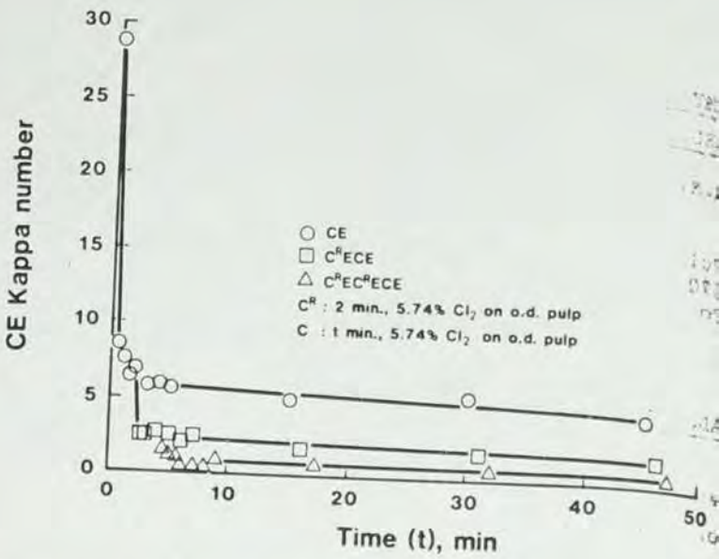


Figure 2. The same sharp transition from a rapid to a slow phase of delignification is found when the chlorination is repeated after extraction. When multiple chlorinations were used (; Δ) the initial chlorinations were done for 2 minutes only. Bleaching conditions were the same as for Figure 1.

after the barrier is removed) must not have been chlorinated. To test this idea we measured the Kappa numbers and chlorine contents of pulps which had been chlorinated and extracted. As shown in Table I, the CE pulp contained a significant amount of chlorine, which is presumably bound to the residual lignin. The conclusion is that chlorine has managed to penetrate throughout the lignin matrix.

Kuang's results [12] are also pertinent. He found that when kraft pulp was chlorinated, the chlorine penetrated to all morphological regions and "the topochemical distribution of the chlorine in chlorinated kraft pulp is similar to that of the lignin." Moreover the photomicrographs of the CE pulp [12] did not show a band of unreacted lignin in the middle of the fibre wall, as one might expect from the theory of Karter and Bobalek; the residual lignin was evenly dispersed throughout the fibre wall.

Table I. Changes in Chlorine Content of CE Pulp with Time of Alkaline Extraction

Extraction Stage Time, min.	Temp., °C	CE Kappa No.,	Organic Chlorine, % on o.d. pulp	Calculated Cl atoms/C_9
2	25	6.4	0.33	1.9
15	70	5.4	0.31	2.1
30	70	5.4	0.24	1.6
45	70	4.9	0.21	1.6
60	70	4.8	0.24	1.8

Unbleached Pulp: black spruce kraft pulp; Kappa No., 30.8.
C-stage: 6.2% Cl_2 on o.d. pulp; 45 min at 25°C; 3.5% consistency.
E-stage: 3.4% NaOH on o.d. pulp; 10% consistency.

In a second experiment, we exposed pulp to excess chlorine. If the reaction is diffusion controlled, the CE Kappa number should eventually reach zero. However, even after 7 days with a 11.5% charge of chlorine, the Kappa number of a bleachable grade pulp (starting Kappa number ~ 30) had not reached zero (Table II). As stated long ago by Giertz [10] "it is impossible to delignify pulp quantitatively in a single chlorination."

Table II. The Limiting CE Kappa Number after Extended Chlorination

Chlorination Time,	Cl_2 Charge, % on o.d. pulp	CE Kappa Number
45 min	5.7	4.5
7 days	5.7*	4.2
7 days	11.5	2.0

* No residual chlorine was present after chlorination

Unbleached Pulp: black spruce kraft pulp; Kappa No., 28.7.
C-stage: 3.5% consistency.
E-stage: 3.2% NaOH on o.d. pulp; 70°C; 10% consistency.

We also compared the bleaching of Douglas fir kraft pulp and balsam fir kraft pulp both made at ~30 Kappa number. On average, Douglas fir fibres are thick-walled (average wall thickness ~3.2 μm [13]). Balsam fir fibres, on average, are thin (average wall thickness ~2.1 μm [13]). If diffusion is rate-controlling in chlorination, the Douglas fir fibres should be less extensively chlorinated than those of balsam fir. Thus, after chlorination, Douglas fir fibres might be expected to contain more unchlorinated lignin and to have a higher CE Kappa number than identically treated balsam fir fibres. Table III shows that this was not the case; the Kappa numbers of identically treated samples of the two furnishes were, within experimental error, the same.

Finally, we compared the bleaching of earlywood and latewood fibres both prepared from the same Douglas fir log. Earlywood fibres have large lumens and thin cell walls (1.3 μm), latewood fibres have thick walls (5.3 μm) [13]. If diffusion is a factor, the lignin in the cell walls of latewood fibres should be less well chlorinated. Chips from each morphological region were selectively cut with a laser and were pulped to approximately the same Kappa number by suitably adjusting the applied alkali charge. The pulps thus obtained were treated with identical charges of chlorine and caustic in a CE sequence. The Kappa numbers of the extracted pulps were identical (Table IV).

Table III. Comparison of the Bleaching of Kraft Pulp from Douglas Fir and Balsam Fir

Pulp Type	Sequence	Kappa Number Initial	Kappa Number Final*
Balsam Fir	CE	29.7	4.9
Douglas Fir	CE	29.1	5.1
Balsam Fir	DE	30.5	6.8
Douglas Fir	DE	31.5	6.9

* Each number represents the average of the results from three bleaching runs.

C-stage: 0.2 x initial Kappa No. (% Cl_2 on o.d. pulp); 45 min at 25°C; 3.5% consistency.
D-stage: 0.076 x initial Kappa No. (% ClO_2 on o.d. pulp); 45 min at 25°C; 3.5% consistency.
E-stage: 0.11 x initial Kappa No. (% NaOH on o.d. pulp); 90 min at 70°C; 10% consistency.

Table IV. Comparison of the Bleaching of Earlywood and Latewood Fibres Obtained from Douglas Fir by Kraft Pulping

Fibre Type	Kappa Number Initial	Kappa Number After CE
Earlywood	29.1	5.2
Latewood	30.4	5.2

C-stage: 0.2 x initial Kappa no. (% Cl_2 on o.d. pulp); 45 min at 25°C; 3.5% consistency.
E-stage: 0.11 x initial Kappa no. (% NaOH on o.d. pulp); 90 min at 70°C; 10% consistency.

The diffusion theories cannot explain all these observations, and thus another hypothesis is needed to answer the original questions which are restated here:

(i) why does some chlorinated lignin refuse to dissolve in alkali?
(ii) why, once it has been treated with alkali, does it behave towards chlorine as though it were normal kraft residual lignin?
(iii) why is there a change from a rapid to a slow chlorination phase?

The only satisfactory response to these questions, in view of the observations made, seems to be that during chlorination, lignin becomes chemically deactivated to attack by chlorine through the formation of 'blocking groups' which are relatively stable under the conditions of chlorination, but which are labile in alkali.

What is the Nature of the 'Blocking Groups'?

Our recent work on the alkaline extraction stage [14] has indicated that large amounts of calcium carbonate as well as sodium chloride are formed during the hydrolysis of chlorinated pulp. We have also observed that, when chlorinated pulps are heated, CO_2 is evolved (Table V). Thus, there are indications that chlorinated pulp contains labile carboxyl groups which may be decomposed to CO_2 or carbonate by the action of heat or dilute alkali.

Table V. Evolution of CO_2 from Chlorinated Pulp when Heated

Analytical Method	Temp., °C	Carbon Dioxide Evolved, % on o.d. pulp	Carbon Dioxide Evolved, mole/kg
Gas Chromatography	125	0.15	0.034
Water Displacement	100	0.12	0.027

Unbleached pulp: black spruce kraft pulp; Kappa No., 30.9

C-stage: 6.2% Cl_2 on o.d. pulp; 45 min at 25°C; 3.5% consistency.

With these reactions in mind, we are put forward two mechanistic schemes which are speculative but might explain all the observations discussed above (Figure 3). The first suggests that the attack of chlorine on certain phenylpropane units may be inhibited by side chain fragments displaced from neighbouring units. The second suggests that the oxidised remnants of aromatic rings are the inhibiting structures. In this paper only the second alternative will be discussed further.

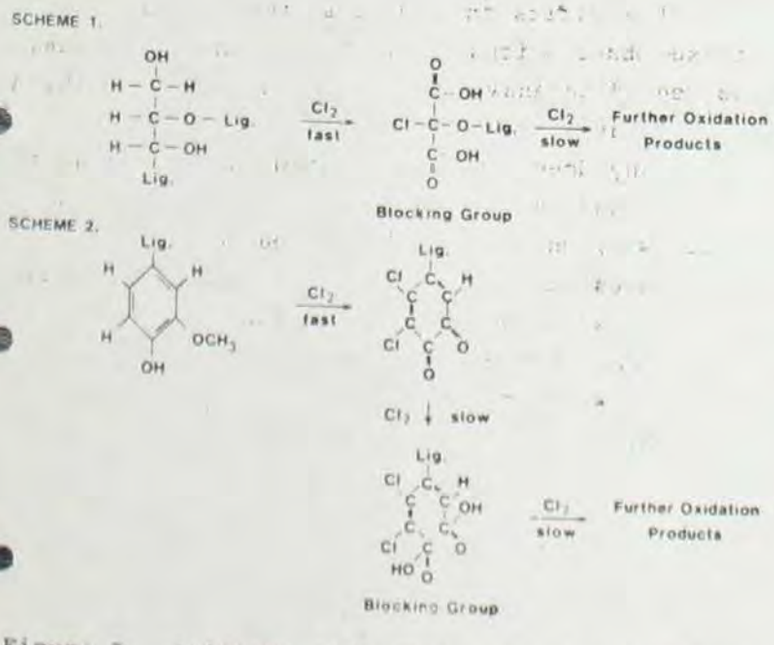


Figure 3. Oxidised side chains or the oxidised remnants of aromatic rings may inhibit chlorination and yet be labile to alkali.

Chloro-o-benzoquinones and chloromuconic acids are likely to be present in chlorinated pulp. A combination of the two might satisfy the requirements for the production of CO_2 and HCl, and each might produce, after hydrolysis, a readily oxidisable fragment.

1. Chloro-o-benzoquinones

Chloro-o-quinones are thought to form when unbleached pulps are chlorinated [15,16,21] and are the likely source of the orange colour in the pulp. Tetrachloro-o-benzoquinone (I) is quite stable under chlorination conditions (see Experimental section) but it is possible that less highly chlorinated o-quinones might be more reactive and undergo ring-opening to form muconic acids [23,24]. Nonetheless, the prevailing orange colour of chlorinated pulps is a good indication that many chloroquinones persist*, and they must therefore be candidate 'blocking groups'.

Table VI shows that tetrachloro-o-benzoquinone was indeed decomposed under the conditions of an alkaline extraction stage yielding about 2 moles of chloride and 0.4 moles of carbonate per mole of chloroquinone. Under the conditions of hot-water treatment [17], only one chlorine atom was released per molecule.

2. Chloromuconic acids

Chloro-muconic acids are formed [18,20] when chloro-o-benzoquinones are treated with peroxide or peracids (Eq. 1); however, it is not known with certainty that this reaction occurs under chlorination conditions [21]. Gess and Dence [22] have reported the isolation of a trichloromethylmuconic acid from chlorination of creosol, but the characterization was not complete. Although the existence of chloromuconic acids in chlorinated pulp is not fully proven, they are certainly candidate 'blocking groups'. Just like chlorinated pulp, tetrachloromuconic acid decomposes yielding HCl and CO_2 when heated in the dry state [18], and it gives carbonate and chloride when heated in water or dilute alkali (Table VI).

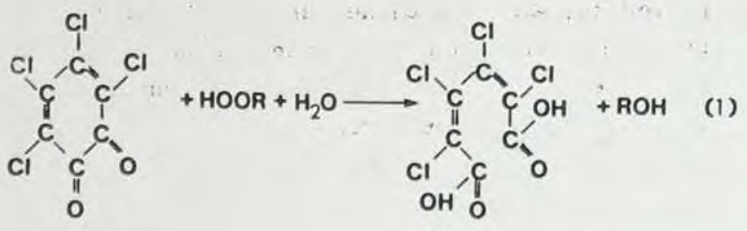
* Gierer and Sundholm isolated five different chloro-o-quinones after lignin model compounds were treated with an excess of chlorine water [25].

Table VI. Chloride and Carbonate from Model Compounds and from Pulp

Substance	Alkaline extraction		Hot-water treatment	
	Chloride, mole %	Carbonate, mole %	Chloride, mole %	Carbonate, mole %
Tetrachloro-o-benzoquinone	195	38	111	51
Tetrachloromuconic acid	305	63	236	80
Chlorinated kraft pulp	0.16*	0.09*	0.09*	0.06*

* expressed as mole/kg

Unbleached pulp: black spruce kraft pulp; Kappa No., 30.9
C-stage: 6.2% Cl_2 on o.d. pulp; 45 min at 25°C; 3.5% consistency.
Hot-water Treatment stage (Wh): 60 min at 90°C; model compounds, 0.0025 moles/L; pulp, 1% consistency.
E-stage: 0.075 moles NaOH/L; 90 min at 70°C; model compounds, 0.0025 moles/L; pulp, 1% consistency



I

R = H or $CH_3.CO$

It is evident from Table VI that the two model compounds chosen gave too much chloride and not enough carbonate compared to pulp. Tetrachloro-compounds were used as model compounds because of their ready availability. In chlorinated lignin, di- and trichloro- compounds would doubtless predominate as they do in the chlorination of creosol [22] and one would therefore expect to obtain a lower chloride to carbonate ratio from pulp than from these model compounds.

Carboxylic Acids and their Precursors – Are They Blocking Groups?

Whereas chloroquinones and chloromuconic acids behave like pulp in yielding chloride and carbonate when treated with alkali, this certainly does not prove that they are necessarily the blocking groups – or even that there are any blocking groups. Some well-devised experiments will be needed to prove or refute the hypothesis put forward. However, there are two observations which are consistent with the 'blocking group' theory.

Potassium permanganate is one of the few acidic oxidants which can decompose carboxylic groups yielding CO_2. It is also one of the few reagents capable of producing a semi-bleached kraft pulp in a single stage. [Unbleached kraft pulp reaches a high brightness in the Kappa number test as a result of complete delignification by permanganate]. The performance of permanganate suggests that if carboxylic groups could be broken down during chlorination then semi-bleached pulps might be obtained directly.

The second piece of evidence comes from the hot-water treatment of chlorinated pulps. Hot-water treatment removes acidic groups from chlorolignin [14,17] without removing the chlorolignin itself. As can be seen in Table VII, increasing the water temperature did not change the Kappa number measured prior to the D-stage, however it did improve the delignification in D_1. When we examined the amount of labile carboxyl groups present in the CW_h pulps (as indicated by the amount of sodium carbonate formed when the pulp was given an

Table VII. Bleaching Kraft Pulp by the Sequences CW_hD and CED

Pre D-Stage Treatment	Kappa No.		Na_2CO_3 formed by alkaline treatment,* mole/kg
	Pre-D	Post-D	
CW_{25}	11.7	5.5	0.088
CW_{70}	11.6	4.8	0.068
CW_{100}	11.6	3.6	0.058
CE	4.9	1.2	-*

* Na_2CO_3 formed if the D-stage is replaced by an E-stage.
* assumed to be zero.

Unbleached pulp: black spruce kraft pulp, Kappa no., 28.1.
C-stage: 5.62% Cl_2 on o.d. pulp; 45 min at 25°C; 3.5% consistency.
Hot-water treatment stage (W_h): 60 min; 10% consistency; subscript denotes temperature.
E-stage: 3.09% NaOH on o.d. pulp; 90 min at 70°C; 10% consistency.
D-stage: 1.25% ClO_2 on o.d. pulp; 3h at 60°C; 10% consistency.

alkaline extraction) we observed that the hot-water stage definitely removes some of these groups (Table VII). The amount of the carbonate formed from labile carboxyl groups roughly parallels the Kappa number after the D-stage.

This is leading us to the conclusion that the importance of the extraction stage may not be in removing chlorinated lignin fragments but rather in breaking down certain carboxylic acids or chloroquinones which are produced during chlorination and which are a hindrance to further oxidation.

CONCLUDING REMARKS

Boundary layer diffusion control of chlorination cannot explain why a second chlorination can only remove a part and not all of the residual lignin remaining after chlorination and extraction. The chloro-lignin barrier theory cannot explain why residual lignin in CE pulp has a substantial chlorine content. Neither can it explain the equal chlorination rates of thin-walled and thick-walled fibres, nor the fact that a C-stage has a limiting CE Kappa number even when considerable time is allowed for diffusion.

Our alternative explanation suggests that chemical 'blocking groups' may inhibit chlorination in adjoining parts of the lignin macromolecule and thus produce a residual lignin which reacts only very slowly with chlorine. These blocking groups must be labile to alkaline attack because an alkaline treatment is able to restore the rapid delignification rate which is characteristic of unbleached kraft lignin. Using the formation of sodium carbonate and chloride in E-stage liquor as an indicator of chlorolignin chemistry, we have selected chloroquinones and chlorocarboxylic acids as candidate 'blocking groups'.

EXPERIMENTAL SECTION

Pulping of Earlywood and Latewood Douglas Fir Samples

Laser cut samples of earlywood and latewood were kindly donated by E.K. Andrews and R.C. Eckert, Weyerhaeuser Co. The samples were cooked in laboratory bombs under the following conditions: Sulphidity, 30%; liquor-to-wood ratio, 7.0 L/kg; max. pulping temperature, 170°C; time to temperature, 90 min; H-factor, 1668; effective alkali, 21.36% on o.d. wood for earlywood, 19.37% for latewood.

Pulping of Douglas Fir and Balsam Fir Samples

Douglas fir and balsam fir chips were cooked in laboratory bombs under the following conditions: sulfidity, 30%; effective alkali, 18%; H-factor: balsam fir, 2700 and 2800; Douglas fir, 2100 and 2250. The resulting Kappa numbers were: Balsam fir, 30.5 and 29.1; Douglas fir, 31.5 and 29.7.

Measurement of CO_2 Evolved from Chlorinated Pulp when Heated

In a water displacement method, a known weight of chlorinated pulp fibres which had been dried over P_2O_5 was placed in a melting point capillary tube and the capillary tube was placed in an apparatus as shown in Figure 4. The amount of CO_2 evolved when the temperature was raised to, and maintained at, 100°C was measured from the difference in the volume of liquid displaced when water and then sodium hydroxide solution occupied the vial.

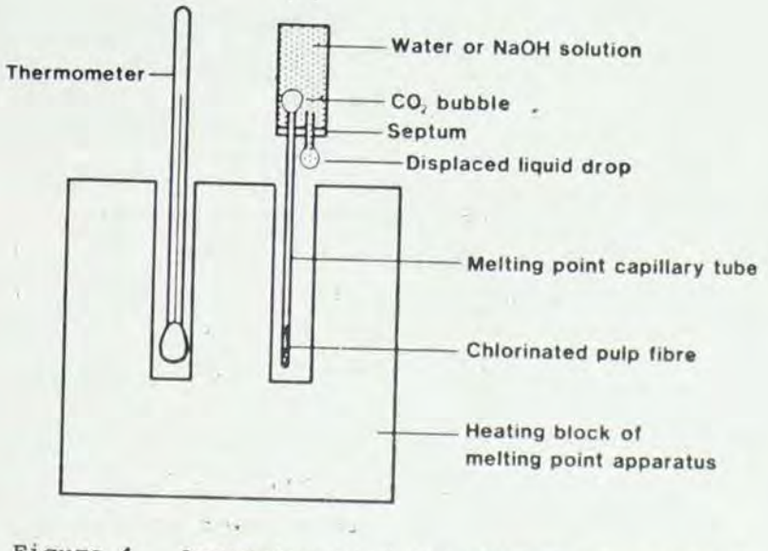


Figure 4. Apparatus used to measure CO_2 evolved when chlorinated pulp is heated.

In a gas chromatographic method, a known weight of chlorinated pulp fibres (0.5 to 1.0 g) were placed in a vial sealed with a septum. The vial was heated for 20 minutes at 125°C and the gas space was sampled. This sample (0.2 mL) was injected into a HP 5720A gas chromatograph equipped with a thermal conductivity detector. A molecular sieve column (Linde 5A, 120 x 0.64 cm id) was used with a helium flow rate of 40 mL/min. The column oven temperature was 180°C.

Chlorination of Tetrachoro-o-Benzoquinone

Tetrachloro-o-benzoquinone (Kodak, m.p. 133-135°, 1.003g) was dissolved in methylene dichloride (25 mL) and chlorine water (25mL, 6g Cl_2/L) was added. The mixture was stored in a glass stoppered flask in the dark at 25°C for 48 hours. The layers were then separated and the CH_2Cl_2 layer was washed with two 10 mL portions

of deionized water. The combined aqueous extract and washings were evaporated and yielded only 2.1 mg of a buff colored solid.

The CH_2Cl_2 layer was evaporated and yielded the starting material (m.p. 130-132°, 0.984g) – a recovery of 98.1%. Evidently tetrachloro-o-benzoquinone is quite stable to chlorine under normal conditons. Had ring-opening reactions occurred, then large quantities of chloromuconic acids would have appeared in the aqueous extract [18].

Preparation of Tetrachloromuconic Acid

Tetrachloromuconic acid was prepared by oxidising tetrachloro-o-benzoquinone (9g) with a mixture of acetic anhydride, sulphuric acid and 30% hydrogen peroxide as described by Shulgin [19]. The reaction was slow, but after 2 hours the white product began to crystallize. After 3 days, 8.9g of product was filtered off. Shulgin's method yields a product which is contaminated with sulphuric acid.

The crude tetrachloromuconic acid was dissolved in ether (10 mL) whereupon 1 to 2 mL of sulphuric acid separated as a dense phase. Benzene (40 mL) was added and more sulphuric acid separated. The upper layer was removed and allowed to evaporate slowly in a fumehood. Shiny white crystals of tetrachloromuconic acid (3.0 g) were deposited, mp: 149-154° (dec., gas evolution). Lit. 148° [20], 156.7° [18].

Bleaching Procedures

Details of the bleaching procedures are given in previous publications [14,17]. Hot-water treatment and alkaline extraction of model compounds and small quantities of pulp were done in 50 mL polyethylene bottles. The CO_2 produced during hot-water treatment was stripped off after the reaction time was completed. This was done by passing CO_2-free nitrogen through the hot-water treatment effluent and then passing the exiting gas through sodium hydroxide solution.

Analyses Used

Kappa number was measured by CPPA standard method, G18. Carbonate and chloride were determined by ion chromatography on a Dionex model 2010 ion chromatograph. Organically bound chlorine was analysed by Guelph Chemical Laboratories, Ontario in a procedure wherein the sample was ashed and the liberated hydrogen chloride measured as silver chloride after absorption in silver nitrate solution.

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We are grateful to Dow Chemical Canada Ltd. for generous financial support. We thank J. Waugh, H. Nugent and P. Wong for careful experimental work and F.J. McPhee for preparing some of the kraft pulps. We are grateful also to J.M. MacLeod for suggesting Douglas fir earlywood and latewood as sources of fibres with widely different wall thicknesses, to E.K. Andrews and R.C. Eckert, Weyerhaeuser Co., for the gift of the laser-cut Douglas fir earlywood and latewood samples, and to N. Liebergott for reviewing the manuscript.

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SULPHITE PROMOTED DELIGNIFICATION

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Approximately 80% of the soluble lignosulphonates (from conifers) have been described as an homologous series of sulphonated lignins having identical repeating units. The remainder (ca. 20%) exists as a group of poorly-define lower molecular weight materials, currently named "hemilignins" (1). Precise structural data for these aforementioned homologues has been presented, but remains a controversial issue due to a lack of convincing published evidence.

It should be emphasised that most of the separations of these lignin-derived substances were carried out using Sephadex column chromatography - a process known to result in limited resolution of mixtures.

Thus, in the light of these extra-ordinary findings, and as a first measure, we developed methodology which established the following:

(i) aqueous high performance liquid chromatography of soluble lignosulphonates which resulted in a much improved resolution of these mixtures (2)

(ii) that the hplc separation of these lignosulphonates was based mainly upon molecular size differences (3)

(iii) during sulphite pulping, two main classes of sulphonated lignins were removed, i.e., paucidisperse (M_W < 3,300) and polydisperse (M_W > 3,300) (2,3)

(iv) only paucidisperse (i.e., resolvable, low molecular-weight lignins) were removed during the early stages of delignification (~ 30% lignin removal). Beyond this point, only widely polydisperse materials were solubilised (4)

(v) prolonged hydrolysis of these polydisperse substances did not result in the genesis of either (a) the single repeating unit reported to occur or (b) additional paucidisperse material (4).

These aqueous lignosulphonates (both pauci- and polydisperse) have been analysed by standard spectroscopic techniques (^1H and ^{13}C nmr, e.g., DEPT, etc.). Certain structural information has clearly been obtained. These findings will be discussed in detail.

Further, because of the tediousness inherent in the manipulation of aqueous samples, we have developed methodology rendering these lignosulphonates organic solvent soluble (4,5). Figure 1 shows the resolution of the paucidisperse components on hplc silica columns. We shall discuss our findings regarding the structures of these materials and their relationship to the original lignin macromolecule.

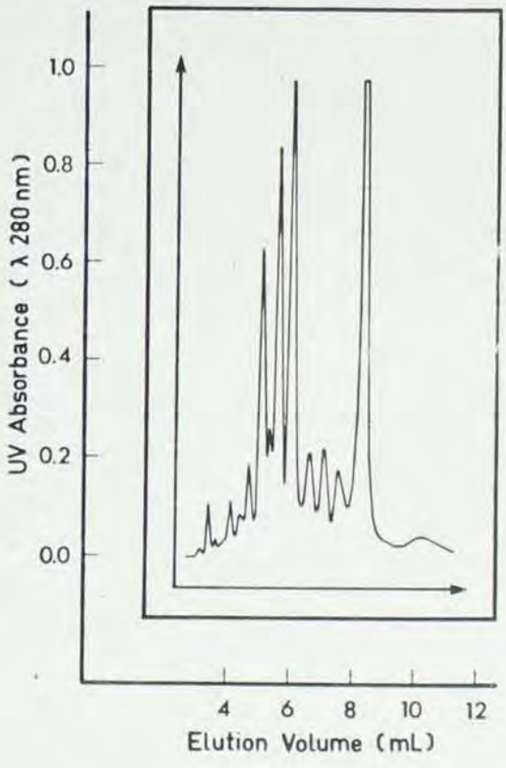

Figure 1. Hplc separation of paucidisperse coniferous, fully methylated, lignin sulphonates. Elution details: Waters μ-porasil column, eluted with 0.25% CH_3OH in CH_2Cl_2. Flow = 1 mL/min.

Our conclusions pertaining to the validity of Forss' model for coniferous lignin and hemi-lignin will also be presented.

In addition, the thermally induced polymerisation of spent sulphite liquor components was also investigated (6). Consequently, a more detailed understanding of the role of the poly- and pauci-disperse lignosulphonates and the carbohydrates during thermosetting has now been achieved. This detailed knowledge has direct applicability to the use of spent sulphite liquor as a composite wood adhesive.

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THIOACIDOLYSE DES LIGNINES : NOUVELLE METHODE DE CARACTERISATION DES ALKYL-ARYL ETHERS.

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ABSTRACT

Part of this work has been previously published (1-3). This paper reports our present knowledge about lignin thioacidolysis (solvolysis in dioxane-ethanethiol 9/1, 0.2 N BF_3 etherate) and confirms its analytical interest.

L'acidolyse selon Lundquist (4) coupe spécifiquement les liaisons alkyl-aryl éthers des lignines. De plus, les produits monomériques issus de cette dégradation présentent le squelette phénylpropane C_6-C_3 caractéristique des unités constitutives des lignines. Cependant, l'acidolyse a deux inconvénients : d'une part, les rendements en produits de dégradation monomériques sont faibles en raison de réactions de condensation catalysées par les acides utilisés en milieu aqueux ; d'autre part le nombre élevé de produits d'acidolyse formés en rend la séparation délicate. Pour conserver les avantages de l'acidolyse (spécificité de dégradation et structure C_6-C_3 des produits monomériques obtenus), nous avons tenté de remédier à ces deux limitations. Dans ce but, nous avons utilisé l'éthérate de trifuorure de bore et l'éthanethiol (EtSH) pour dégrader les lignines dans le dioxanne anhydre. Le système (BF_3 éthérate - EtSH) est en effet un réactif efficace de coupure des liaisons éthers en conditions douces (5).

La thioacidolyse (solvolyse en milieu dioxanne - éthanéthiol, 9/1, 0.2 N BF_3 éthérate, 4 heures à 100°C) permet effectivement de dégrader les structures alkyl-aryl éthers non condensées des lignines en produits monomériques thioéthylphénylpropanes (figure 1).

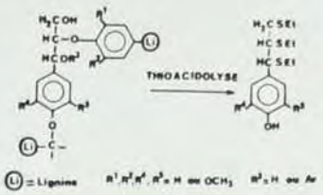

Figure 1. Dégradation des structures alkyl-aryl éthers non condensées par thioacidolyse.

Le mélange de produits de dégradation monomériques obtenus est donc beaucoup plus simple que celui de l'acidolyse (figure 2). La réaction n'est pas stéréospécifique : à partir d'un dimère alkyl-aryl éther thréo ou érythro, on obtient un mélange des diastéréoisomères monomériques. Des études cinétiques réalisées sur lignines ou sur résidu pariétal ont montré que la durée de 4 heures de réaction est optimale. Les résultats comparés obtenus pour des échantillons de lignines de bois moulu (M W L) sont indiqués dans le tableau 1. Ils sont exprimés en pourcentage pondéral équivalent à celui des diastéréoisomères p-hydroxyphényles (H), guaïacyles (G) ou syringyles (S) obtenus par thioacidolyse.

M W L de :	Peuplier		Pin (bois de réaction)		Pin (bois opposé)	
Monomères %	A	T	A	T	A	T
- H	-	-	1.7	4.6	traces	0.46
- G	12.4	16.1	11.8	21.7	13.9	27.8
- S	9.4	21.0	traces	0.8	traces	0.30
- total	21.8	37.1	13.5	27.1	13.9	28.6
- S/G	0.76	1.30	-	0.04	-	0.01
- H/G	-	-	0.14	0.21	-	0.02

Tableau 1. Résultats comparés des acidolyses A et des thioacidolyses T de lignines de bois moulu.

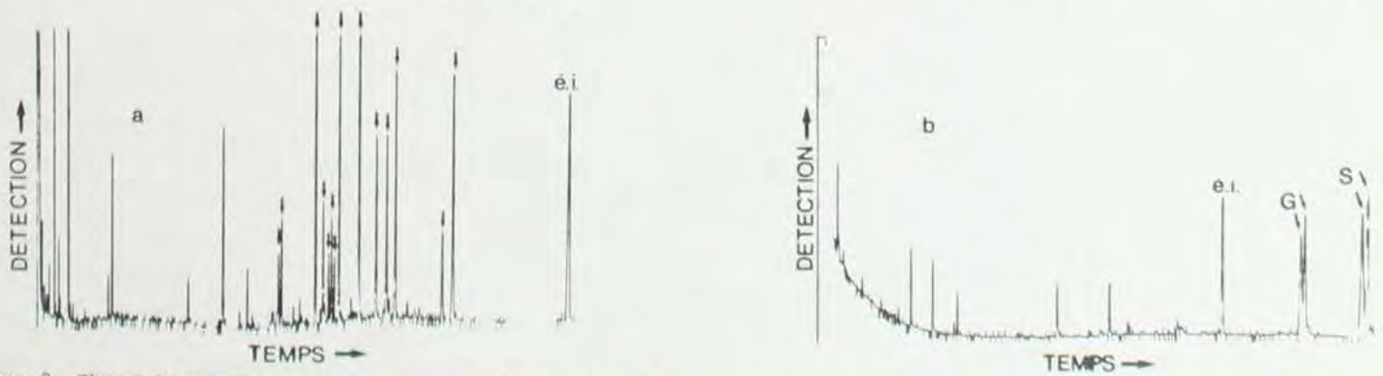

Figure 2. Chromatogrammes en phase gazeuse des produits monomères triméthylsilylés guaïacyles (G) et syringyles (S), issus a) de l'acidolyse (indiqués par une flèche) et b) de la thioacidolyse d'une lignine de Peuplier (é.i:étalon int.)

Le rendement total de thioacidolyse est environ le
uble de celui de l'acidolyse. L'amélioration du ren-
ment est plus forte pour les unités S et H que pour les
ités G. La thioacidolyse donne donc un reflet plus
dèle de la quantité et de la composition des structures
lvolysées que l'acidolyse.

La thioacidolyse a permis de confirmer l'hétérogénéité
ucturale des fractions de lignines extraites successi-
ent de bois de Peupliers, par des méthodes douces.
un nombre élevé d'échantillons, issus de Peupliers ou
Blé, elle a permis la mise en évidence d'une forte
rélation linéaire positive entre le rapport S/G et la
me (S + G) des diastéréoisomères syringyles et guaïa-
es. Plus la teneur en unités syringyles est forte, plus
liaisons alkyl-aryl éthers non condensées sont fré-
ntes. Ce résultat concorde avec celui obtenu par
sser et al (6). L'optimisation de certains paramètres
rimentaux et l'analyse des dimères de thioacidolyse
titueront la suite de ce travail.

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Le rendement total de thioacidolyse est environ le double de celui de l'acidolyse. L'amélioration du rendement est plus forte pour les unités S et H que pour les unités G. La thioacidolyse donne donc un reflet plus fidèle de la quantité et de la composition des structures solvolysées que l'acidolyse.

La thioacidolyse a permis de confirmer l'hétérogénéité structurale des fractions de lignines extraites successivement de bois de Peupliers, par des méthodes douces. Sur un nombre élevé d'échantillons, issus de Peupliers ou de Blé, elle a permis la mise en évidence d'une forte corrélation linéaire positive entre le rapport S/G et la somme (S + G) des diastéréoisomères syringyles et guaïacyles. Plus la teneur en unités syringyles est forte, plus les liaisons alkyl-aryl éthers non condensées sont fréquentes. Ce résultat concorde avec celui obtenu par Glasser et al (6). L'optimisation de certains paramètres expérimentaux et l'analyse des dimères de thioacidolyse constitueront la suite de ce travail.

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REACTIONS OF PHENYLCOUMARAN LIGNIN MODEL QUINONE METHIDES WITH AHQ/ANTHRANOL

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ABSTRACT

Quinone methides prepared in situ from phenylcoumaran lignin models, which did not contain a γ-hydroxymethyl group, readily formed addition products with anthranol but not with anthrahydroquinone (AHQ). For phenylcoumaran lignin models containing the hydroxymethyl group the retro-aldol reaction (liberating formaldehyde) was so facile and rapid under the conditions used that stilbene formation from the quinone methide took precedence over adduct formation.

KEYWORDS: Lignin model, phenylcoumaran, quinone methide, anthraquinone, anthranol

INTRODUCTION

A great deal of activity has been directed toward the study of the reactions of AHQ and anthranol with β-aryl ether quinone methides. It is primarily the reactions of these lignin units under alkaline/additive pulping conditions which are responsible for the accelerated cleavage of the lignin macromolecule in, for example, AQ pulping.

Loss of AQ from the pulping cycle has also received considerable attention[1]. We have been interested in ascertaining how, and to what degree, the reactions of additives with other lignin unit quinone methides contribute to their overall function in the pulping process.

Although there is considerable speculation[2] as to whether adducts between AHQ (or anthranol, a reduction product of AQ which is also present in alkaline cooking liquors) are intermediates in the catalytic cleavage of β-ether bonds under alkaline conditions, there is no question that such adducts are readily formed[3]: furthermore, their formation may not be as reversible as many tend to believe.

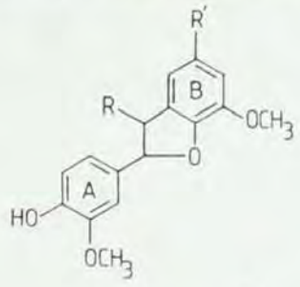
β-aryl ether quinone methides are not the only quinone methides which can form under pulping conditions. Indeed, any free-phenolic unit with an α-leaving group (OH, OAr, or OR) can form quinone methides[4]. We wished to know if these quinone methides can also trap AHQ or anthranol and, if so, how this affects the AQ cycle and the reaction pathways of these other units.

The main objective of the work described in this paper was to determine if quinone methides from β-C linked structures react with AHQ and anthranol and to characterise any adducts formed. Only the phenylcoumaran structure is considered here, although studies on β-Cl and other β-C linked models are also in progress in our laboratories.

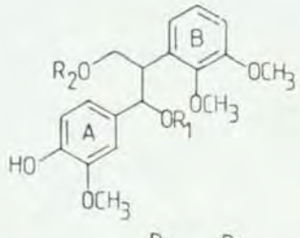
RESULTS AND DISCUSSION

Models

The most readily available phenylcoumaran models are dehydrodiisoeugenol 1[5], and its reduction product dihydrodehydrodiisoeugenol 2 (Fig. 1). Use of 2 rather than 1 removes the complication of further reactions of the vinyl sidechain which are not characteristic of the phenylcoumaran moiety.



	R	R'
1	CH_3	$CH{=}CH{-}CH_3$
2	CH_3	$CH_2CH_2CH_3$
3	CH_2OH	H
4	CH_2OAc	H



	R_1	R_2
5	H	H
6	Ac	Ac

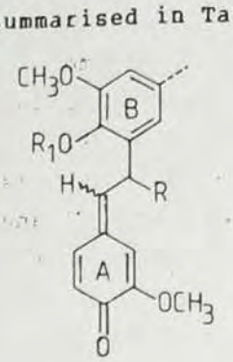
Fig. 1. Phenylcoumaran and 'opened' Phenylcoumaran models used.

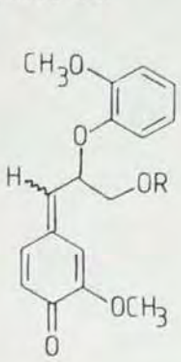
Although the use of these models is valuable in developing methods for the study of adduct formation, it is preferable to use a more representative model such as 3 (Fig. 1) which possesses the γ-hydroxymethyl group present in most lignin sidechains. The presence of this group markedly influences the course of important reactions.

A model representing a 'ring-opened' phenylcoumaran (which could not re-cyclise) was also required in our studies. Model 5 (Fig. 1), in which the B-ring phenolic group is methylated, was prepared using essentially the method of Brunow and Lundquist[6].

Anthranol and AHQ Adducts with β-5 Models

Alpha-aryl ethers such as compounds 1-4 (Fig. 1) are known[4] to (reversibly) generate quinone methides at a significant rate even at 10°C in 1M NaOH (Fig. 3). Therefore, attempts to form adducts from quinone methides 7-9 (Fig. 2) were made by addition of models 1 to 4 directly to solutions of anthranol or AHQ in base. These reactions gave products as summarised in Table 1.





12

	R	R_1
7	CH_3	H
8	CH_2OH	H
9	CH_2OAc	H
10	CH_2OH	CH_3
11	CH_2OAc	CH_3

Fig. 2. Quinone methides.

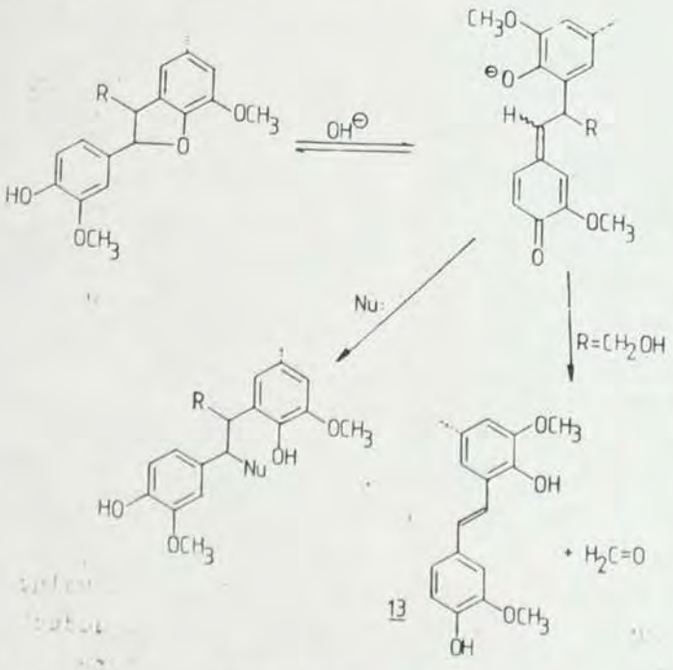


Fig. 3. Reactions of phenylcoumarans.

Generation of the quinone methide 10 from the ring-opened phenylcoumaran model 5 at moderate temperatures required the α-OH to be replaced with a better leaving group. Attempts to form the α-bromide of 5 using TMSBr[7] were unsuccessful due to spontaneous loss of formaldehyde, and formation of stilbene 13 from the bromide. However, the required quinone methide 11 was obtained in situ from the free phenolic diacetylated model 6 in base. As there was no possibility of quinone methide 11 reverting back to a phenylcoumaran by an internal cyclisation, the yield (Table 1) of adduct was substantially higher from model 6 than from the true phenylcoumarans 1-4.

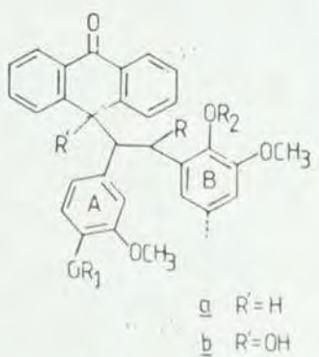
TABLE 1

Approximate yield data for adduct reactions. Conditions: 2 eq anthranol or AHQ; 1M NaOH (except 0.3 M for 4 to minimise hydrolysis of the γ-OAc group); 50°C; 1 hr (15 min for 6).

Model	Anthranol			AHQ		
	Adduct#	S/M**	Stilbene	Adduct	S/M	Stilbene
1	70(97:3)	30	0	0	100	
2	70	30	0	0	100	
3	0	0	100	0	0	100
4	50(90:10)	50	0	-	-	
6	*90(75:25)	0	0	0	.	

\# Ratio of erythro:threo isomers (in bracket determined from H-1 NMR.
* 75% yield after flash chromatography.
** Starting material.

Despite the high stereoselectivity observed[1] for threo adducts from β-ether quinone methides (e.g., 12), both adduct isomers can be detected from attack of anthranol on any of the β-C5 quinone methides, Figure 5 and Table 1.



	R	R_1	R_2
14	CH_3	H	H
15	CH_3	Ac	Ac
16	CH_2OH	H	H
17	CH_2OH	H	CH_3
18	CH_2OAc	Ac	Ac
19	CH_2OAc	Ac	CH_3

a R'=H
b R'=OH

Fig. 4. Adduct structures.

The β-C5 adducts 14-19 (Fig. 4), like the β-aryl ether adducts[1,8-9], have fascinating NMR characteristics due to their conformations in solution. In the erythro isomer of 19 (which is analogous to the 'threo' isomer in β-ether adducts because of the way the groups are assigned) the A ring is again[1,9] clearly situated over the anthracenyl ring system as is evidenced by the highly shielded ring A methoxy and the ring A protons (Fig. 5). However, the minor threo isomer is quite unlike the 'erythro'

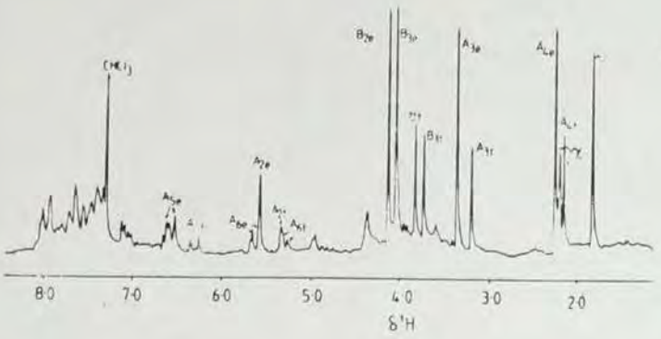


Fig. 5. 90 MHz H-1 NMR spectra of adducts 19.

isomer[8] of ß-ether adducts in that ring A is even more intensely shielded. Examination of the NMR spectra leads to the postulated conformations shown in Fig. 6.

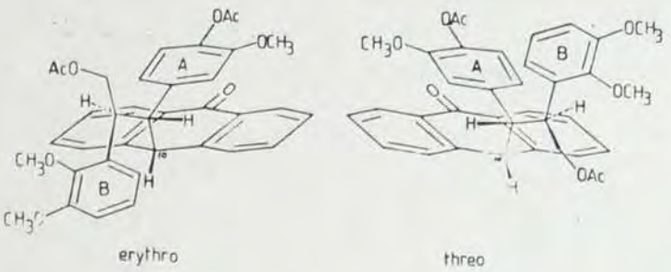


Fig. 6. Postulated conformations of erythro and threo isomers of compound 19.

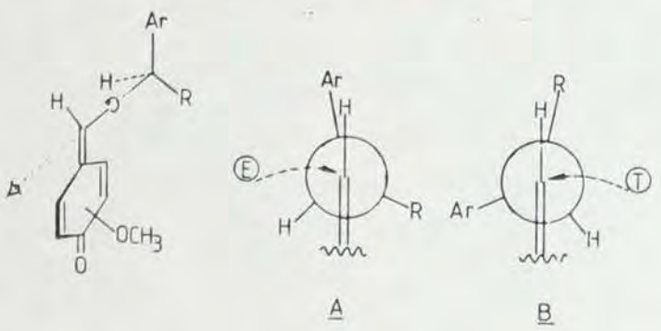


Fig. 7. Major rotamers of ß-5 quinone methides.

The observed stereoselectivity can reasonably be attributed to the quinone methide conformations. Fig. 7 shows the two major rotamers expected[10] for ß-5 quinone methides. If R is sterically less demanding than Ar (as expected for R=Me, CH_2OH, CH_2OAc), A would be the major rotamer. Attack from the less hindered side would lead to the erythro adduct.

For reasons that are not clear, these ß-5 quinone methides seem to be markedly less stable toward polymerisation than ß-aryl ether quinone methides and, at modest concentrations, are observed only transiently at room temperature. Attempts to characterise them by NMR techniques (analogous to those used for the ß-ether quinone methides) are in progress.

Several further important points are apparent from Table 1.

1. Whereas anthranol adducts form readily from these quinone methides, it was not possible to form AHQ adducts (R'=OH, Fig. 4), presumably for a combination of steric and electronic reasons. It has been noted previously[1] that AHQ adds less readily than anthranol to ß-aryl ether quinone methides and it has also been shown[1] that, in competition studies, anthranol adducts are formed in overwhelming preference.
2. Formation of quinone methides from phenylcoumarans 1-4 is clearly reversible, but anthranol addition competes reasonably effectively for the quinone methide. In a 5-minute reaction where the quinone methide 7 was generated from the α-iodide at room temperature, the ratio of adduct 14a to phenylcoumaran 2 was about 10:90. Hence, anthranol attack seems to be about 10% as rapid as the recyclisation reaction.
3. In compound 3, with a γ-CH_2OH, not even anthranol can compete with the quinone methide against the retro-aldol elimination of formaldehyde and generation of the stilbene. The reaction therefore follows the same course as in the absence of the additive (Fig. 3)[11].

This last point illustrates the pitfalls in using inappropriately substituted or derivatised models. Acetylated models[1,12], or acetylated lignin itself[13,14], are frequently used to allow in-situ generation of quinone methides at room temperature. But the protection afforded to the γ-CH_2OH group by acetylation means that formaldehyde loss by a retro-aldol reaction cannot compete for the quinone methide. This is not so critical in the case of ß-aryl ether quinone methides since anthranol, and possibly AHQ, can add to quinone methide 12 (R=H) efficiently before the retro-aldol reaction (to give the styryl ether) can occur. However, in these ß-C5 models, the retro-aldol reaction entirely dominated the reaction of representative quinone methides 8 or 10 (with the γ-CH_2OH group) whereas the adduct readily formed from the acetylated quinone methides 9 or 11. Thus, reactions on acetylated milled wood lignin with anthranol, where adducts other than ß-ether adducts appear to be observed in the C-13 NMR spectra[13,14], may not be representative of reactions of the underivatised quinone methides.

CLUSIONS

Adduct formation between ß-C5 quinone
nides and anthranol, but not AHQ, occurs
dily, but only when the possibility of
naldehyde elimination from the quinone
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CONCLUSIONS

Adduct formation between β-C5 quinone methides and anthranol, but not AHQ, occurs adily, but only when the possibility of maldehyde elimination from the quinone methide is removed. Consequently, the reactivity of lignin phenylcoumaran units in soda-additive pulping is not expected to be altered by the additive. Conversely, it is not expected that AQ losses can be attributed to reactions with β-C5 quinone methides.

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HYDRODYNAMIC ASPECTS OF POLYMER BONDING IN PAPERMAKING

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ABSTRACT

Retention of fillers and fines in papermaking is governed by several mechanisms, the most important being: (i) the efficiency of shear-coagulation or deposition; (ii) the strength of the bonds between fillers or fines and fibers and (iii) the efficiency of entrapment in the forming sheet. Polymeric retention aids affect these efficiencies to various degrees.

KEYWORDS: Retention, fines, fillers, retention aids, hydrodynamics.

INTRODUCTION

Papermaking suspensions contain, besides the pulp fibers that are made into a sheet of paper on the wire section of the paper machine, many more non-soluble materials, such as fines and fillers. Usually it is desirable to retain as many of these small particles as possible. Increased efficiency can be achieved by adding retention aids to the papermaking furnish, usually high molecular weight cationic polyelectrolytes. Their efficiency is determined by many factors that are at present poorly or not understood. In this paper we will present some remarks on the hydrodynamic aspects of papermaking, which are crucial in the retention mechanisms.

Selective coagulation

The main task in papermaking is producing a homogeneous sheet of paper and therefore polymer bridging between fibers must be avoided as this leads to fiber flocs and thus a inhomogeneous fiber distribution. On the other hand bridging between fibers and fines or fillers is very desirable. Bridging between fines or fillers among themselves could be either desirable or not depending on the end use of the paper.

From these arguments it follows that coagulation must be extremely selective. Hydrodynamic conditions favor selective coagulation(1) in which polymers play an important role(2). In general under hydrodynamic conditions aggregates of unequal sized particles are more likely to remain intact.

Hydrodynamic vs. colloidal forces.

The ratio of colloidal to hydrodynamic forces determines the efficiency of the shear coagulation process. Polymers can affect this efficiency to a large extend. They affect both the efficiency of aggregate formation and also of aggregate break-up.

Some of the parameters that determine hydrodynamic and colloidal forces are summarized in Table I.

Table I

factors affecting hydrodynamic and colloidal forces

forces:	hydrodynamic	colloidal
parameters:	velocity distribution	Hamaker constant
	system boundaries	surface charge
	particle size & shape	ionic strength
	viscosity	particle size & shape
		diffusion constant
		polymer bridging

Shear coagulation or deposition

For small particles the coagulation in turbulent flow can be described by coagulation in shear flow in which the rate of shear is replaced by an average value characteristic of the strength of the turbulent flow. In case of small particles depositing on pulp fibers the rate can be estimated from

$$J \approx \sigma (4/3) n G_{eff} R^2 L.$$

Here J is the nuber of small particles captured per fiber per unit time; σ is the capture efficiency, n the number of fines or fillers per unit volume, G_{eff} the effective average rate of shear, R the fiber radius and L the fiber length. The effective average rate of shear can be estimated from the theory of isotropic fully developped turbulence:

$$G_{eff} = \mu Re^{3/2}/dl^2,$$

where μ and d are the viscosity and the density of the medium (water) resp. and Re is the Reynolds number based on the average macroscopic fluid velocity and a characteristic dimension l (e.g. the width of the slice of the headbox).

One of the mechanisms of fines retention with polymeric retention aids is to increase the value of . This is possible because particles can be captured at larger distances from the fiber surface. As an example we studied the deposition of titanium dioxide particles on cellophane, using the impinging jet technique(3). This technique allows for a precise control of the hydrodynamic forces acting on the colloidal particles. In the absence of retention aids we found that the deposition increases from almost zero till the values characteristic for fast deposition (no energy barrier, $\sigma \approx 1$) at a critical 1-1 electrolyte concentration of about 5mM. Adding a cationic polyelectrolyte of molecular weigth 500,000 resulted in an increase of the efficiency by a factor of four.

Particle detachment

After particle deposition the possibility exists that the deposited particles are removed by the shear forces. Obviously one would like to retain as many particles as possible on the fibers. The rate at which particles detach depends on the bond strength and the hydrodynamic forces exerted on the deposited particles. An obvious way to increase retention is to increase the bond strength between the fines or fillers and the fibers. Again high molecular cationic polyelectrolytes are ideal as they adsorp on the negatively charged surfaces of fines and

fibers. The bond strength depends very much on the conditions under which the bond was formed as well as conditions prior to and after the formation of the bond. The bond strength may depend on the fact that a particle has been stuck to a fiber before but was removed afterwards. This could have changed or ruptured the polymer on its surface. Also the bond strength depends on conditions during bond formation. At high shear, weak bonds do not survive and usually stronger bonds are formed at higher shear. After bond formation the bond strength can either increase with time due to an increase in the number of polymer segments participating in bonding, or it can decrease with time if a competion exists for bonding sites between the bridging polymer and non-adsorbed polymer or o ıer surface active materials. In model experiments on detachment of polymer coated particles in impinging jets, we have observed both phenomena (increasing and decreasing bond strength). The bond strength of titanium dioxide particles deposited by sedimentation on cellophane has been observed by Hubbe(4). He found that such particles are removed typically at wall shear stresses in the range 10-100 Pa. Pelton et. al.(5) descibe similar results for the detachment of latex particles from glass surfaces. One must bare in mind that in these experiments the bonds were formed by sedimentation and one must be careful in extrapolating these data to papermaking conditions. The history effects in polymer bridging are summarized in Table II.

Table II
History effects in polymer bridging

1. Deposition efficiency and bondstrength depend on conditions prior to bond formation (previously broken bonds, polymer transfer, polymer rupture)
2. Bondstrength depends on conditions of bond formation. In general stronger bonds are formed at higher shear.
3. Bond strength depends on time. Usually bond strength increases with time.
4. Bond strength depends on conditions after bond formation

The weakening of the bond due to excess freely suspended polymer is comparable to the exchange of adsorbed and non-adsorbed polymer. Freely suspended polymer can be exchanged with polymer engaging in bond formation, thus reducing the bond strength. This is shown schematically in Fig.1.

Figure 1. Weakening of a bond by free polymer.

Particle entrapment

A third mechanism for fines retention is particle entrapment in the forming sheet. This mechanism is particularly important for fines particles whose dimensions are comparable to the pores of the forming sheet. The average pore radius, r, in a porous sheet can be estimated from

$$r = R\epsilon/(1-\epsilon),$$

where ϵ is the porosity or void fraction of the sheet. However there exist pores of size much smaller than the average pore radius and the smallest pore sizes will determine which fines can pass through.

The entrapment of fillers and small fines (<10µm) is extremely inefficient and does not contribute to retention(6). Polymers are not expected to increase this efficiency very much, especially at low concentrations. At higher concentrations the polymer could form a kind of web in which small particles can be trapped, similar to the large fines in the forming sheet. Polymers that form gels at low concentration will be the most effective in trapping particles thic way.

Concluding remarks

Several fines retention mechanisms have been discussed with emphasis on the role of polymers and hydrodynamic forces. It can be concluded that high molecular weigth cationic retention aids can increase retention in a variety of ways.

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EFFECT OF ANTHRAQUINONE ON THE ALKALINE DEGRADATION OF POLYSACCHARIDES

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ABSTRACT

Soda-anthraquinone (AQ) digestions of cotton cellulose at 170°C gave higher yields of residual cellulose with increased carboxyl contents and lower viscosities than soda digestions. However, when reduced AQ (as 9,10-diacetoxy-anthracene (DAA)) was added to soda cooks of cotton cellulose containing sodium dithionite, no change in yield and carboxyl content and only a small viscosity decrease early in the cook was observed. Soda and soda-AQ pulping of P. radiata wood gave pulps which after chlorite delignification had lower zero span tensile indexes and slightly lower viscosities with increasing AQ charge. The data suggest that AQ promotes the scission of glucosidic bonds of cellulose under alkaline pulping conditions.

INTRODUCTION

The addition of catalytic amounts of AQ and its derivatives to alkaline wood pulping systems results in higher pulp yields and increased rates of delignification. The higher pulp yields are due in part to the ability of AQ to oxidize the terminal aldehyde groups of polysaccharides to aldonic acids (1), thereby stabilizing the polysaccharides towards endwise depolymerization (peeling) reactions. To explain the effectiveness of such small amounts of AQ, a cyclic mechanism has been proposed in which AQ is continually reduced by the polysaccharides and the reduced AQ species is oxidized back to AQ by the lignin (2,3).

Although the oxidation of terminal aldehyde groups of polysaccharides by AQ under alkaline pulping conditions is well documented, the effect of AQ on the random alkaline cleavage of glycosidic bonds is less well understood. AQ-assisted random alkaline scission of glucosidic bonds occurs in solutions of amylose both in the presence and absence of oxygen (4). For alkaline degradation of cellulose at 170°C, although AQ promotes random cleavage in the presence of oxygen (5), the effect of AQ and its derivatives without oxygen is less clear. Whereas Carlson and Samuelson (5) found that addition of 5% AQ (cellulose basis) to soda cooks of cotton cellulose under nitrogen gave increased yields and slightly lower viscosities (indicative of chain cleavage), other studies showed that addition of 0.1% AQ and its derivatives (6) or tetrahydro-AQ (7) gave increased yields and slightly higher viscosities.

Investigations of wood-derived polysaccharides require consideration of the contribution of both cellulose and hemicelluloses to the properties of the pulps. Soda-AQ cooking of wood holocelluloses has been reported to give pulps with higher yields and higher viscosities (8) and lower zero span tensile strengths (9) than the soda controls. For wood samples, AQ addition to soda cooks of spruce caused reductions in pulp viscosities (10), whereas no change was noted in the viscosities of soda-AQ pulps from black spruce within the range 0.1-0.5% AQ addition (11). Because of the contradictory nature of the above observations, we undertook an investigation of the effect of AQ on the alkaline degradation of cotton cellulose and P. radiata wood.

EXPERIMENTAL

General

Pulp viscosities were measured as 0.5% cuene solutions by Tappi method T230 om-82.

Carboxyl contents of the pulps were obtained by the methylene blue method (12).

Cellulose tricarbanilates were prepared by the procedure of Schroeder and Haigh (13), and their molecular weight distributions (MWDs) were obtained by chromatography on a series of three Showdex columns, KF-806, 805 and 804, with tetrahydrofuran as the eluting solvent.

Alkaline treatment of cotton cellulose

Bleached cotton linters (4.0 g) and 200 mL 1M sodium hydroxide were placed in 500 mL steel vessels under nitrogen. Various additives were introduced, and the vessels were rotated, six at a time, in a hot air bath at 170°C. After cooling and filtration, the treated pulps were kept at 60°C with a solution of 0.1M sodium dithionite and 0.25M sodium hydroxide and then filtered. The procedure was repeated until the red colour of reduced AQ was no longer evident. As additives, AQ (208 mg, 1 mmol), 9,10-diacetoxy-anthracene (DAA) (294 mg, 1 mmol), 1,4-diacetoxybenzene (194 mg, 1 mmol), glucose (1.8 g, 10 mmol) and sodium dithionite

(582 mg, 3.3 mmol) were used.

Additional experiments were performed in 180 mL vessels, with 5 g samples of cellulose in 50 mL 1M sodium hydroxide, and AQ (52 and 5.2 mg) the additive.

Soda and soda-AQ pulping of P. radiata

P. radiata woodchips were digested at 170°C with 15.3% active alkali as Na_2O and varying amounts of AQ. The liquor:wood ratio was 4:1, time to 170°C, 1.5 h, and time at 170°C, 1.6 h.

RESULTS AND DISCUSSION

Alkaline degradation of cotton cellulose

Comparative studies were carried out on the soda and soda-AQ digestion of cotton cellulose, with AQ additions of 5,1 and 0.1% based on cellulose. The larger AQ charges were used in an attempt to simulate the soda-AQ pulping of wood, during which AQ is continually regenerated.

In an oxygen atmosphere, soda-5% AQ digestion of cellulose gave higher yields and lower viscosities than did soda cooking. The same trend was noted in a nitrogen atmosphe

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In an oxygen atmosphere, soda-5% AQ digestion of cellulose gave higher yields and lower viscosities than did soda cooking. The same trend was noted in a nitrogen atmosphere, although the effect was smaller (Figure 1), and for soda-1% AQ and soda-0.1% AQ cooks of cellulose, the yield increase and viscosity decrease was still lower. Addition of 5% AQ to kraft cooks of cellulose gave less viscosity drop than soda cooks. These observations on cotton cellulose corroborate those of Carlson and Samuelson (5), and contrast with those in which viscosity increases were noted (6,7).

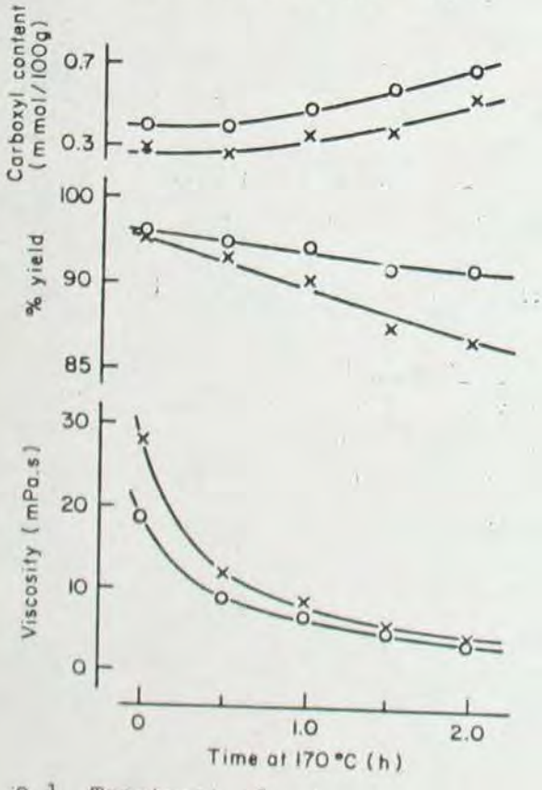

Figure 1. Treatment of cotton cellulose at 170°C with 1M NaOH, without AQ (X) and with 5% AQ addition (O).

The carboxyl contents of all the AQ-treated celluloses were higher than the controls, due to oxidation of cellulose end groups by AQ to aldonic acids (1). The MWDs of the tricarbanilates of the treated celluloses were determined by size exclusion chromatography, and showed that the loss in DP of the cellulose in the AQ cooks took place across the whole range of molecular weight (Figure 2).

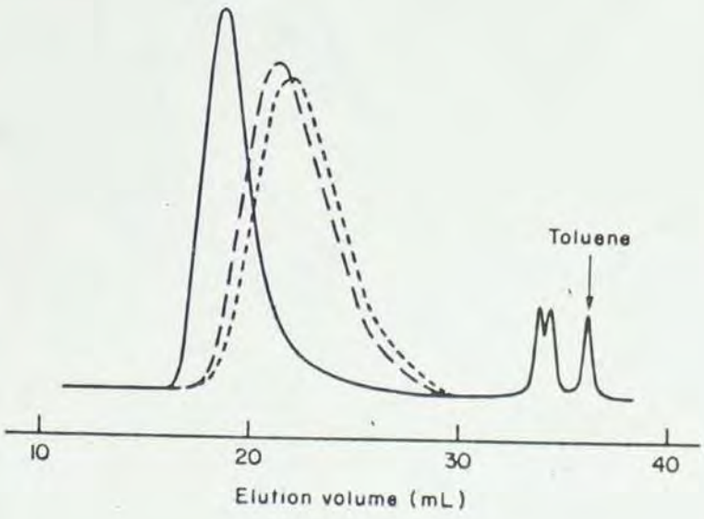

Figure 2. Size exclusion chromatograms of tricarbanilates of cotton cellulose (——) and cellulose treated for 2 h with 1M NaOH without AQ (— — —) and with 5% AQ (--------)

Addition of 5% AQ to soda cooks of cellulose containing the reducing agent glucose gave little yield enhancement and only small viscosity reductions compared to the soda cooks. When glucose was replaced by sodium dithionite, no yield enhancement was observed with the AQ cooks, although a small viscosity drop again ensued. However, addition of either DAA or 1,4-diacetoxybenzene (sources of anthrahydroquinone or hydroquinone, respectively) to soda-dithionite cooks of cellulose gave no yield increases and, except for the early stages of the DAA cook (Figure 3), no viscosity reductions. The MWDs of the DAA-treated celluloses were identical with the soda controls.

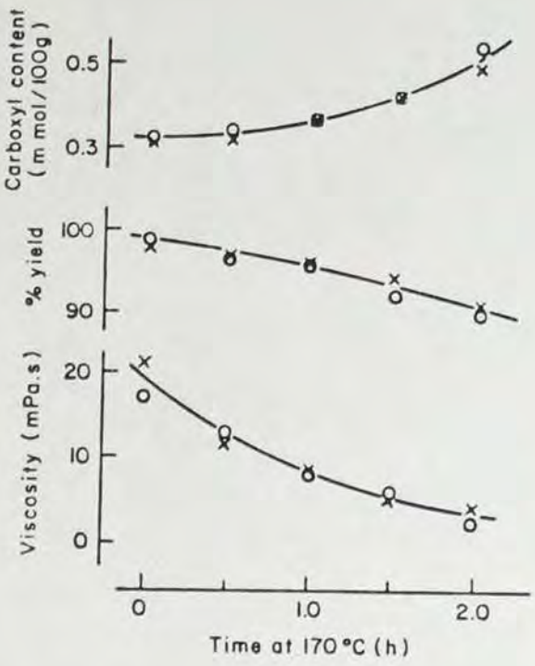

Figure 3. Treatment of cotton cellulose at 170°C with 1M NaOH and 0.017M $Na_2S_2O_4$ without DAA (X) and with 7.3% DAA addition (O)

Thus it appears that both the yield enhancement and decrease in viscosity observed when AQ is added to soda cooks of cellulose are due to oxidation. This is in accordance with the proposal of Gierer et al. (14) that AQ pretreatment of pine wood oxidizes the polysaccharides, rendering them more labile towards degradation during kraft pulping. However, although the results with cotton cellulose suggest that AQ itself is the oxidant causing random cleavage of the chains, the involvement of peroxide which may be formed from anthrahydroquinone and trace amounts of oxygen remaining in the early stages of the cook, as has been previously suggested (5), cannot be ruled out.

Soda-AQ cooking of P. radiata wood

The effect of AQ on the soda pulping of P. radiata wood was investigated by carrying out a series of cooks using the same time/temperature program and alkali charge but with addition of varying amounts (0-1%) of AQ (Table 1).

The pulps resulting from cooks with increasing AQ charges had lower lignin and higher carbohydrate contents. With the exception of the soda cook with no AQ addition, the zero span tensile index (ZSTI) values of the pulps

% AQ	% scr. pulp yield	% lignin in pulp	ZSTI Nm/g	% α-Cell. (a)	visc. mPa.s (a)	ZSTI Nm/g (a)
0	51.3	15.4	150	81.5	22.1	171
0.05	50.7	9.4	165	81.4	20.4	159
0.1	49.0	7.4	161	80.9	20.3	159
0.2	49.2	5.3	155	82.2	18.4	160
0.5	49.3	4.5	151	81.4	18.9	154
1.0	50.0	3.2	148	80.9	18.5	142

a) chlorite delignified pulps

Table 1 Effect of AQ on the soda pulping of P. radiata

decreased with increasing AQ charge. The ZSTI values may be dependent on the chemical composition of the fibre, and thus attempts at correlation of fibre strength with cellulose degradation from these results is difficult.

After chlorite delignification, the pulps had similar α-cellulose contents (Table 1), although with increasing AQ charge the lignin contents were somewhat lower, and the carbohydrate contents, particularly the glucomannan (15), were higher. The pulps thus had similar contents of fibrous material.

Both the cuene viscosities and ZSTI values for the delignified pulps decreased with increasing AQ charge. The lower viscosity of the soda-1.0% AQ pulp compared to the soda pulp was indicative of a DP decrease of ca.9% (16). Basta and Samuelson (10) have noted similar small viscosity decreases in soda-AQ compared to soda pulps, while Kubes et al. found for black spruce soda-AQ pulps, no change in viscosities in the range 0.1-0.5% AQ addition. The decrease in ZSTI with increasing AQ charge shows that the presence of AQ in the digester leads to fibre weakening. These data indicate that AQ does promote random cleavage of glucosidic bonds in cellulose. The possibility of modification of cellulose by AQ which leads to fibre weakening without chain cleavage, as has been proposed by Eachus (9) for soda-AQ cooking of holocellulose fibres, must also be considered.

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ACETYL XYLAN ESTERASES - A NOVEL CLASS OF MICROBIAL ENZYMES INVOLVED IN THE DEGRADATION OF HEMICELLULOSE

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ABSTRACT

Fungal cellulolytic systems contain esterases that deacetylate naturally occurring plant acetyl xylans. The esterases act synergistically with xylanases in the degradation of the acetylated polymers.

INTRODUCTION

The xylan of several wood species is acetylated. Consequently, microorganisms in at least some natural habitats face the task of degrading an acetylated, rather than a deacetylated polymer. To date, studies of xylan degradation by microbial enzymes have used as a substrate only the deacetylated material obtained on alkaline extraction of delignified holocellulose, hence a polymer that does not occur naturally.

The sequence of enzymic reactions involved in the degradation of the acetylated polymer is unknown. One possibility is that enzymic deacetylation is a prerequisite for subsequent hydrolysis by xylanases and xylosidases. While the existence of enzymes that deacetylate xylan might have been anticipated, they do not seem to be described previously. The present study points to a wide occurrence of esterases of this type and delineates aspect of their role in the degradation of acetyl xylan.

RESULTS

The substrates used were: a non-dialysable fraction of water-soluble hemicellulose produced by the steaming of birch, and a water-soluble polysaccharide extracted from beechwood holocellulose by dimethyl sulfoxide. Both polymers were characterized by ^{13}C-NMR spectroscopy as highly acetylated xylans. Acetic acid content exceeded 10% in both samples.

Acetyl xylan esterase activity was found in commercial preparations of cellulase enzymes from Trichoderma reesei (Novo), T. viride (Onozuka), and Aspergillus niger (Sigma). The activity was found also in media of cultures of Schizophyllum commune grown on cellulose and Aureobasidium pullulans grown on xylan. The liberation of acetic acid from acetyl xylan showed characteristics of an enzyme-catalyzed reaction. The rate of acid liberation was proportional to the amount of enzyme and the time of incubation. The pH optimum was about pH 6.5. Reaction did not occur with heat-denatured enzyme preparations.

The fungal esterases differed from purified orange peel acetylesterase, porcine liver esterase and pectinesterase in specific activities towards acetyl xylan and 4-nitrophenyl acetate. The fungal preparations were relatively more active on acetyl xylan as shown by the ratio of esterase activities measured (Table 1). The specific activities of fungal preparations on acetyl xylan were invariably greater, even though these preparations were crude protein mixtures. Acetyl xylan esterase activity was not associated with a pectinesterase.

Table 1

Enzyme preparation	4-Nitrophenyl acetate esterase	Acetyl xylan esterase	Ratio
	*U/mg prot.		
T. reesei cellulase	0.061	0.043	1.4
T. viride cellulase	0.027	0.08	0.34
A. niger cellulase	0.135	0.041	3.3
S. commune cellulase	0.363	0.072	5.0
A. pullulans xylanase	1.75	0.39	4.5
Acetylesterase (orange)	1.47	0.022	66.8
Esterase (porcine liver)	49.7	0.011	4518.2
Pectinesterase (orange)	0.16	0.004	40.0

*1 μmol/min

Separation of components of the cellulolytic systems of T. reesei and S. commune by HPLC on a TSK DEAE-3SW column resulted in fractions containing acetyl xylan esterases and xylanases that were not mutually contaminated. As with the crude fungal preparations, the xylanase-free esterase fractions showed much higher reactivity towards acetyl xylan than the plant and animal esterases. Based on these observations, the T. reesei and S. commune esterases are considered to represent a novel class of carbohydrate esterases involved in the degradation of native hemicellulose.

The availability of xylanases and acetyl xylan esterases that were not mutually contaminated enabled investigation of the ability of xylanases to hydrolyze acetyl xylan as well as to assess the role of the esterases in the overall degradation. Xylanases alone hydrolyzed acetylated xylan to a much lesser extent than in the presence of an acetyl xylan esterase. An example of the birch acetyl xylan degradation by S. commune enzymes is shown in Table 2. The table also shows that the

same number of units (4-nitrophenyl actetate used as substrate) of orange peel acetylesterase had ly slight effect on the reaction, substantiating the view that the esterase of S. commune is relatively specific for acetyl xylan.

Table 2

Reaction time	Reducing sugars released by xylanase alone	xylanase+ acetyl xylan esterase	xylanase+ orange peel esterase
min	umol xylose equivalents/ml		
10	0.27	0.22	0.18
30	0.78	0.71	0.59
60	1.12	1.47	1.00
120	1.30	2.03	1.30
180	1.36	2.35	1.53
240	1.39	2.40	1.62

The kinetics of acetyl xylan degradation by xylanase plus or minus esterase correlated well with the results of the analysis of the hydrolysates by thin-layer chromatography (Fig. 1).

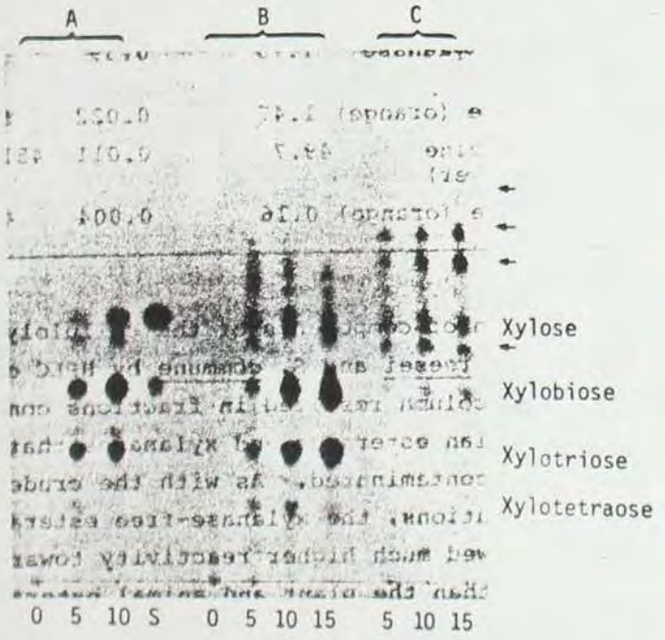

Figure 1. Thin-layer chromatography of the products of hydrolysis of deacetylated birch xylan (A) and acetylated birch xylan by a Schizophyllum commune xylanase in the presence (B) and in the absence (C) of acetyl xylan esterase from the same organism. The numbers indicate the time of incubation in hours. S, standards; arrows, acetylated xylooligosaccharides.

ylanase alone released small quantities of both acetylated and non-acetylated xylooligosaccharides. When an acetyl xylan esterase was added, the majority of the products corresponded to non-acetylated xylooligosaccharides, such as those formed upon the action of xylanase on deacetylated xylan.

The presence of xylanase increased the rate of acetic acid liberation from acetyl xylan by esterases. Table 3 summarizes the effect of a S. commune xylanase on acetic acid liberation from the birch acetyl xylan by an acetyl xylan esterase from T. reesei.

Table 3

Reaction time (h)	Concentration of released acetic acid (%) Xylanase absent	Xylanase present
1.5	0.026	0.041
3.5	0.05	0.071
5.5	0.082	0.13
21	0.23	0.52
45	0.35	0.55

DISCUSSION

The synergistic action of xylanases and esterases during the degradation of acetyl xylan could be interpreted as follows. Esterases, by liberating acetic acid, created new sites on the polysaccharide backbone suitable for subsequent productive binding with xylanases. The positive effect of xylanases on the deesterification of acetyl xylan by esterases was due to a preference of esterases to deacetylate shorter fragments rather than the original high molecular weight polysaccharide. A decrease in the polymerization degree of the substrate by xylanases also contributed to the frequency of esterase-substrate interaction by decreasing the viscosity of the reaction medium.

LESS ORDERED REGIONS (LOR) OF CELLULOSE - NEW CHEMICAL APPROACHES

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ABSTRACT

While the crystalline domains of cellulose have been extensively investigated by chemical as well as physical methods, little attention has been paid to the non-crystalline, less ordered regions of the fibers. In the following, several new systems dealing with the average size of a less ordered region, with the dynamic nature of accessibility and with new aspects of water absorption are discussed.

A two-step procedure is used for the determination of the average size of an LOR. First, active carbonyl groups are produced by a controlled mild oxidation of the cellulose. In the second step, the oxidized cellulose is exhaustively extracted with a mild bicarbonate solution under reflux, whereby the "peeling" reaction initiated by the active carbonyls is proceeding along the chains in the LOR, producing isosaccharinic acid and the characteristic yellow chromophore. It is stopped at the edge of the crystalline regions. From the knowledge of the number of active carbonyls and the amount of cellulose dissolved, the average length of a chain in the LOR can be calculated by means of a statistical theory of alkaline depolymerization.

In another system, the accurate determination of accessibility is achieved by determining the reversible sorption of bromine from bromine water on cellulose, which was shown to proceed according to the Langmuir isotherm. This method correlates linearly with IR and X-ray determinations of crystallinity as shown for 16 celluloses ranging from 4 to 70% accessibility.

The accessibility values obtained were shown, at bromine concentrations higher than 0.02 m/l to change with the contact time of the cellulose with the bromine solution, with the concentration of the bromine solution and with the nature of the fiber. Decrystallization and crystallization rates studied were found to be of the first order, both to the LOR concentration in the fiber and to the bromine concentration. The activation energies were in the range of 5-12 Kcal/mole, being higher above the Tg of cellulose in water, e.g. 25°C. The rates of crystallization varies for celluloses of different origins by over 4 orders of magnitude, whereas the activation energy is the same.

The rate of crystallization increases with the orientation factor of the cellulose. Yields and rates of crystallization increase at higher temperatures and orientations which create more favorable conditions for the formation of intermediate liquid crystalline structures inside the polymer phase.

The increase in crystallinity brings about a decrease in water absorption in the LOR as distinct from the absorption on the walls of the crystallites. Linear relationships are obtained between accessibility and water absorption for any series of celluloses produced from an initial basic cellulose by crystallization with bromine to increasing levels. Extrapolation to zero accessibility yields a value for water absorbed on the walls of the crystallites which is characteristic for the series and defines the size of the crystalline regions.

MASS LOSS OF WOOD AND ITS COMPONENTS DURING TRANSMISSION ELECTRON MICROSCOPY

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When a sample of biological material is under observation in a transmission electron microscope (TEM), it is severely damaged by electron irradiation [1]. The most important result of this damage is a rapid loss of mass which can range from 10 to 90% depending on the chemical composition of the specimen [2-4].

Wood is a composite of three biological macromolecules and the extent of its damage during electron microscopy is not known. The goal of the present work is to quantify the damage by measuring the decrease in weight of the whole wood as well as of its three major constituents when they are in a TEM for imaging or for microbeam analysis.

As electrons pass through a specimen, characteristic X-rays are emitted corresponding to the different elements. In addition, a continuum of X radiation (also called Bremsstrahlung or "white" radiation) is generated. The decrease in intensity of this X-ray continuum while the electronic irradiation proceeds corresponds to the change in the specimen mass per unit area [5]. Thus the mass loss of a specimen may be measured by use of an X-ray spectrometer on a transmission electron microscope.

Figure 1 shows the mass loss of the whole wood plotted against the dose for doses smaller than 10^{-9} c/μm^2. The trend is linear and extrapolation to the original mass of the sample is precise. The vertical dashed line represents the dose at which the crystallinity of the cellulose as detected by electron diffraction disappears, and corresponds to a total dose of about $2 \cdot 10^{-11}$ c/μm^2. The mass loss at this level of irradiation is negligible.

In Figure 2 the mass loss is plotted against the dose for much higher levels of irradiation. The decrease of the mass is quite rapid until it reaches an approximately constant value for doses higher than $5 \cdot 10^{-8}$ c/μm^2. The percentage of mass remaining in the whole wood at this level of irradiation is only 42%.

When the electron beam current (flux of the electrons) was varied, essentially no change was found in the curve of mass loss versus dose.

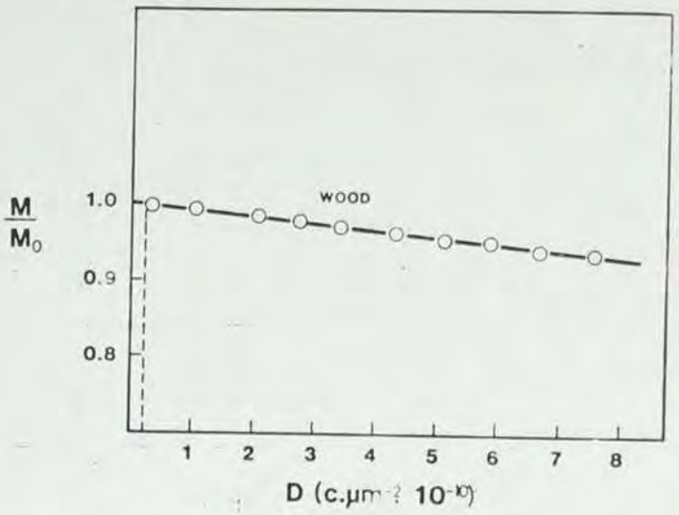

Figure 1. Mass loss of black spruce wood due to an irradiation with 100 keV electrons at room temperature. The thickness of the sample is < 500 nm.

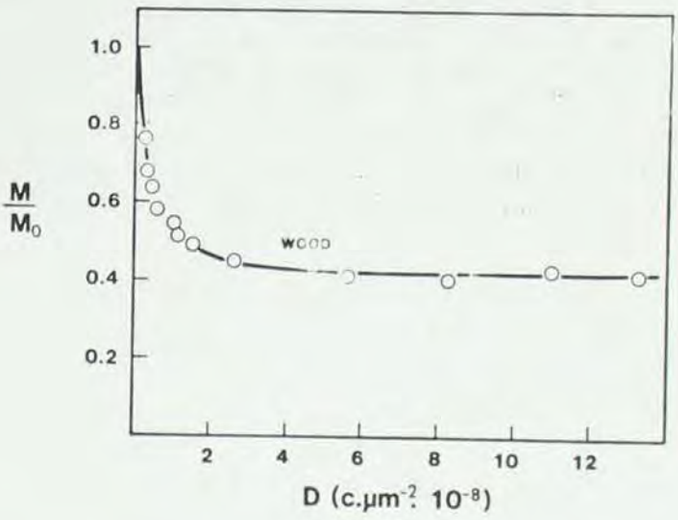

Figure 2. Same as Figure 1 but for higher electron irradiation doses.

Furthermore, no change was noted when the thickness of the sample was varied from 150 nm to 500 nm. Thus, the loss of mass in a TEM operated at 100 kV is independent of the dose rate and of the specimen thickness up to 500 nm.

Figure 3 shows a series of curves representing the mass loss of wood, cellulose from Valonia ventricosa, periodate lignin and xylan. The curves are similar in shape, decreasing to a constant value of mass loss after a dose of about $5 \cdot 10^{-8}$ c/μm^2. However, this constant value is different for each type of sample. The proportion of mass remaining after long irradiation is 32% for cellulose, 45% for xylan and 70% for periodate lignin. By assuming that these three samples are representative of the cellulose, hemicellulose and lignin in black spruce wood in the proportions 50:25:25, respectively, it is possible to calculate the mass loss of the whole wood. The value thus obtained is 44.7% which is in good agreement with our result obtained by direct measurement, i.e., 42%.

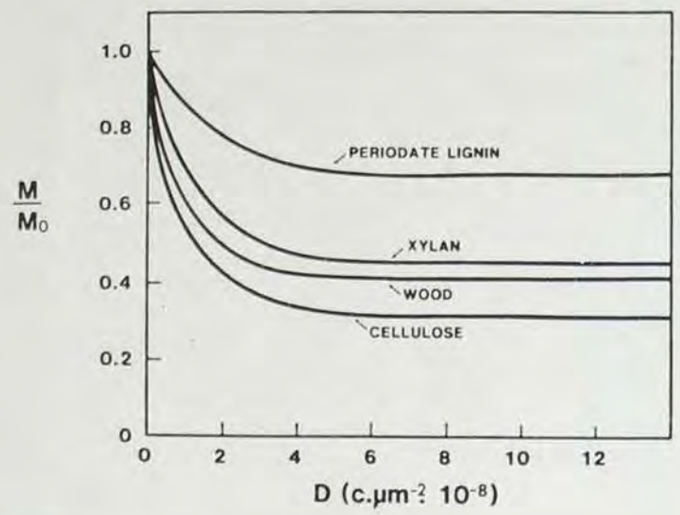

Figure 3. Mass loss of black spruce wood and its components due to an irradiation with 100 keV electrons at room temperature. The thickness of the samples is < 500 nm.

The difference in mass loss between lignin and the carbohydrates will lead to differences in contrast between the TEM images of the middle lamella and the secondary wall of the cell, and a more accurate interpretation of the images becomes possible if mass loss is taken into account. Examples are given.

Several papers have recently been published from this laboratory [6-9] and elsewhere [10-15] in which the microscopic distribution of certain elements in wood has been measured by electron microscopy coupled with an energy-dispersive X-ray analyser (SEM-EDXA or TEM-EDXA). In some cases, the sensitivity of the signal to the time of irradiation was measured and no change in intensity was found [7-12]. However, in general, irradiation greater than 10^{-7} c/µm^2 is required for quantitative microbeam analysis. For such high doses, it is likely that mass loss will occur even before the first measurement can be made. All observations will correspond, therefore, to the level-off intensities shown in Figures 2 and 3. Clearly such effects should be taken into account in the interpretation of quantitative results.

Unfortunately with the sensitivity presently available it is difficult to make measurement of initial mass loss (as shown in Figure 1) with a spot size less than 40 µm in diameter. This resolution is several orders of magnitude too coarse to allow measurements in morphological regions in wood such as the middle lamella or ie torus. No doubt the loss in weight could be educed by keeping the sample at low temperatures in a cooling stage [5,16]. However, even at very low temperatures, such as that of liquid helium, some damage is still present [17,18].

It seems likely, therefore, that, in the high-resolution microbeam analysis of woody material, the effects of mass loss will be elucidated only when the sensitivity of the method has been improved considerably. In the meantime caution should be exercised in the interpretation of the results obtained.

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BIOLOGICAL PULPING

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ABSTRACT

At the Swedish Forest Products Research Laboratory (STFI) one approach to save energy in the production of both mechanical and chemical pulp has been to use cellulase-less (Cel^-) mutants of white-rot fungi to degrade, or structurally modify, part of the lignin in wood chips (1-6). White-rot fungi are able to degrade both lignin and the other wood components. To degrade lignin, they need polysaccharides and/or low molecular weight sugars, partly to provide the energy for growth and metabolism and partly to produce hydrogen peroxide which appears to be important for lignin degradation (8-9). A totally specific attack on the lignin component probably does not occur.

If the capacity of white-rot fungi to degrade lignin could be made more specific we thought that it would be possible to save energy in mechanical pulping and probably also in chemical pulp production. In addition, it would probably also be possible to produce a more easily digestible and also a more energy-rich fodder for ruminants from agricultural waste such as straw and bagasse if the lignin could be specifically deleted.

We have tried to reach these goals at STFI by isolation and utilization of cellulase-less (Cel^-) mutants of white-rot fungi. The original technique for producing these mutants was by UV-irradiation of asexual spores (1-2). Practical trials to delignify wood chips with the mutants obtained certainly led to energy saving in mechanical pulping but the process also led to a discoloration of the pulp (5). The rate of delignification achieved with these first mutants was also too low.

From our experiments we understood that Cel^--mutants produced only by random mutation of conidiospores were unlikely to become technically valuable unless their delignifying capacity was increased. After much difficulty, we succeeded in "constructing" Cel^--strains with an increased phenol oxidase and xylanase production (6). However, although the new mutants were considerably better than their predecessors, they still had a lower capacity for lignin degradation in wood than to the wildtype (6).

Another method for obtaining a more specific delignification of wood is to impregnate wood chips with sugar before inoculation with the wildtype fungus. The presence of glucose will repress the production of polysaccharide-attacking enzymes and a specific attack on the lignin is obtained (10). This is illustrated in Fig. 1 where it is demonstrated by transmission electron microscopy that cellulosic fibrills become exposed (arrows) by the solubilization of the lignin matrix. Unfortunately, even though very specific delignification can be obtained in this way, it is probably not economically or technically feasible to impregnate wood with sugars.

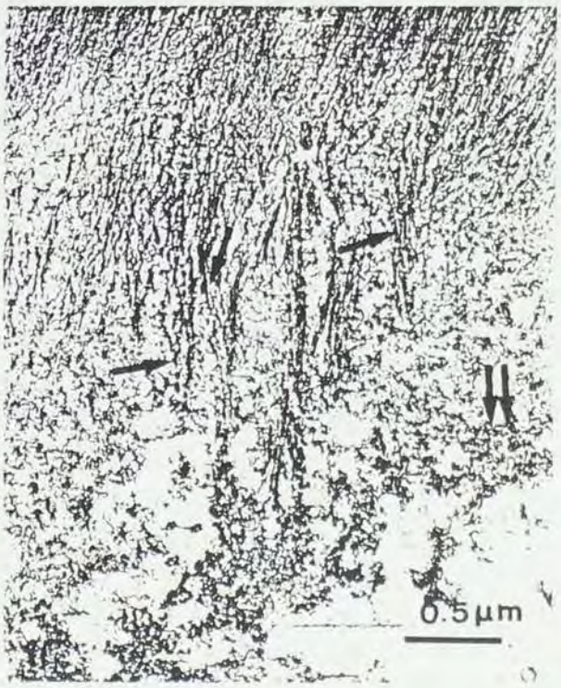

Figure 1. Transmission electron micrograph of glucose-impregnated spruce wood incubated with the wild-type of the white-rot fungus Sporotrichum pulverulentum. Due to the glucose impregnation, the polysaccharide-attacking enzymes are repressed and a specific attack on the lignin is obtained. In the picture, the cellulose fibrils have been exposed (arrows) by the solubilization of the lignin matrix which is still visible in some areas (double arrow), from (10).

At this stage, we decided that a return to basics was necessary for a better understanding of the biology and physiology of the fungi and f the mechanisms by which they degrade lignin. It was discovered during this work that the fungus Sporotrichum pulverulentum was a Basidiomycete, Phanerochaete chrysosporium, with a full sexual cycle (Johnsrud, S.C., in preparation). This made possible the use of classical genetics in order to obtain the strains we were seeking, i.e. cellulase-less variants with a high lignin-degrading power. To accomplish this, homokaryotic Cel$^-$-strains, selected for their superior ability to degrade lignin, were crossed with wild-type strains of equally high lignin-degrading capacity. How these crossings of the different strains were carried out is described in Fig. 2. The new mutants are equal to, or even better than, the wildtype in their lignin-degrading capacity (11).

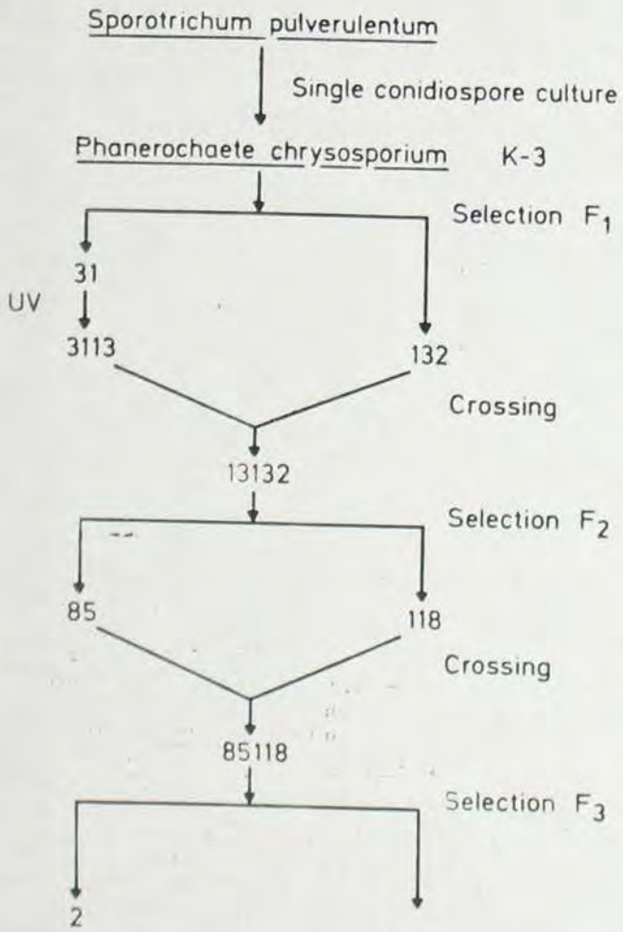

Figure 2. Scheme for the selection, mutation and intercrossing of homokaryotic strains of Phanerochaete chrysosporium K-3. (P. chrysosporium K-3 is a single conidiospore culture of Sporotrichum pulverulentum). Cellulase positive strains: K-3, 31, 132, 13132. Cellulase deficient strains: 3113, 3132-85, 13132-118, 85118 from (11).

The inability of the mutants to degrade cellulose was investigated in several ways, one of which was by studies of $^{14}CO_2$-development from ^{14}C-[U]-labelled cellulose. The ability to degrade lignin was studied partly by measurement of the amount of $^{14}CO_2$ developed from ^{14}C ring-labelled synthetic lignin and partly by estimation of the lignin and weight losses caused by the new mutants in wood. The lignin-degrading and cellulose--degrading capacities of different strains of P. chrysosporium and their Cel$^-$-mutants can be seen in Fig. 3. It is obvious that the

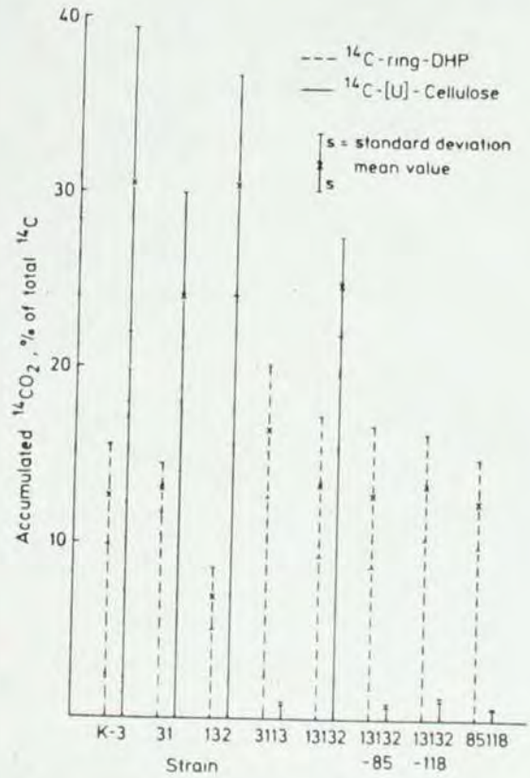

Figure 3. Release of $^{14}CO_2$ from ^{14}C-ring-labelled DHP (3.0×10^4 dpm) and from ^{14}C-[U]-cellulose (3.0×10^4 dpm) by Phanerochaete chrysosporium K-3 and isolates of the F_1, F_2 and F_3 generations. Cellulase positive strains: K-3, 31, 132, 13132. Cellulase deficient strains: 3113, 13132-85, 13132-118, 85118 from (11).

Cel$^-$-strains degrade lignin as well as or even better than the wild-type and the cellulase-positive strains. This is also true of the degradation of lignin in wood. The weight and lignin losses in birch wood caused by the wild-type K-3 and four new Cel$^-$-strains are shown in table 1. After two weeks,

CHEMICALLY MODIFIED LIGNIN FOR THE USE IN CONTROLLED-RELEASE DEVICES

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ABSTRACT

Kraft lignin and organosolv lignin have been modified by acylation and alkylation in such a way that they can be used in the formation of homogeneous blends by solvent alloying of appropriate resins.

The brittleness of these alloys has been reduced by adding another compatible polymer to the mixture which has a low glass-rubber transition temperature. Several examples will be presented showing the optimization of the compatibility of ternary and quaternary mixtures.

The swellability of these blends in water, being 30-50 times their own weight, provides a good indication of their structural homogeneity.

In order to evaluate potential matrices for controlled-release systems we have determined some water-swelling characteristics such as swell ratio, swell rate, and sorption behaviour depending on pH and ionic strength.

The thermoplastic processability and flexibility of the most promising ternary mixtures have been tested by measuring melt-index, mechanical properties and glass-rubber transition temperature.

INTRODUCTION

Polymer blends with high water absorption have been recognized as interesting materials when designing controlled-release devices for bioactive materials. Examples are polymer-polymer complexes consisting of oppositely charged polyelectrolytes which absorb large amounts of water, forming elastic hydrogels[1-4]. However, these polyelectrolyte complexes are insoluble in organic solvents and do not exhibit thermoplastic behaviour. As they cannot be processed by casting, moulding or extrusion, the applicability of hydrogel polymers in controlled-release systems is limited. Other disadvantages are the limited number of parameters to adjust optimal release profile (e.g. equilibrium swelling, swell kinetics, and pH dependence of swelling), and the complex and costly production techniques. Likewise, a hydrogel polymer matrix is too expensive for large-scale applications in agriculture.

Recently, a new and unique polymer concept has been developed overcoming most of the disadvantages of the presently available hydrogel polymers. The concept is based on hydrogels, which consist of homogeneous mixtures of water-phobic polymers such as polyvinyl acetate (PVAc), cellulose acetate, polyethyl acrylate or polymethyl methacrylate[5]. The polymer mixtures exhibit a one-phase morphology, have a lower ciritical solution temperature (LCST) of ca. 140°C, are thermoplastic, and swell in water up to 80 times their dry weight.

These blends, called Aqualloy polymers, have been used as release matrix because of their potential to control water sorption and sorption rate by simply choosing the right mixing ratio.

We have investigated the feasibility of preparing water-swellable polymers comparable with the Aqualloy polymers in which type of polymers the polyvinyl esters etc. are replaced in part by acylated and/or alkylated derivatives of kraft pine lignin and organosolv birch lignin. The characteristics of these hydrophylic polymer alloys, which are relevant for controlled-release applications, will be discussed.

ALLOY CHARACTERISTICS

Most polymer mixtures are not completely miscible and do show phase-separation. However, due to polymer-specific interactions the mixtures may become miscible, forming under certain conditions blends with a one-phase morphology. One-phase mixtures are only thermodynamically stable when $\frac{\delta^2 \Delta G_m}{\delta \phi^2} > 0$, where ΔG_m is the free energy of mixing and ϕ resembles the volume fraction of one of the blend constituents. If specific interactions play an important role in blend formation, the enthalpy of mixing, ΔH_m becomes negative (exothermic), while the $\Delta H_m/\phi$-relation is parabolic and shows a minimum. Then, the above miscibility criterium is fulfilled for all blend ratios, because the entropy of mixing is negligible for high molecular weight blend constituents. Specific interactions may arise from several mechanisms but dipole-dipole interactions and hydrogen bonding are the most relevant interactions in mixtures with exothermic heat of mixing.

Generally, besides these exothermic interactions also dispersive or Van der Waals forces between the remaining parts of the polymer constituents, not involved in specific interactions play an important role in the homogeneous, one-phase blend.

These forces contribute endothermically to the mixing enthalpy. However, dispersive forces are indispensable at the formation of non-disintegrating elastic hydrogels. They analogize with the covalent bonds in cross-linked polymers. We studied the miscibility and sorption behaviour of a series of binary, ternary and quaternary blends comprising modified lignin as one of the constituents. For instance, optically clear films, cast from a 20% w/v solution of a 1:1 blend of polystyrene-maleic anhydride copolymer (PS-MA), M_w 2.10^5 and an acylated lignin, swell about 60 times their own weight in distilled water, cf. Figure 1.

Strain	Time (weeks)	Weight loss, (%)	Lignin loss[a], (%)
	0		
K-3	2	18.5	17.7
	3	19.9	17.2
	4	24.4	19.9
3113	2	6.0	5.9
	3	14.0	18.5
	4	19.0	29.5
13132-85	2	11.3	16.0
	3	18.2	28.5
	4	19.6	25.6
13132-118	2	6.9	13.3
	3	11.7	13.9
	4	10.5	18.4
85118	2	10.6	21.4
	3	14.5	22.7
	4	16.6	26.0

a) As a percentage of the initial amount of lignin.

Table 1. Weight loss and lignin loss of birch (Betula verrucosa) wood wafers (2 x 20 x 50 mm) determined after 2, 3 and 4 weeks of degradation by K-3 and four Cel⁻-strains.

one Cel⁻-strain can remove as much as 21 % of the intitial amount of lignin in birch wood and another strain 28.5 % after three weeks. The lignin losses obtained with spruce and pine wood are lower, 6 and 10 % respectively after four weeks rotting but these losses are considerably higher than for earlier Cel⁻--strains. Some of the new Cel⁻-mutant can also be used to delignify straw and sugar cane bagasse thereby increasing their digestibility for ruminants.

We are now concerned with the production of mechanical and chemical pulps from both wood and bagasse.

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We have investigated the feasibility of preparing water-swellable polymers comparable with the Aqualloy polymers in which type of polymers the polyvinyl esters etc. are replaced in part by acylated and/or alkylated derivatives of kraft pine lignin and organosolv birch lignin. The characteristics of these hydrophylic polymer alloys, which are relevant for controlled-release applications, will be discussed.

ALLOY CHARACTERISTICS

Most polymer mixtures are not completely miscible and do show phase-separation. However, due to polymer-specific interactions the mixtures may become miscible, forming under certain conditions blends with a one-phase morphology. One-phase mixtures are only thermodynamically stable when $\frac{\delta^2 \Delta G_m}{\delta \phi^2} > 0$, where ΔG_m is the free energy of mixing and ϕ resembles the volume fraction of one of the blend constituents. If specific interactions play an important role in blend formation, the enthalpy of mixing, ΔH_m becomes negative (exothermic), while the $\Delta H_m/\phi$-relation is parabolic and shows a minimum. Then, the above miscibility criterium is fulfilled for all blend ratios, because the entropy of mixing is negligible for high molecular weight blend constituents. Specific interactions may arise from several mechanisms but dipole-dipole interactions and hydrogen bonding are the most relevant interactions in mixtures with exothermic heat of mixing.

Generally, besides these exothermic interactions also dispersive or Van der Waals forces between the remaining parts of the polymer constituents, not involved in specific interactions play an important role in the homogeneous, one-phase blend.

These forces contribute endothermically to the mixing enthalpy. However, dispersive forces are indispensable at the formation of non-disintegrating elastic hydrogels. They analogize with the covalent bonds in cross-linked polymers. We studied the miscibility and sorption behaviour of a series of binary, ternary and quaternary blends comprising modified lignin as one of the constituents. For instance, optically clear films, cast from a 20% w/v solution of a 1:1 blend of polystyrene-maleic anhydride copolymer (PS-MA), M_w 2.10^5 and an acylated lignin, swell about 60 times their own weight in distilled water, cf. Figure 1.

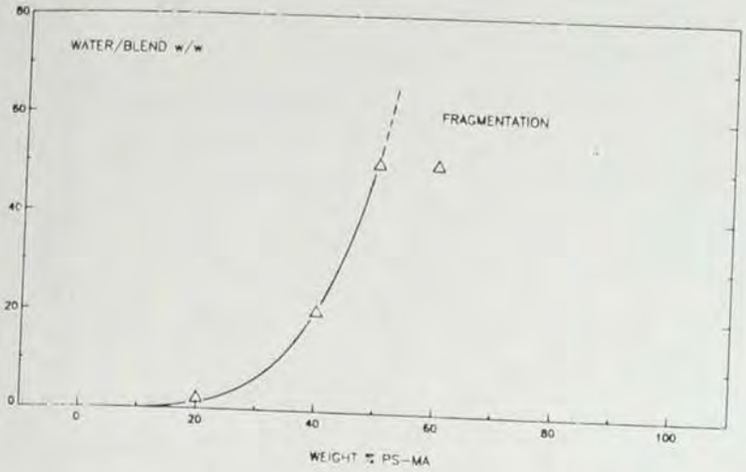

Figure 1. Equilibrium sorption of distilled water in a one-phase alloy of PS-MA/Acylated lignin

The phase-separation temperature, also called lower critical solution temperature (LCST), strongly depends on the degree of protolysis of the anhydride groups. E.g. the LCST of a 50/50 w/w PS-MA/PVAc alloy increases from 40 to 140°C when only 20% of the anhydride groups are hydrolized, Figure 2. The increase is due to formation of hydrogen bonds generated during hydrolysis of the anhydride groups. Such increase of LCST permits thermoplastic processing of the homogeneous one-phase alloy without phase-separation, thus holding their interesting water sorption characteristics.

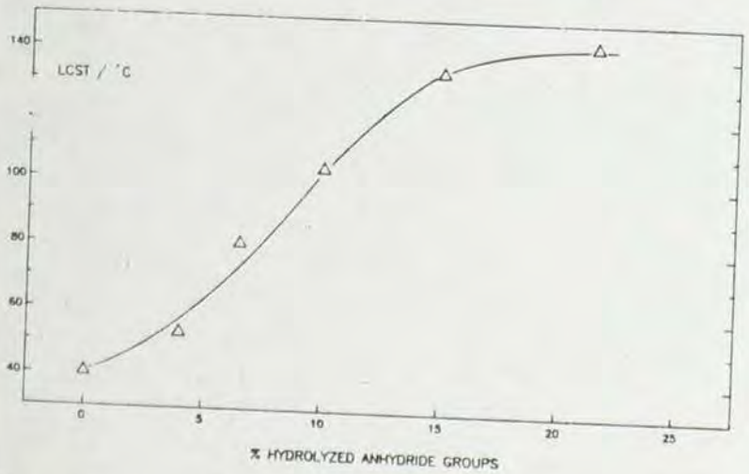

Figure 2. LCST for a 20% w/v solution of 50/50 w/w PS-MA/PVAc blend in butanone as a function of the percentage hydrolyzed anhydride groups in PS-MA.

ALLOYING RATIO

In the hydrophylic polymer alloys the nature of the hydrogel and the degree of sorption is a function of alloying ratio, as is illustrated in Figure 1. The transport of low molecular weight agents through hydrogels can be described either by a pore or by a dissolution/diffusion mechanism. This depends on the nature of the permeating agent, on the nature of the hydrogel, and on the amount of sorbed water[6]. Up to 50% water sorption, the main part of the water molecules are bound to the hydrogel polymer, while the rest is present as free water. The higher the water fraction, the better the pore model describes the transport of active agents, because the amount of free water increases[7].

IONIC STRENGTH

As illustrated in Table 1, neither acidity nor the presence of sodium chloride dramatically influences the swellability of the polyblends comprising an acylated lignin. In contrast, the swellabilities of Aqualloy polymers are much more sensitive to changes in pH, choice of electrolyte or ionic strength.

Table 1. Swelling characteristics of films of an alloy of polymethyl vinylether-maleic anhydride (PMVE-MA) and acylated organosolv lignin (MA 2240) in various aqueous electrolytes

Ratio MA 2240/PMVE-MA		Swelling, water/blend w/w
30/70	1. in 1% w/w NH_4OH 10 min.	125
	2. then in 1% w/w NaCl, acidified with 2M acetic acid (pH 3) 24 hrs.	19
	72 hrs.	7
	3. as under 1, then in a solution of 1% w/w $CaCl_2$ 1 hr.	5

TYPE OF LIGNIN DERIVATIVE

The swelling behaviour of these binary blends hardly varies utilizing kraft of organosolv lignin derivatives. The swelling behaviour of mixtures comprising anhydride copolymer and acylated lignin with a long aliphatic chain is rather poor. Apparently, these polymers are not completely miscible. We have increased the specific interactions between the dissimilar polymers by influencing the hydrophylic/hydrophobic block-character of the lignin derivatives. Thus, introducing ethylene glycol moieties in the aliphatic chain, e.g. lignin-$O(CH_2)_nCO(OCH_2CH_2)_mOCH_3$, high swellabilities are obtained.

DEGREE OF PROTOLYSIS

The kinetics of the water sorption depends strongly on the fraction of the anhydride groups which are protolyzed. The water sorption exhibits three stages: Hydrolysis of the anhydride groups (I), hydration of the maleic anhydride copolymer (II) and osmotic sorption (III). In the overall-sorption process stage I is rate-determining. The initial degree of protolysis determines the period of stage I-sorption. At a degree of protolysis of 100%, the sorption starts directly in stage II. The sorption-rates in stages II and III can be five orders of magnitude higher than the sorption rates in stage I. These features are of particular interest in designing formations with a built-in time-lag.

The dependence of the time-lag upon the degree of protolysis is schematically given in Figure 3.

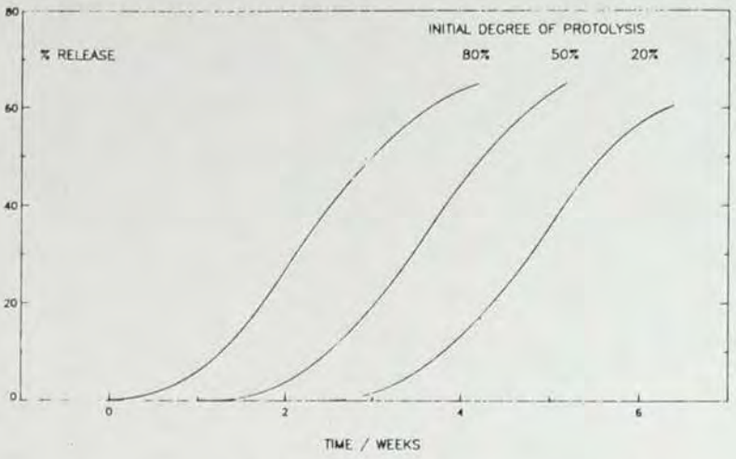

Figure 3. Influence of the degree of protolysis of the anhydride groups in a 30/70 w/w PS-MA alloy on the initial period of zero-release (time-lag).

Such formulations might be advantageously used in agriculture, when the active material is only needed several weeks after application.

GLASS-RUBBER TRANSITION TEMPERATURE, Tg

By using the Aqualloy alloying technique modified lignin can be used in the formation of homogeneous blends. Generally, binary polymer alloys appear to be fairly brittle. This behaviour may be caused by a too low average molecular weight of the blend components. The brittleness of the swellable, binary blends could be reduced by adding another compatible polymer to the mixture, which has a low Tg-value (e.g. PVAc (Tg = 28°C), and vinyl acetate-vinyl laurate copolymers).

An example of the sorption behaviour of ternary and quaternary blends is compiled in Table 2. Films, cast from 20% w/v blend solutions in butanone, are optically clear, flexible and fairly strong, and possess excellent swelling properties.

MECHANICAL PROPERTIES

The blends were tested on their thermoplastic processability and flexibility by measuring tensile properties, melt-index and glass-rubber transition temperature. The data obtained, as examplified in Table 2, indicate that no high demands can be made on the mechanical properties of the blends. However, with regard to the evaluation of potential matrices for controlled-release devices, this is of minor importance.

Table 2. Swelling characteristics and mechanical properties of some alloys containing modified lignin (L-OR)

Ratio in % w/w		L-OR/PS-MA/PVAc	L-OR/PMVE-MA/PVAc/PVAc-VL
Swelling, water/blend w/w		33/33/33	33/32/25/10
1% w/w NH_4OH	10 min.	10	
dist.H_2O	24 hrs.	45	55
Tensile strength	N/mm^2	12.7	10.5
Strain-at-break	%	5	0.53
E-modulus	N/mm^2	1200	2050

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ROTATING FELT TO STUDY THE BEHAVIOUR OF ORGANIC COLLOIDS IN PAPERMAKING STOCK

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ABSTRACT

Behaviour and interactions of organic colloids, such as fines, fillers, polymers and pitch, in papermaking process play an important role in process operation and properties of paper products. To understand the nature of aggregation and deposition of organic colloidal particles, simple device consist of a beaker and rotating felt was developed in our laboratory. Potential of pitch deposition in papermaking machinary can easily predicted using this device. Although this device was developed primarily to study the nature of pitch particles, it can be used for studying other colloidal system. Application of rotating felt device to suspensions of latex and hot melt is discussed.

KEYWORDS: Felt, Pitch, Latex, Hot Melt, Deposition

INTRODUCTION

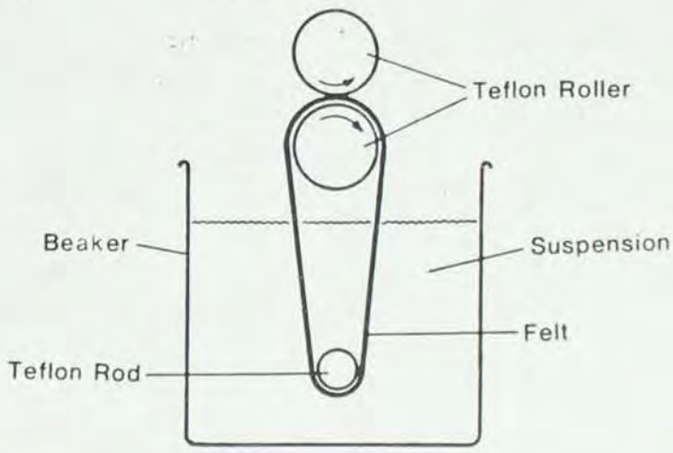
Major component of papermaking stock is wood fiber, which is hardly considered to be colloidal particle. However there are many kind of colloidal particles in papermaking stock. For example, fines of wood fiber, polymers, latex and pitch particles are in the range of colloids. Thus it is important to understand the behavior of these collidal particles, particularly to understand interactions among themselves and with other particles including non-colloidal materials.

Retentions of fines and fillers during papermaking process depend not only on surface chemical properties of particles and wood fibers, but also network structure of fiber matrix. Papermakers wish to have maximum retention without aggregation of particles, so that particles are well distributed in a bulk of paper. Higher retention and good dispersion are two opposite properties required, thus difficult to achieve both simultaneously.

Pitch, whatever it is defined, usually exist as colloidal form in pulp and paper making process. It can stick to any part of machinary to form a deposit or aggregate into large particles which again deposit or form pitch speck in paper products. In order to understand the behavior of pitch desopition, a simple device of rotating felt was developed, which is proven to be a useful tool for predicting pitch deposition. On the other hand the device itself is also useful for study on behavior of other organic colloids in papermaking stock.

ROTATING FELT DEVICE

Schematic diagram of rotating felt is shown in Fig. 1. Felt or felt-like material of 50mm wide is formed into a roop, which can be rotated by a Teflon rotor at the speed of 47cm/sec. Half of felt roop is dipped into a suspension to be studied. The amount of deposition on felt can easily determined by light absorption or turbidity measurement of remaining suspension.



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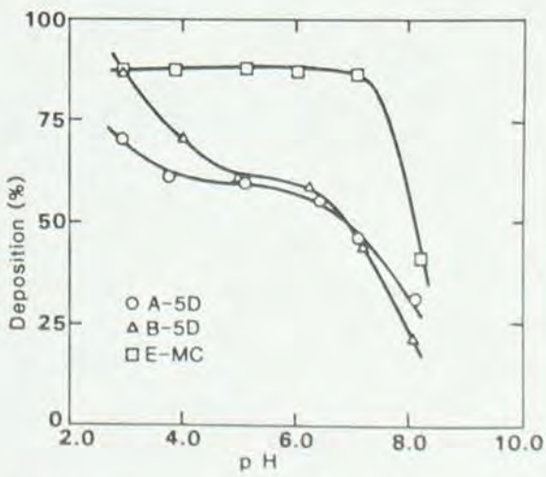

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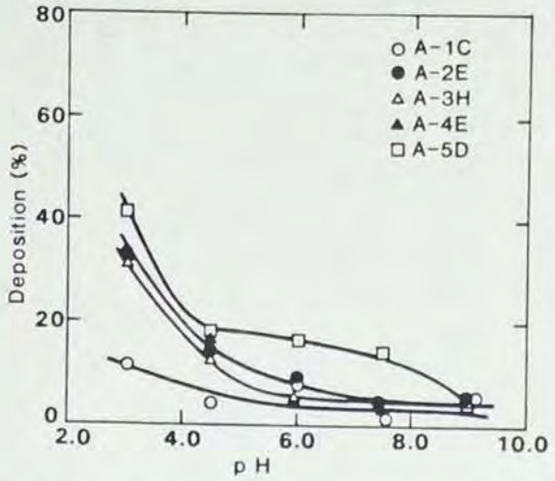
Sequential change in pitch deposition during five bleaching stages(C-E-H-E-D) of hardwood pulp is shown in Fig. 3. Deposition tendency of pitch increases as the bleaching sequence progresses, reaching maximum at the last chlorine dioxide bleaching. Deposition test of pitch in bleach effluent revealed that deposition ability undergo oscillatory change with bleaching sequence.



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BEHAVIOR OF LATEX

Synthetic latex has been accepted for their application to many fields, including pulp and paper industry. Thus it is important to know how they behave in the changing environment of pulp and paper making process. Fig. 4. is an example of latex deposition measured by rotating felt device. Measured deposition was parallel to the change in mobility of latex, not influenced by the surface characteristics of felt.

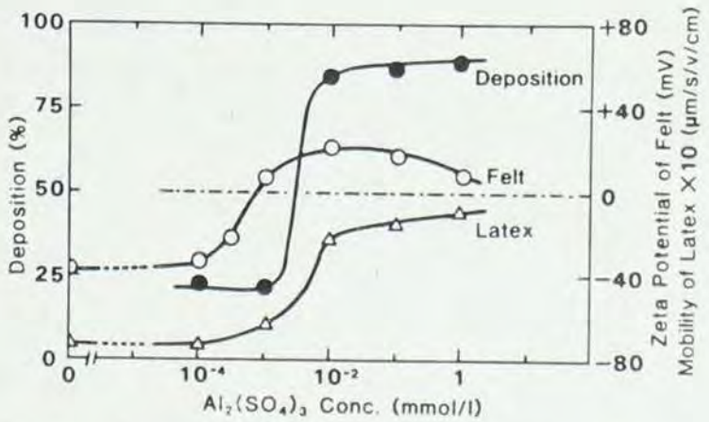
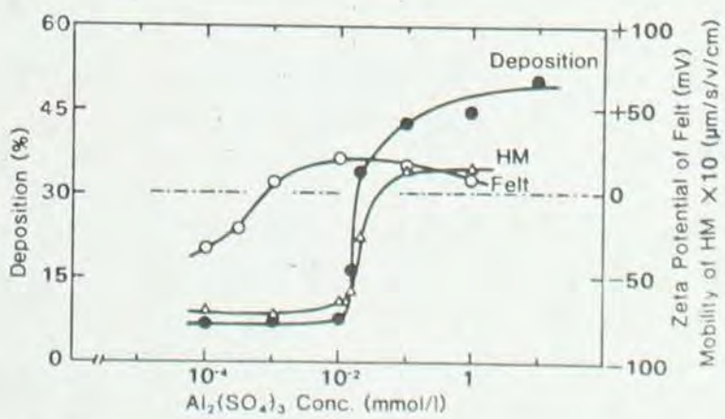


Fig.4. Deposition of Latex on Felt, and Electrokinetic Properties of Latex and Felt.

BEHAVIOR OF HOT MELT

Sticky material in recycled paper was transformed into colloidal particles during the course of repulping. Fig. 5. shows the effect of Alum addition on the deposition of hot melt suspension on a felt. Deposition was very closely related to the surface potential of hot melt particles.

These examples indicate that the rotating felt device is an useful tool for studing nature of organic colloids.



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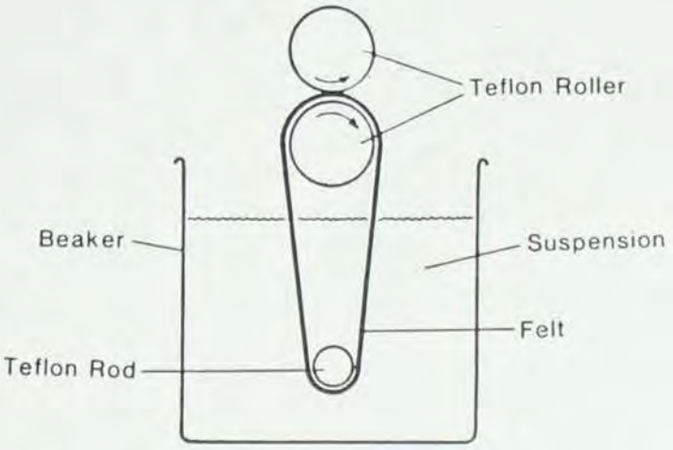

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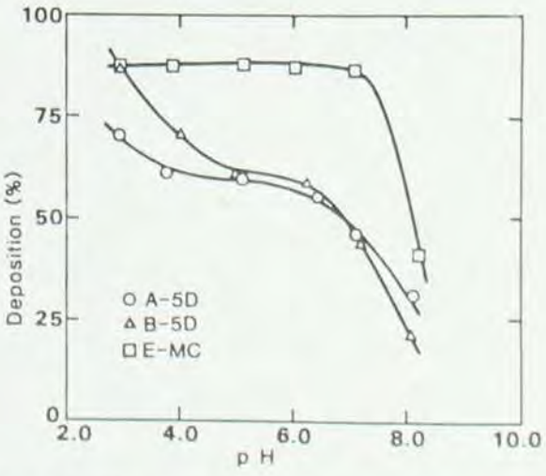

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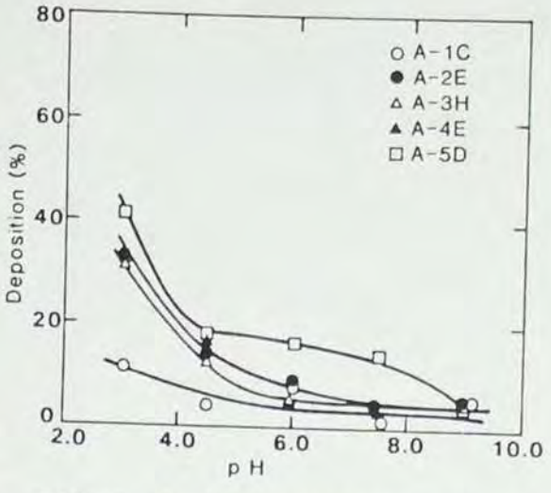

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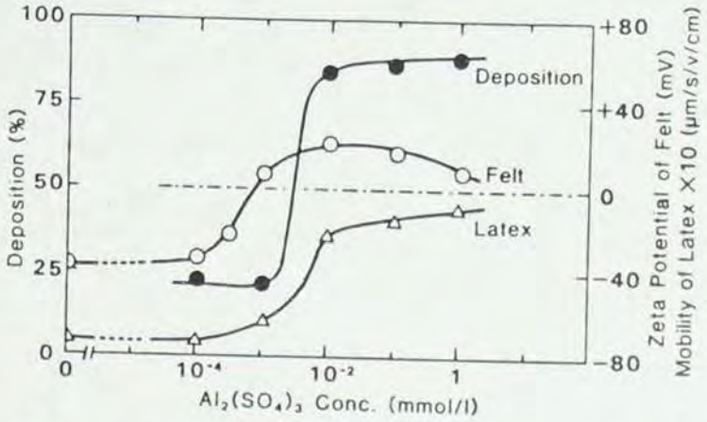

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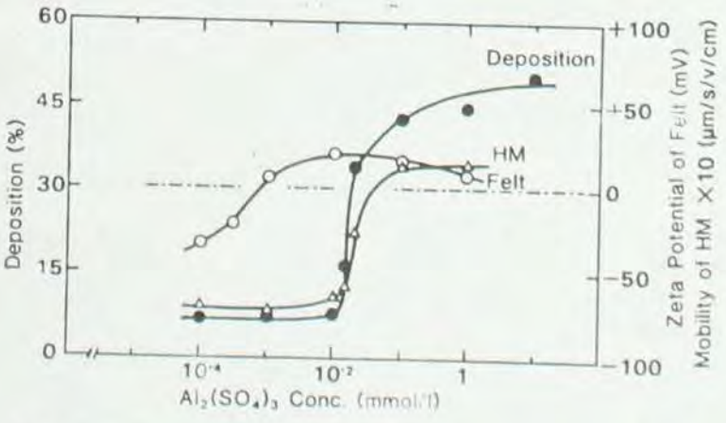

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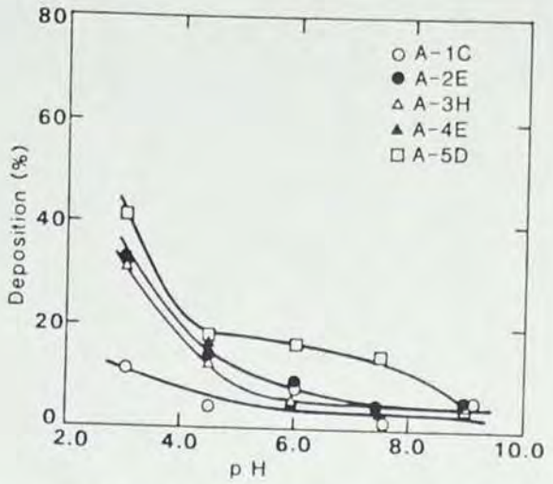

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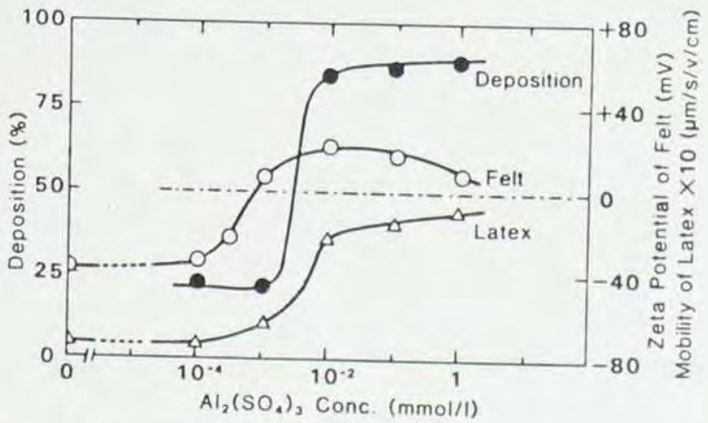

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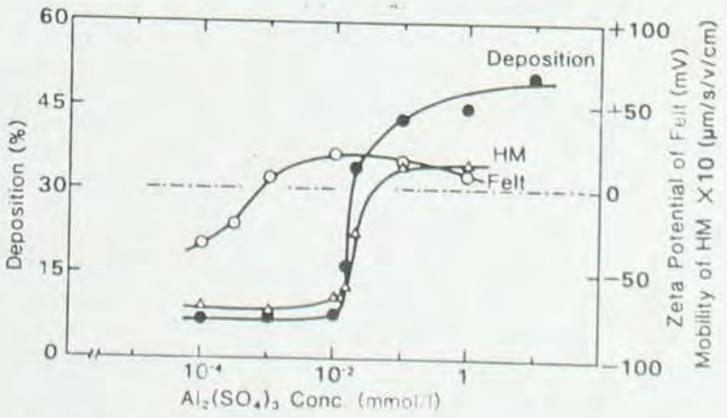

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CHEMICAL STRUCTURE AND REACTIVITY OF THE MIDDLE LAMELLA LIGNIN

ULLA WESTERMARK

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ABSTRACT

The isolation of a middle lamella fraction by a sieving technique is described. Analytical data for this fraction is compared with published data for a middle lamella fraction isolated by the density gradient fractionation technique. The content of p-hydroxyphenylpropane units and the bromination behaviour of the middle lamella fractions were studied. In conflict with earlier published results, no indications of p-hydroxyphenylpropane units or of a lower bromination ability of the middle lamella lignin than of the whole wood were obtained in our sample. It was noted that the density-separated material had many properties similar to compression wood. The possibility that this can be due to either a contamination of compression wood lignin in the density-separated material or that the techniques separate different parts of the middle lamella is discussed.

KEYWORDS: Middle lamella, p-hydroxyphenylpropane, bromination, lignin

The reactivity and composition of the middle lamella and outer cell walls in softwood fibers are important for the defibration of wood and also to a certain degree for the surface properties of pulp fibers. UV-spectrophotometric analysis of thin wood sections has served as the basis for much of the present knowledge about the composition and reactivity of the compound middle lamella. The UV-technique also showed that the middle lamella reacted differently from the secondary wall during alkaline pulping processes (Procter et al. 1). Differences in the chemical structure of the lignin in different parts of the fiber were also found by this technique (Yang et al. 2). However, the UV-technique involves several assumptions whose correctness is difficult to verify. To confirm the UV-result and to obtain more detailed information on the structure and reactivity of the middle lamella it would be of great interest to be able to analyse isolated middle lamella. Direct isolation is, however, a very tedious procedure which gives only small amounts of material (Bailey 3). Different fractionation techniques have therefore been used to separate fractions enriched in middle lamella.

Whiting et al. (4) have used a "density gradient separation" technique to enrich middle lamella based on the lower density of lignin-rich material. Using this technique, a fraction with high lignin content assumed to come from the middle lamella was separated. The basis of the density gradient technique is that the middle lamella has a higher degree of lignification than other parts of the wood.

Hardell et al. (5) developed a technique based on sieving to isolate different wood elements from spruce, including a fraction enriched in middle lamella/primary wall material. This technique has been further developed by Westermark (6) and a fraction of middle lamella particles has been isolated. The middle lamella particles can be isolated either from wood or from thermomechanical pulp. The advantage of this technique is that the middle lamella fragments can be recognized and checked under a microscope. Fig. 1 shows a picture of

Figure 1. The appearance of the middle lamella fragments. Scanning electron microscopy.

isolated middle lamella particles. By SEM and light microscopy investigations it has been established that a considerable part of the particles also contains the middle lamella cell corners. The fraction has a lignin content of 43 % lignin as measured by Klason analysis and methoxyl content.

The lignin in the tissue isolated by the density gradient technique is much different from the rest of the wood lignin (Whiting et al. 7). It has a lower methoxyl content and can contain up to one third of p-hydroxyphenyl-

propane units. It also shows a different bromination behaviour from that of the rest of the wood lignin (Saka et al. 8).

In the present work, the p-hydroxyphenylpropane units and the bromination behaviour of middle lamella fragments isolated by the above-mentioned technique of Westermark have been studied. The content of p-hydroxyphenylpropane units in the lignin has been analysed by acidolysis and nitrobenzene oxidation.

Compression wood contains a lignin with a low methoxyl content and a considerable amount of p-hydroxyphenylpropane units and was therefore included as a comparison in the analysis. The chromatograms from the acidolysis mixture are shown in Fig. 2. Several degradation

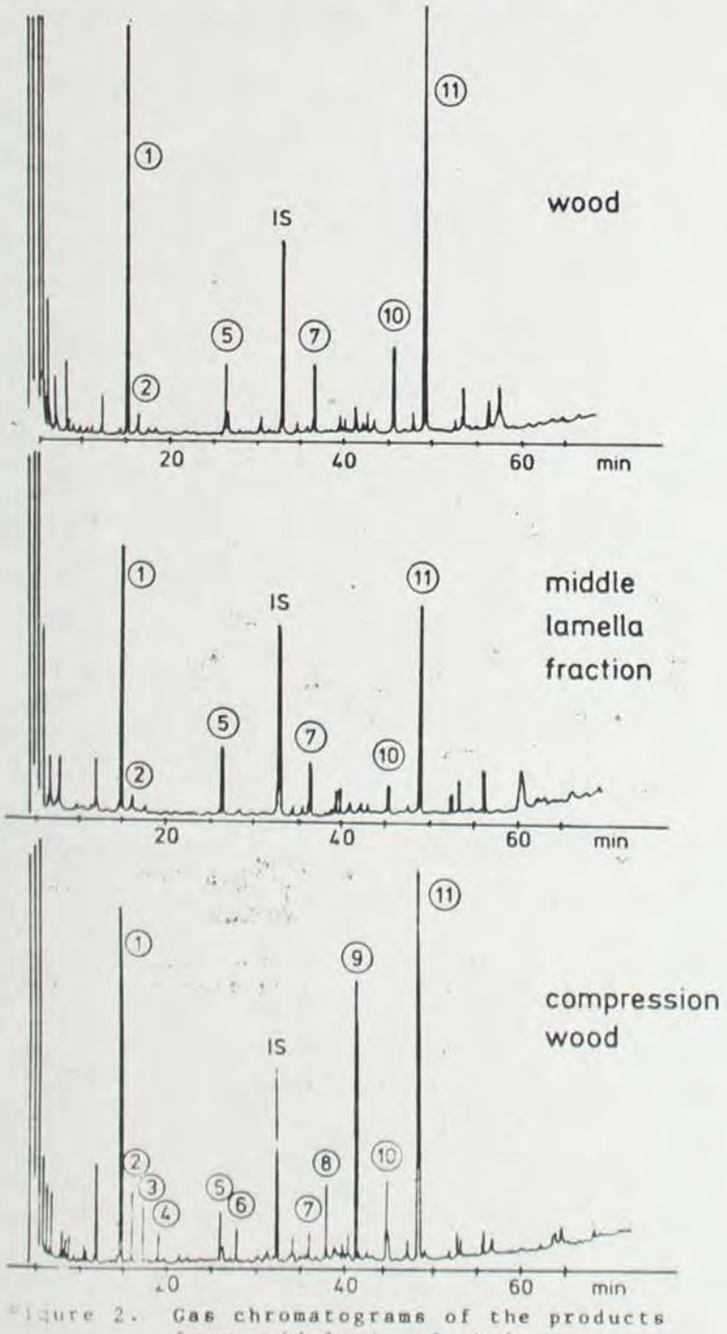

Figure 2. Gas chromatograms of the products from acidolysis of whole-wood, middle-lamella and compression-wood lignin. Product (3) is p-hydroxybenzaldehyde, (8) is 2-hydroxy-1-(4-hydroxyphenyl)-1-propanone and (9) is 3-hydroxy-1-(4-hydroxyphenyl)-2-propanone.

products originating from p-hydroxyphenylpropane units were identified in the compression wood sample (compounds 3, 8, 9). None of these was, however, detected in the whole wood or in the middle lamella fraction. In the nitrobenzene oxidation, a considerable amount of p-hydroxybenzaldehyde was also detected from the compression wood whereas only traces were found in the whole wood and in the middle lamella sample. This means that the considerable amount of p-hydroxyphenylpropane units indicated in the density-separated middle lamella sample could not be confirmed in the sample separated by the technique described in this paper.

Bromination of wood has recently attracted interest since it has been used for lignin determination by the SEM and TEM-EDXA techniques (7). The response to bromination of different morphological parts of the fiber is therefore of importance for the quantification of the lignin distribution over the cell wall. The lignin separated by the density fractionation technique brominates to a lesser degree than the whole wood lignin. The bromination behaviour of our fraction is shown in Fig. 3.

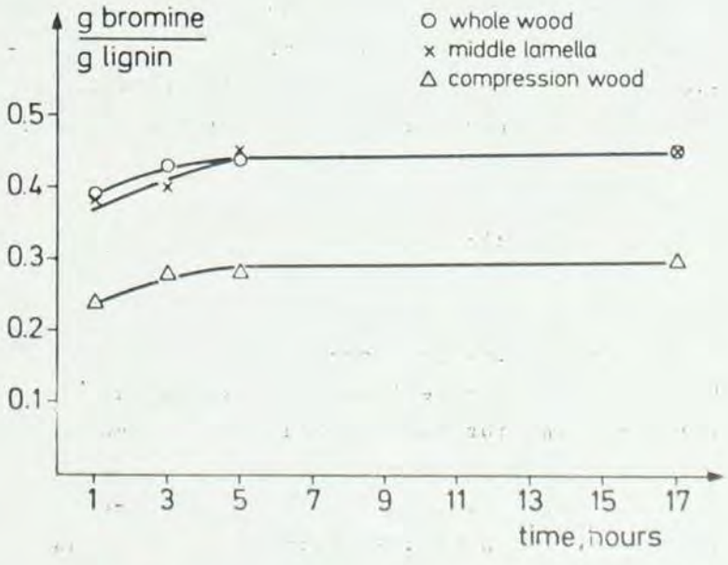

Figure 3. Incorporation of bromine at 60°C into the lignin of normal wood, middle lamella and compression wood.

From the curves it is obvious that the lignin in the middle lamella fraction isolated by our technique brominates to the same extent as the whole wood lignin. Compression wood lignin is, however, brominated to a lesser extent. The value for the compression wood is in fact similar to the value obtained by Saka et al. (8) for the density-separated middle lamella. A similar reactivity of the middle lamella and

cell wall lignin to bromination would mean that the lignin concentration in the middle lamella measured by bromination-EDXA would be considerably lower than has earlier been measured by the UV-technique (9). It is obvious from the results of the acidolysis and bromination that the middle lamella fraction isolated by the technique described here reacts quite differently from the fraction isolated by the density fractionation technique.

In fact, the density separated middle lamella behaves in a similar manner to the compression wood in our study. The possibility either that this can be due to a contamination of compression wood lignin in the density-separated material or that the techniques separate different parts of the middle lamella is discussed.

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PATHWAYS AND MECHANISM OF DEGRADATION FOR ARYLGLYCEROL-β-APYL ETHER SUBSTRUCTURE MODELS BY Phanerochaete chrysosporium AND Coriolus versicolor

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ABSTRACT

It was found by isotopic experiments with ligninolytic culture of P. chrysosporium that arylglycerol-β-aryl ether models were cleaved between Cα and Cβ of the glycerol side chain to give benzyl alcohol derivatives (C6Cα) and glycol (Cβ-Cγ) without hydrogen abstraction, and that ligninase reaction was consistent with the in vivo experiment results. Some of the arylglycerol-β-aryl ether models gave the arylglycerols via the cyclic carbonate or formate of the arylglycerols by the cleavage of β-ehterated aromatic rings mediated by other ligninases.

KEYWORDS: Arylglycerol-β-aryl ether, Ligninase, P. chrysosporium, C. versicolor, Aromatic ring cleavage

INTRODUCTION

The arylglycerol-β-aryl ether bond (β-O-4 substructure) is the most frequent interphenylpropane linkage which roles to connect main lignin substructures such as β-5, β-β', β-1 in lignin macromolecule. It is, therefore, very important related to the depolymerization of lignin to elucidate the degradation mechanism for β-O-4 substructure by lignin degrading fungi which cleave β-O-4 linkage at the initial stage of lignin catabolism. Indeed, many researchers (1-7) have attempted to elucidate the cleavage mechanism for β-O-4 linkage using several lignin degrading microorganisms, and recently the enzyme which catalyzes Cα-Cβ cleavage of β-1 substructure models as well as β-O-4 models was isolated from a lignin degrading fungus, Phanerochaete chrysosporium (8-10).

The results so far obtained by these researchers could be summarized as illustrated in Fig. 1. Earlier studies (1-4) showed that guaiacylglycerol and guaiacol were formed from veratrylglycerol-β-guaiacyl ether in the cultures of several lignin degrading fungi. Later, the formation of these compounds were confirmed in the ligninolytic culture of P. chrysosporium (5-7). However, in earlier investigations without used $^{18}O_2$ and $H_2{}^{18}O$ only analogical interpretation, hydrolysis and β-hydroxylation, was made without adequate experimental evidence for the cleavage mechanism of β-O-4 substructure to give arylglycerol (Fig. 1, pathway A).

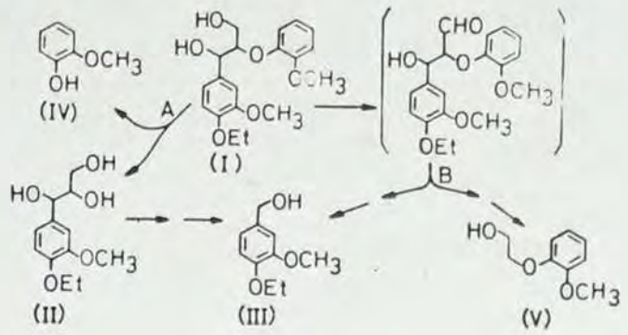

Figure 1. Degradation pathways of non-phenolic arylglycerol-β-aryl ether models by P. chrysosporium.

This paper deals with the degradation pathways of β-O-4 substructure models by P. chrysosporium and C. versicolor, and some reaction mechanism of C-C and ether cleavage of lignin substructure models mediated by ligninase.

RESULTS AND DISCUSSION

in vivo Experiments

P. chrysosporium and C. versicolor were cultured in ligninolytic condition and the β-O-4 models were added as DMF solution into the 5,6 day-cultures which showed a strong ligninolytic activity, and flushed with oxygen. Usually the degradation products were extracted with ethyl acetate, acetylated, separated by TLC, and analyzed by GC-MS and NMR. When we started degradation study on β-O-4 models using P. chrysosporium arylglycerol (II), guaiacol (IV), C6-Cα (benzyl alcohol) derivatives (III) and guaiacoxyethanol (V) had been identified as degradation products of arylglycerol-β-guaiacyl ether (I) by P. chrysosporium (Fig. 1), but no informations had been obtained on Cβ-Cγ fragment compounds which could be formed as counterpart compounds for C6Cα derivatives, nor the formation mechanism of arylglycerol.

Since Cβ-Cγ fragment compounds which could be derived from arylglycerol side chain such as glycol derivatives are supposed to be difficult to detect by further metabolism we synthesized a trimer composed of β-O-4 and α-O-γ substructure, i.e., γ-benzyl ether of β-O-4 substructure model (VI) as substrate (11). As degradation product benzyloxy ethanol (VIII), a Cβ-Cγ fragment compound was identified for the first time, in addition to a C6Cα derivative (III) and an arylglycerol derivative (VII). Thus, we now know that the arylglycerol moiety of β-O-4 models is cleaved between Cα and Cβ to give a C6Cα derivative (III) and glycol (VIII) (Cβ-Cγ fragment compound) via

a pathway (pathway B, Fig. 2).

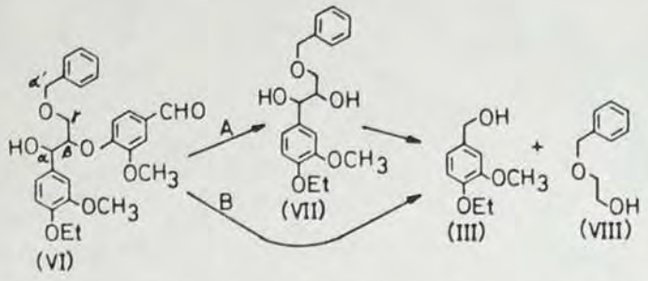

Figure 2. Degradation pathways of a trimer composed of β-O-4 and α-O-γ substructures by P. chrysosporium.

We propose that at least some of the C6Cα compound (III) is produced by the Cα-Cβ cleavage which does not involve arylglycerol (VII) (pathway B, Fig. 2), in addition to the C6Cα compound (III) produced via Cα-Cβ cleavage of arylglycerol (VII) previously formed by other pathways (pathway A, Fig. 2). Because we found that $^{18}O_2$ is incorporated into the benzyl alcohol derivative (III) derived from β-O-4 substructure model, but is not incorporated into the benzyl alcohol derivative from arylglycerol (VII) used as substrate in ligninolytic culture of P. chrysosporium. It seems that the incorporation of ^{18}O into benzyl alcohol derivative (III) from β-O-4 substructure models (VI) can not be explained by the mechanism of Cα-Cβ cleavage proposed by Kirk et al., (9), incorporation of oxygen into Cβ as in the Cα-Cβ cleavage of β-1 substructure models.

To elucidate the mechanism for the formation of arylglycerol from β-O-4 substructure models we synthesized Cα and Cβ double deuterated β-O-4 model compound with (VI-α, β-2D) and without α-O-γ bond (IX-α, β-2D) and used as substrates for ligninolytic cultures of P. chrysosporium (11, 12). We found that the isolated arylglycerols, (VII-α, β-2D) and (II-α, β-2D), retained deuterium almost 100%. We (13, 14) further investigated the degradation of β-O-4 model (I) under $^{16}O_2$ with $H_2{}^{18}O$. ^{18}O was not incorporated into Cβ of arylglycerol from $H_2{}^{18}O$, whereas about half of the Cα oxygen of the glycerol was derived from $H_2{}^{18}O$ and the other was from the Cα oxygen of substrate (I). The results are summarized and illustrated in Fig. 3.

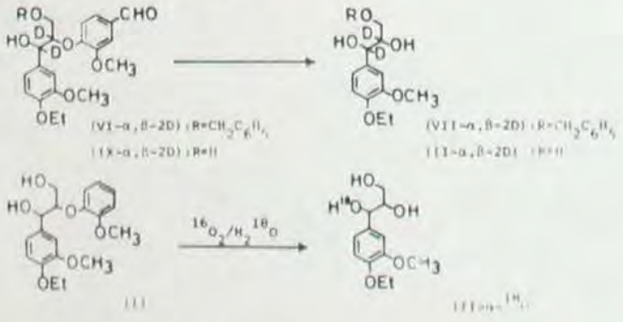

Figure 3. Degradation pathways (based on isotopic experiments) of 4-ethoxy-3-methoxyphenylglycerol-β-aryl ethers by P. chrysosporium.

The results clearly indicated that Cβ hydroxylation and hydrolysis of β-O-4 models as suggested by earlier papers (1-4) did not occur in the formation of arylglycerol.

So, as the next step of the investigation we synthesized arylglycerol-^{18}O-guaiacyl ether (I-β-^{18}O) as substrate (15). MS analysis of the arylglycerol and guaiacol isolated from the ligninolytic culture showed that ^{18}O was retained almost 100% at Cβ of the arylglycerol and hydroxyl group of the guaiacol, respectively. The result clearly indicated that the cleavage occurred between ^{18}O and guaiacol in the formation of arylglycerol. The formation of guaiacol-^{18}O could be reasonably explained as derived from an intermediate hemiketal which could be formed by the direct Cα-Cβ cleavage of β-O-4 models mediated by the ligninase characterized by Kirk et al (9).

Two possible mechanisms which involve and/or do not involve aromatic ring cleavage are supposed for arylglycerol formation. Hence, we first searched for ring cleavage products in the culture with β-O-4 models and could identify an unknown compound, which always appeared as a peak with a little later retention time than that of arylglycerol in GC-MS analysis, to be a β-γ cyclic carbonate of arylglycerol (X).

Our interest was then focussed on the origin of the carbonate carbon of the compound. We synthesized 4-ethoxy-3-methoxyphenylglycerol-β-guaiacol-^{13}C ether (I-^{13}C) and added to the ligninolytic culture of P. chrysosporium (16). The carbonate was isolated from the culture and analyzed by MS. The spectrum is shown in Fig. 4.

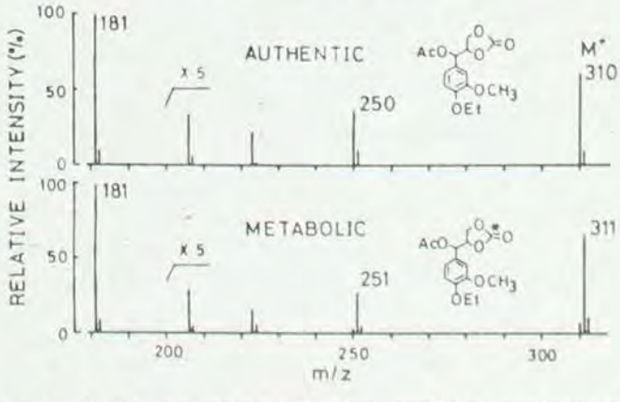

Figure 4. Mass spectra of the cyclic carbonate of 4-ethoxy-3-methoxyphenylglycerol (X) (acetate). *: ^{13}C

It was clearly shown that the carbonate carbon was derived from guaiacyl ring carbon, indicating that the ring cleavage of β-etherated guaiacol occurred

In a separate investigation (17) using C. versicolor with 4-ethoxy-3-methoxyphenylglycerol-β-guaiacol-^{13}C ether (I-^{13}C) the cyclic carbonate (X-^{13}C) was also identified and confirmed that the carbonate carbon was derived from the guaiacyl ring. Furthermore, it was found that the cultures of both P. chrysosporium and C. versicolor with

4-ethoxy-3-methoxyphenylglycerol-β-2,6-dimethoxyphenyl ether (XI) gave 4-ethoxy-3-methoxyphenylglycerol-γ-formate ester (XII), and that the formate carbon was derived from 2,6-dimethoxyphenyl ring by using 4-ethoxy-3-methoxyphenylglycerol-β-2,6-dimethoxyphenol-^{13}C ether (XI-^{13}C) as substrate (17). It was further shown that both the cyclic carbonate and γ-formate of arylglycerol, (X) and (XII) respectively, were degraded to give arylglycerol (II) in the cultures. These results as shown in Fig. 5, clearly indicated that some of the arylglycerol is formed by the cleavage of aromatic ring of β-etherated aryl groups.

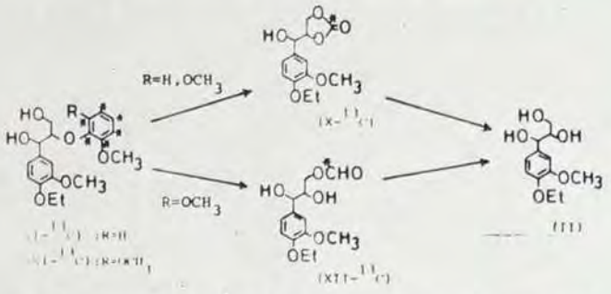

Figure 5. Formation pathways of arylglycerol via aromatic ring cleavage products from β-O-4 models by P. chrysosporium and C. versicolor. *: ^{13}C.

In addition, we found that guaiacoxy ethanol is formed in considerable amounts from 4-ethoxy-3-methoxyphenylglycerol-β-guaiacyl ether (I) in the ligninolytic culture of P. chrysosporium (18). The formation of this compound from 4-ethoxy-3-methoxyphenylglycerol-β-guaiacyl ether (I) was found by Enoki et al. (5). They proposed that the compound is probably formed via retroaldol reaction of γ-aldehydic β-O-4 dimers (Fig. 1, pathway B). However, no such aldehyde derivative has been detected in the culture of P. chrysosporium. We propose that the guaiacoxyethanol (V) is not formed via retroaldol reaction of the γ-aldehydic β-O-4 dimer (Fig. 1, pathway B). Because the guaiacoxyethanol formed from 4-ethoxy-3-methoxyphenylglycerol-β-^{18}O-guaiacyl ether (I-β-^{18}O) by ligninolytic culture of P. chrysosporium contained no ^{18}O at all (Fig. 6). If the mechanism (Fig. 1, pathway B) is true, the ethereal ^{18}O must be retained in the product, guaiacoxyethanol (V).

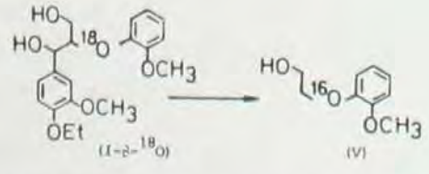

Figure 6. Formation of guaiacoxyethanol from 4-ethoxy-3-methoxyphenylglycerol-β-guaiacyl ether by P. chrysosporium

We further identified 4-ethoxy-3-methoxyphenyl-β-deoxydiol (22), and, tentatively, glycol ester of 4-ethoxy-3-methoxybenzoic acid (23) as degradation products of 4-ethoxy-3-methoxyphenylglycerol-β-syringaldehyde ether by C. versicolor. The formation of the latter compound could be explained by secondary connection of glycol to 4-ethoxy-3-methoxybenzoic acid, both of which could be formed by C_α-C_β Cleavage of 4-ethoxy-3-methoxyphenylglycerol-β-syringaldehyde ether by the fungus.

in vitro Experiments

Recent research on lignin biodegradation has rapidly been progressing towards elucidation of its molecular mechanism of a hemoprotein ligninase isolated from P. chrysosporium (8-10). We have recently established (24-26) the simple biomimetic model system with the iron-porphyrin catalyst which exhibits an important oxygenase action of the ligninase. Here, we report one electron transfer reaction mechanism to rationalize apparently different types of oxidations with lignin and its related compounds on the basis of a lines of evidence obtained in the in vivo and in vitro systems.

The culture filtrate of 6,7-day ligninolytic cultures of P. chrysosporium was concentrated by a membrane filter, dialyzed and used as a crude enzyme solution for the oxidative cleavage reaction of lignin substructure models, deuterated arylglycerol-β-aryl ethers, (VI-α,β-2D) and (XIII-α,β-2D), and 1,2-diarylpropanes, (XVI-β-D) and (XVI-α-D), as shown in Figs. 7 and 8, respectively.

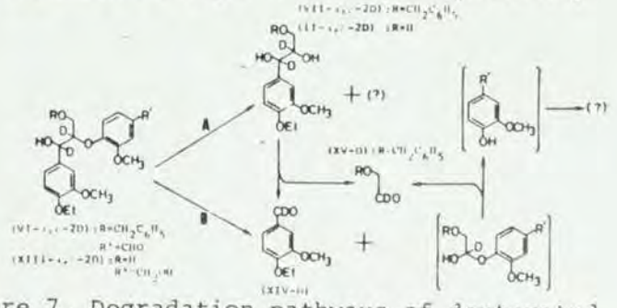

Figure 7. Degradation pathways of deuterated arylglycerol-β-aryl ether models by ligninase

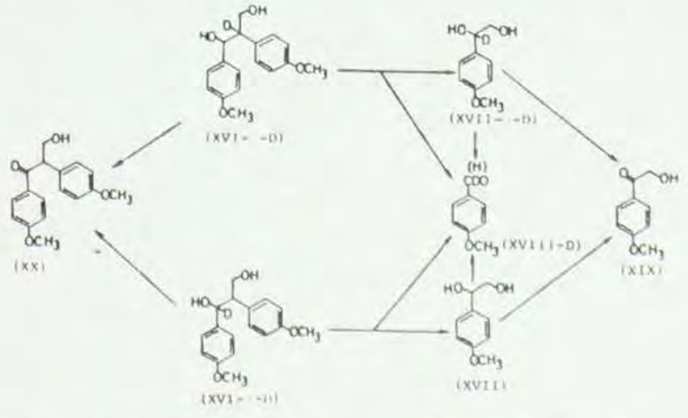

Figure 8. Degradation pathways of deuterated β-1 models by ligninase

The results obtained demonstrate that the D-labels at C_α or C_β of the substrates were almost quantitatively retained in the products after the C_α-C_β and ether bond cleavages as summarized in Table I. The present evidence clearly shows that hydrogen abstraction is not involved in both the

C-C and ether bond cleavages, which is consistent with the in vivo system (11,12).

DD IN (S) (%)		DD in (P) (%)		Retention (%)
(VI-α,β-2D)	α 98	(XIV-D)	98	100
	β 80	(XV-D)	78	98
(XIII-α,β-2D)	α 98	(XIV-D)	93	95
	β 80	----------		---
	total 89	(II-α,β-2D)	89	100
(VII-α,β-2D)	α 98	(XIV-D)	96	98
	β 93	(XV-D)	93	100
(II-α,β-2D)	α 98	(XIV-D)	95	97
	β 93	----------		---
(XVI-β-D)	α 0			---
	β 91	(XVIII-D)	33	
		(XVII-α-D)	94	100
(XVI-α-D)				
	α 98	(XVIII-D)	72	---
	β 0	(XVII)	0	---
(XVII-α-D)	α 98	(XVIII-D)	96	98

Table I. Deuterium retention calculated from degrees of deuteration (DD) of the substrates (S) and the products (P)

Alternatively, we have established that the heme-enzyme model system catalyzes the C-C bond cleavage of the lignin substructure models (β-1, β-O-4, β-5) together with the quantitative D-retention patterns and ^{18}O incorporation (83%) from dioxygen into the cleaved product, phenylglycol, of the diarylpropanediol.

On account of the one-electron oxidizing role of high-valent oxo-ironporphyrin complex (Compound I of peroxidase) formed in the presence of hydroperoxide, one electron might be transfered to the complex from the arylpropane substrate to form the cation radical intermediate, which undergoes the C-C bond cleavages homolytically or heterolytcally producing the carbon-centered radical intermediate. Consequently, the radical intermediate is readily attacked by molecular oxygen to form the dioxygen adduct and the corresponding hydroperoxide, which are eventually converted to the hydroxylated phenylglycol product. The reaction mechanism proposed with our own enzyme model is in good agreement with the recent evidence for the aryl cation radical detected by ESR spectrometry in the ligninase system. Although the elucidation of the detailed reaction mechanism requires further investigation, the ligninase should be denoted as a type of peroxidase rather than H_2O_2-requiring oxygenase.

However, it is not known that what enzyme mediates the formation of arylglycerol via the cyclic carbonate and formate of arylglycerol which contain C_1 fragments from β-etherated aromatic rings. Further investigations are in progress in our laboratory.

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Figure 2 shows that the decrease in the electrophoretic mobility is directly related to a transfer of ^{3}H-C-PAM from the MCC to the coarse fiber fraction, the reason for this transfer being that the adsorption is slower onto the coarse fiber fraction (slow penetration of the polymer into the porous cell wall of the fibers) than onto the MCC fraction. The faster rate of adsorption onto the MCC fraction is probably due to the smaller size of the substrate and correspondingly smaller diffusion distances into this substrate.

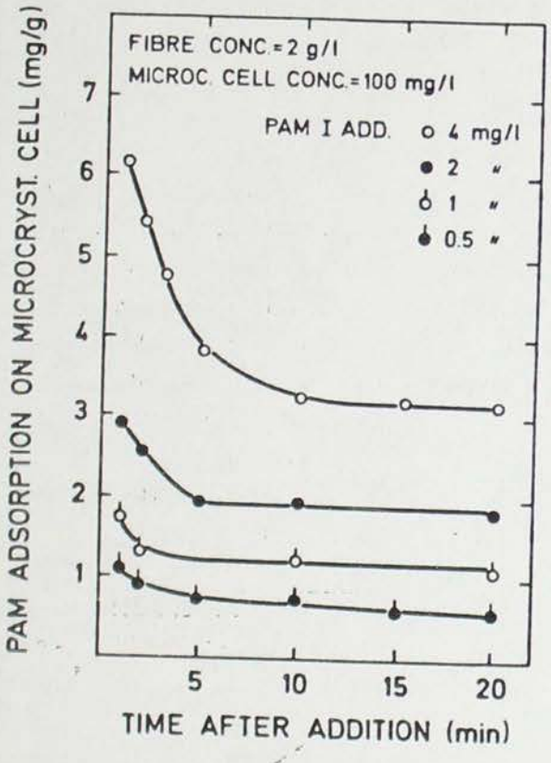

Figure 2. ^{3}H-C-PAM adsorption onto microcrystalline cellulose. ^{3}H-C-PAM added to a suspension containing 2 g/l bleached softwood kraft fibers and 100 mg/l microcrystalline cellulose. Same experiment as in Fig. 1.

These experiments are further substantiated by data showing different adsorption kinetics onto the fiber fraction and onto the MCC fraction, and by experiments with non-porous fibers (nylon) where these transient surface potential effects and polymer transfer effects are absent.

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CELLULOSE SUSPENSIONS AND POLYELECTROLYTES - SOME KINETIC ASPECTS

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KEYWORDS: Adsorption, Radioactive tracers, Electrophoresis

INTRODUCTION

In the practical application of various retention aids such as high molecular weight cationic polyacrylamides in the papermaking process, the contact time between the polymeric additive and the pulp suspension is of the order of seconds. The kinetics of polyelectrolyte adsorption onto the pulp and the flocculation of the stock are therefore of decisive importance. Transient surface potentials, i.e. changes in the z-potential with time after the addition of a charged polymer to a cellulose pulp suspension, were apparently first recorded (by means of microelectrophoresis) by Strazdins (1,2).

Later, studies in this laboratory (3) confirmed these observations when a cationic polyacrylamide (C-PAM) was added to a fiber suspension. The unexpected observation in these studies was that the electrophoretic mobility of the fines fraction decreases from a positive value to a negative value with time instead of increasing from a negative to a positive value. The rate of adsorption of C-PAM onto the coarse fiber fraction was found to be much slower than onto the fibril (crill or fines) fraction (3), and it was suggested that the C-PAM initially adsorbs to the fines and recharges them. As the coarse fiber material starts to adsorb the polymer, the fines desorb the polymer and the electrophoretic mobility of the fines decreases at a rate corresponding to the rate of adsorption of the polymer onto the coarse fiber material. The object of the present investigation was to substantiate this hypothesis with direct experimental evidence for such a transfer mechanism.

RESULTS

In order to follow the adsorption of C-PAM onto the cellulose substrates, a series of cationic polyacrylamides (copolymers of acrylamide and N,N diethylaminoetylacrylate quaternized with dimethylsulphate; courtesy of Allied Colloids, U.K.) were tritiated by means of $^3H_2$ (^{3}H-C-PAM). In a typical experiment, the coarse fiber fraction of an unbeaten bleached softwood kraft pulp was dispersed at a concentration of 2 g/l in a Britt Dynamic Drainage Jar (BDDJ) equipped with a 100 mesh wire. Microcrystalline cellulose, MCC (model substance for fines), was then added to a concentration of 100 mg/l. Each experiment started with the addition of a given amount of ^{3}H-C-PAM. Samples of the MCC were withdrawn from the BDDJ and the electrophoretic mobility was determined together with the amount of adsorbed ^{3}H-C-PAM. In order to determine the amount of adsorbed ^{3}H-C-PAM onto the MCC, the samples were filtered on a filterpaper on a Büchner funnel immediately after separation from the BDDJ.

Figure 1 shows the electrophoretic mobility of the MCC at different times after addition of the ^{3}H-C-PAM to the fiber and MCC suspension in the BDDJ. The high positive initial electrophoretic mobility followed by a decrease with time is typical.

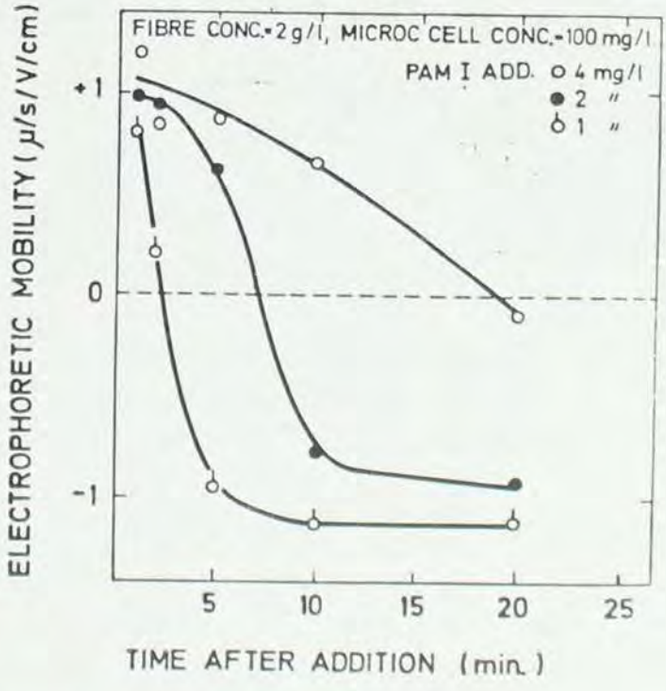
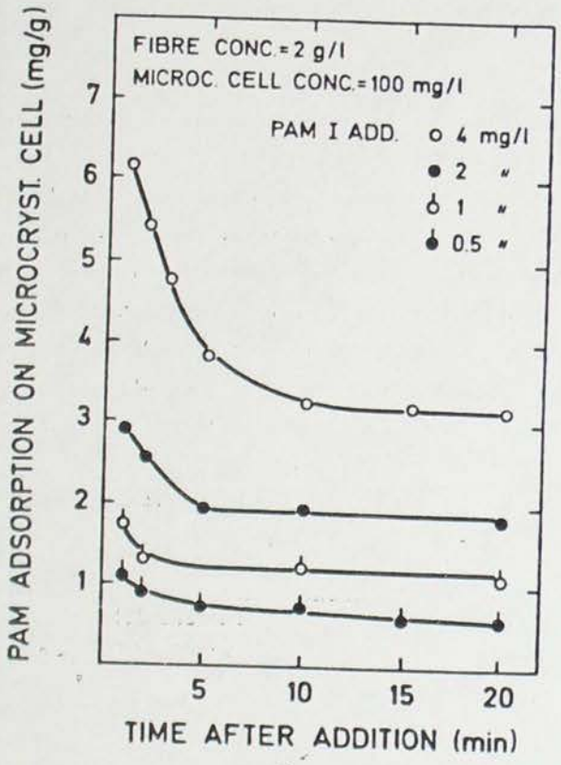


Figure 1. The electrophoretic mobility of microcrystalline cellulose particles (conc.=100 mg/l) separated from a bleached softwood kraft fiber fraction (fiber conc.= 2 g/l) at different times after addition of ^{3}H-C-PAM (PAM 1). Various levels of addition of ^{3}H-C-PAM.

Figure 2 shows that the decrease in the electrophoretic mobility is directly related to a transfer of ^{3}H-C-PAM from the MCC to the coarse fiber fraction, the reason for this transfer being that the adsorption is slower onto the coarse fiber fraction (slow penetration of the polymer into the porous cell wall of the fibers) than onto the MCC fraction. The faster rate of adsorption onto the MCC fraction is probably due to the smaller size of the substrate and correspondingly smaller diffusion distances into this substrate.



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ANALYSIS OF POLYPHENOL-DERIVED AROMATICS IN WOOD

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ABSTRACT

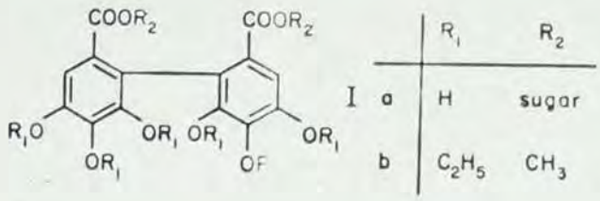
Difficulties encountered in the estimation of lignin and polyphenol contents of certain woods are outlined. Methods for the determination of polyphenols in wood involving degradation of wood and measurement of the resulting products by gas chromatography (GC) are discussed. A four-step procedure, based on permanganate oxidation of ethylated wood, allowed the estimation of proanthocyanidins and related polyphenols as the methyl ethoxybenzoates IVa-c. Two approaches to the determination of ellagitannins in wood, by alkaline treatment of ethylated wood to give the diphenic acid derivative Ib, and by alkaline decarboxylation of wood to the hexahydroxybiphenyl (HHBP) V, were unsuccessful.

INTRODUCTION

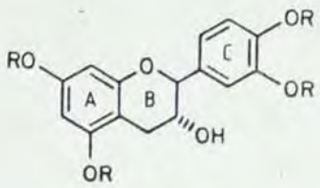
Klason lignin analyses of Eucalyptus woods which contain polyphenols can give anomalously high values because the polyphenols are included in the acid-insoluble Klason lignin residue. In certain Eucalyptus woods, the polyphenols cannot be extracted with neutral solvents, and boiling aqueous sodium hydroxide is often required for their complete removal (1). Under these alkaline conditions, appreciable amounts of lignin and hemicelluloses may become solubilized, particularly from the heartwoods.

Determination of Klason lignins corrected for polyphenols may be carried out by a method based on the methoxyl contents of Klason lignin residues from both unextracted and alkali-extracted woods (2,3). An assumption in the method is that the lignin in both the unextracted and alkali-extracted woods has the same methoxyl content. However, this assumption must be treated with caution, as lignin extracted from E. regnans wood has been shown to be richer in guaiacyl relative to syringyl groups than the original lignin (4). Methods for detection and direct estimation of polyphenols in wood were therefore sought.

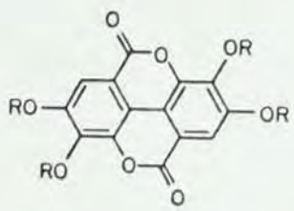
Polyphenolic extractives in eucalypt woods occur typically as hydrolysable tannins, chiefly sugar diesters of hexahydroxydiphenic acid (Ia) (ellagitannins); condensed tannins, which are proanthocyanidin polymers possessing units of structure IIa; ellagic acid (IIIa) and stilbenes (5). Existing methods for the determination of these substances in wood rely on examination of extracts. We present new approaches to the analysis of wood polyphenols which involve direct degradation of wood either by oxidation with permanganate or by treatment with alkali.



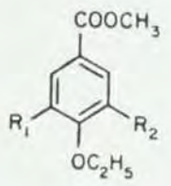
		R_1	R_2
I	a	H	sugar
	b	C_2H_5	CH_3



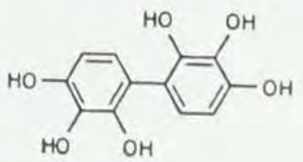
II a R = H
b R = C_2H_5



III a R = H
b R = C_2H_5



		R_1	R_2
IV	a	H	H
	b	OC_2H_5	H
	c	OC_2H_5	OC_2H_5



V

EXPERIMENTAL

Wood samples were Wiley milled to pass through a 1 mm sieve. The woodmeals were extracted with boiling water and boiling 0.1M sodium hydroxide according to the Appita standard methods P4m-61 and P5m-68, respectively. Cold alkali extractions of woodmeals were carried out with 0.1M sodium hydroxide at 20°C for 24 h. Additional samples were Soxhlet extracted for 18 h periods sequentially with acetone and methanol.

Ethylation of woodmeal

Woodmeal (1.0 g) was suspended in a mixture of

30 mL methanol-dimethoxyethane-water (21:21:18, v/v/v) adjusted to pH 11.0 with 2M sodium hydroxide, and 2 mL diethylsulphate was added. The mixture was kept under nitrogen at 20°C for 24 h and the pH was maintained at 11.0 by periodic addition of 2M sodium hydroxide with the aid of an automatic titrimeter. After acidification with 1M hydrochloric acid, the mixture was kept at 80°C for 30 min. The mixture was cooled, filtered and the ethylated woodmeal was washed with cold water and dried.

Permanganate oxidation of ethylated wood

A suspension of ethylated woodmeal (200 mg) in t-butanol (10 mL), 2M sodium hydroxide (10 mL), 0.03M potassium permanganate (20 mL) and 0.12M sodium periodate (50 mL) was shaken and then heated under reflux for 6 h. Additional solid potassium permanganate was added periodically so that the mixture remained purple in colour. After cooling, ethanol (10 mL) was added and the mixture was left to stand for 18 h. The treated woodmeal was collected by filtration and washed with 1% sodium carbonate solution. The combined filtrate and washings were acidified to pH 4.0, concentrated to ca. 30 mL in a rotary evaporator, and after addition of sodium carbonate (900 mg) 30% hydrogen peroxide (5 ml), kept at 50°C for 10 min. The solution was cooled, and manganese dioxide (100 mg) was added. After the evolution of gas ceased, the mixture was filtered and the residue washed with 1% sodium carbonate. The filtrate was acidified to pH 2 with 5M sulphuric acid, extracted with 50% acetone-chloroform (3 x 50 mL) and dried. The product was obtained after evaporation of the solvent.

Methylation and GC analysis

A large excess of diazomethane in diethyl ether was added to a solution of the oxidized product in methanol (2 mL) and the mixture was kept at 4°C for 18 h. After evaporation of the solvent, dichloromethane (1 mL) containing pyromellitic acid tetramethyl ester (6.0 mg) as internal standard was added. The GC analysis was carried out with a SE30 bonded phase vitreous silica capillary column (12 m x 0.22 mm ID) (SGE Scientific, Melbourne) in the splitter mode, and detection was by flame ionization.

Alkaline treatment of ethylated wood

Samples of ethylated woodmeal (200 mg) were heated under reflux with 0.1M sodium hydroxide (20 mL) for 1 h. The woodmeal was collected by filtration and washed with warm water. The combined filtrate and washings were acidified to pH 2 and extracted with 50% acetone-chloroform (3 x 30 mL). The extracts were dried and the residue after evaporation of the solvent was methylated with diazomethane and examined by GC after addition of pyromellitic acid tetramethyl ester as the internal standard.

Preparation of the HHBP (V)

A suspension of ellagic acid (1.0 g) in 4M sodium hydroxide (10 mL) was sealed under nitrogen in a 20 mL steel autoclave and was kept at 170°C for 2 h in a rocking air bath. After cooling, the contents of the autoclave were immediately acidified to pH 2 with 5M hydrochloric acid and cooled in an ice bath. The precipitate which formed was filtered and washed with cold distilled water. The dried material (405 mg) was dissolved in hot water, purified with charcoal, and the white needles of V which were obtained on cooling had a mp > 350°C.

Estimation of ellagic acid as the HHBP (V)

Ellagic acid (12-50 mg) and 0.5M potassium hydroxide (5 mL) were sealed under nitrogen in 15 mL glass vials, and the vials were kept at 105°C for periods of 18-96 h. After opening the vials, the contents were immediately acidified to pH 4, transferred to 100 mL flasks and freeze-dried. Methanol (5 ml) containing disyringylmethane (6 mg) as internal standard, was added and the mixture shaken. An aliquot (ca. 2 mL) was evaporated under nitrogen and the residue was silylated with N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA)(100 µL) at 100°C for 24 h. Excess BSTFA was removed under nitrogen, and dichoromethane (1 mL) was added prior to GC analysis on a SE30 bonded phase capillary column, with a column temperature of 230°C.

Additional experiments were carried out with ellagic acid in the presence of woodmeals (500 mg) and alkali extracts from woodmeals, as well as with woodmeals themselves.

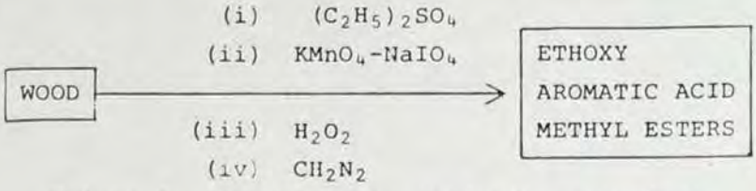
RESULTS AND DISCUSSION

Permanganate oxidation of wood

Oxidative methods for the estimation of polyphenol-derived aromatics in wood were explored. The polyphenol-derived products can be distinguished from lignin-derived aromatics by the absence of methoxyl substituents on the aromatic rings of the former. An exception is the p-hydroxyphenyl moiety, which may occur in both lignin and polyphenolic extractives.

Initial experiments showed that alkaline nitrobenzene and alkaline cupric oxide oxidation at 170°C were not appropriate methods for the

analysis of polyphenols in wood, as protocatechualdehyde and protocatechuic acid, typical of the expected oxidation products, were not stable under the reaction conditions. Application of these oxidants to ethylated polyphenols was also not a useful approach, because tetraethylcatechin (IIb), a model for ethylated proanthocyanidins in wood, did not yield products identifiable by GC.



Scheme 1 Permanganate oxidation procedure

The adopted method (Scheme 1) is a modification of the permanganate oxidation procedure which has been used for lignin structural studies (6,7). The initial step is the ethylation of the phenolic hydroxyl groups in the wood samples with diethylsulphate at pH 11. Sequential oxidation of the ethylated wood with alkaline potassium permanganate - sodium periodate, and hydrogen peroxide, gave substituted aromatic acids, which after treatment with diazomethane were determined as their methyl esters by GC. The products were identified by comparison with authentic samples by GC-mass spectrometry.

Oxidation of tetraethylcatechin (IIb) by the above procedure gave the methyl benzoate IVb in 86% yield. When the hydrogen peroxide step was omitted, the yield of IVb was reduced to 55%. Compound IVb originates from the C-ring of the ethylated catechin, and no product deriving from the A-ring was identified. Application of the oxidation to tetraethylellagic acid (IIIb) gave no product identified by GC.

When various eucalypt woodmeals were subjected to the oxidation procedure, a series of substituted methyl benzoates were obtained. Of the woodmeals from the four eucalypt species in Table 1, E. regnans gave no diethoxybenzoate IVb, whereas the other species yielded 1-3% on oxidation. E. regnans is representative of a pale-brown heartwood species and the other three species form part of the red-coloured group of species (5). The latter group are known to contain proanthocyanidins (5,8,9), and compound IVb may derived from the C-ring of units of structure IIa. The origin of ethoxybenzoate IVa could be lignin, proanthocyanidins, or hydroxystilbenes. Compound IVc, the gallic acid derivative, may either originate from gallotannins or proanthocyanidins.

The components which give rise to ethoxybenzoates IVa and IVb are only extracted to a limited extent with boiling water or acetone-methanol, and require an alkaline extraction for their removal. However, the substances which yield the gallic acid derivative IVc are removed with boiling water or organic solvents. The latter substances are more likely to be gallotannins or gallic acid itself rather than polymers of the delphinidin type, which would not be expected to be removed with neutral solvents.

Wood Sample	% Yield (w/w) of Benzoic Acid Derivative		
	IVa	IVb	IVc
E. regnans			
heartwood	0.1	-	tr.
E. tetrodonta			
heartwood	0.1	1.1	0.3
E. diversicolor			
heartwood	0.3	2.2	0.6
boiling water extracted	0.5	2.0	tr.
acetone-methanol extracted	0.3	2.0	tr.
cold alkali extracted	-	0.2	-
boiling alkali extracted	tr.	0.2	-
E. diversicolor			
sapwood	0.2	1.2	0.1
boiling water extracted	0.2	0.8	tr.
acetone-methanol extracted	0.1	0.8	-
cold alkali extracted	-	0.2	-
boiling alkali extracted	tr.	0.1	-
E. marginata			
heartwood	0.2	2.7	0.7
cold alkali extracted	0.1	0.9	0.2
boiling alkali extracted	tr.	0.2	-
E. marginata			
sapwood	0.1	1.2	1.5
boiling water extracted	0.1	0.8	0.4

Table 1 Permanganate Oxidation of Woodmeals

Alkaline degradation of polyphenols

1 Alkaline hydrolysis of ethylated wood

Estimation of the aromatic groups in the hydrolysable tannins was attempted by a method in which the ethylated tannins were hydrolysed to their parent acids and measured as the methyl esters by GC. Thus the diphenic acid derivative Ib and the methyl triethylgallate IVc would be the expected products from ethylated ellagitannins and gallotannins, respectively.

Sequential treatment of ethylated eucalypt wood samples with boiling 0.1M sodium hydroxide and diazomethane afforded the triethoxybenzoate IVc with smaller amounts of the diethoxybenzoate IVb (Table 2). No trace was found of the ellagitannin-derived diphenic acid ester Ib. The detection of compound IVb was unexpected, as esters of protocatechuic acid are not known structural features of lignin or polyphenols.

2 Alkaline treatment of ellagitannins in wood

An attempt was made to estimate the polyphenol moieties in ellagitannins as the hexahydroxybiphenyl (HHBP) V, based on the observation of Hemingway and Hillis (10) that ellagic acid

Wood Sample	% Yield (w/w% wood basis) IVb	IVc
E. diversicolor heartwood	0.1	0.3
E. marginata sapwood	0.1	0.6
E. marginata heartwood	0.1	0.1
E. tetrodonta heartwood	trace	0.4

Table 2 Alkaline Hydrolysis Products

treated with 0.5M sodium hydroxide at 160°C gave the decarboxylated product V. The present approach would allow the measurement of both ellagic acid and the aromatic groups in ellagitannins, and would supplement the method of Hillis et al. (11) for estimation of free ellagic acid in wood.

Reaction of ellagic acid with 0.5M potassium hydroxide at 105°C for 48 h gave the HHBP (V) (estimated by GC as the trimethylsilyl ether) in 76% yield. However, when various eucalypt woods were digested with alkali at 105°C or 170°C, neither the HHBP (V) nor pyrogallol, which could arise from decarboxylation of gallic acid, were identified as products. Furthermore, when the decarboxylation reaction of ellagic acid was carried out in the presence of eucalypt woods or alkaline extracts of these woods, the yield of V was reduced to ca. 5%. The eucalypt woods would be expected to contain ellagitannins, and the HHBP (V) formed by hydrolysis/decarboxylation probably undergoes alkali-catalysed condensation reactions with lignin extracted from the woods. The approach for analysis of ellagitannins was not pursued further.

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OXYGEN BLEACHING FOLLOWING PREOXIDATION OF WOOD PULPS WITH NO_2/O_2

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ABSTRACT

Preoxidation of sulphate pulp from pine gave rise to a larger increase in selectivity (viscosity at a given kappa number) after oxygen bleaching than that observed with birch sulphate pulp. Larger amounts of CO_2 and N_2O were produced from birch than from pine pulp. The production continued long after the added NO_2 was consumed completely, indicating a massive regeneration of NO_2. Insufficient regeneration can, therefore, not explain the unfavourable results with birch pulp.

Experiments with pine pulp showed that addition of oxygen is not a prerequisite for a massive regeneration. Treatment of lignin with acid nitrate solution gave rise to large amounts of NO_2 + NO even when no oxygen was added. This suggests that NO_2 can be generated in connection with the recovery of spent liquors from the process.

KEYWORDS: Nitrogen dioxide, Nitric acid, Oxygen, Bleaching, Lignins, Dinitrogen oxide, Carbon dioxide.

INTRODUCTION

The PRENOX® process invented by the author and described in several patent applications to Mo och Domsjö AB and publications from Chalmers University of Technology will shortly be studied in a pilot plant built by Sunds Defibrator at the Oestrand kraft mill. The process is based on a preoxidation of unbleached pulp in the presence of NO_2 and O_2 followed by an alkaline treatment preferably oxygen bleaching. A main feature is that the conditions during the preoxidation are such that NO_2 is regenerated from produced and added nitrate and utilized repeatedly (1).

The preoxidation results in a protection of the carbohydrates reflected in a suppressed depolymerization rate during the oxygen bleaching. Under most conditions the delignification after the oxygen bleaching is improved (2). Both factors contribute to an enhanced selectivity, defined as viscosity at a given kappa number. This report deals with preoxidation of different types of pulp and an alternative method to regenerate nitrogen dioxide.

DIFFERENT PULPS (Coworker PER SJÖGREN)

Kraft pulps from softwood received in wet condition have been used in most previous work. Remaining inorganic constituents which neutralize the nitric acid produced during the preoxidation can exert a serious effect on the results (3). If not otherwise stated the pulps used in our laboratory were washed carefully with demineralized water subjected to distillation in quartz glass equipment. By this procedure the serious effect of trace metals (mainly copper) present in tap water and distilled water was eliminated.

During the preoxidation or before this stage metal ions present in the pulp are dissolved in produced or added nitric acid. In laboratory experiments it is tedious to recirculate the liquors in a manner simulating the conditions in a plant with continuous preoxidation, oxygen bleaching and recovery of the spent liquors. To avoid the difficulties we have in the present work used pulps soaked with 0.1 M hydrochloric acid at room temperature for 30 min before washing with the purified water.

Most previous reports are based on experiments with industrial kraft pulps of high viscosity. Even in the same mill the viscosity and kappa number can vary from time to time. A pulp of higher kappa number and a lower viscosity than most pulps used in our previous wash, was therefore studied.

The pulp was impregnated with 0.3 molal $NaNO_3$ in 0.1 molal HNO_3 before the preoxidation (4). In addition a programmed temperature (3) and a programmed introduction of oxygen (5) were used. Under proper conditions all these precautions lead to an increased selectivity. In the preoxidation 1% NO_2 was introduced into the evacuated reactor at 52°C (zero time) followed by 1% NO_2 after 3 min. Air, 300 ml, was introduced after a total time of 5 min. The temperature was raised to 65°C during the period 7-17 min and 300 ml air added after 17 min. After 30 min air was introduced to atmospheric pressure. The preoxidation was interrupted after a total time of 60 min. All treatments referred to in this paragraph were carried out with 75 g pulp in a 2-Litre reactor.

The plots of viscosity versus kappa number (Fig. 1) show that preoxidation at either 15 or 27 % consistency resulted in a markedly improved selectivity after the oxygen bleaching. The preoxidized pulps were delignified to kappa number 9 before the viscosity decreased to 950 dm^3/kg. In

the blank with acid-soaked pulp the viscosity dropped to this value at a kappa number of about 16. After any given duration of the oxygen bleaching the kappa numbers were lowered markedly as a result of the preoxidation. The loss in viscosity during the preoxidation was counterbalanced by the protection effect. Since an acid soaked pulp was used as reference the improved selectivity cannot be related to a removal of detrimental trace metals.

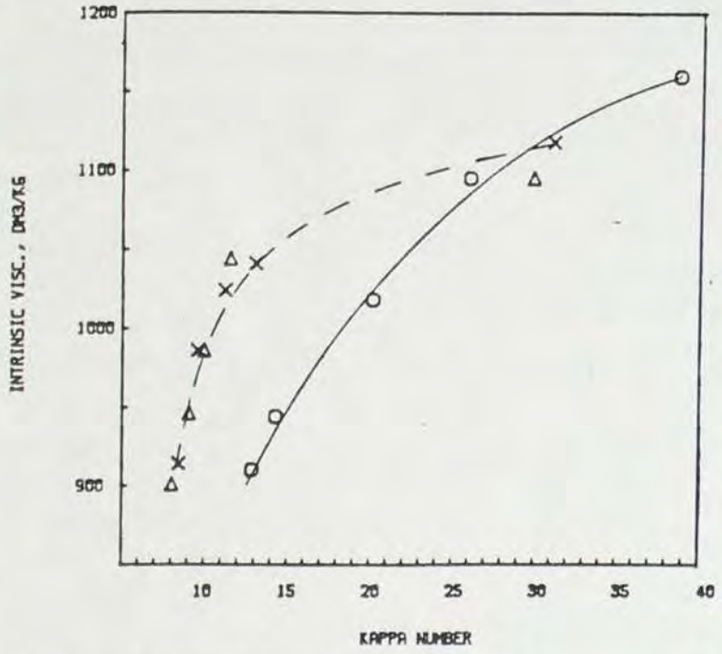

Fig. 1. Intrinsic viscosity versus kappa number after oxygen bleaching of kraft pulp from softwood (mainly Pinus sylvestris). The highest kappa numbers and viscosities in each series refer to pulps before oxygen bleaching.
x Preoxidation at 15 and Δ 27% consistency
o Blank, no preoxidation

A comparison with results obtained with other kraft pulps shows that a low viscosity of the unbleached pulp has a larger detrimental effect on the selectivity after oxygen bleaching than a high kappa number.

Table I. Duration of the oxygen bleaching and kappa number (interpolated values) at an intrinsic viscosity of 950 dm^3/kg.

Consistency during preoxidation %	Washing with distilled water Time min	Kappa number	Soaking with 0.1 M HCl [a] Time min	Kappa number
-	30	11.5	100	9.0
10	120	9.0	110	8.5
27	110	9.0	100	8.5

a. The soaking with acid for 30 min at 20°C decreased the ash content from 0.73 to 0.16%; Cu from 3 to 1, Fe from 20 to 12 and Mn from 90 to 4 mg per kg pulp.

The effects of preoxidation of an industrial birch sulphate pulp and of soaking are shown in Table I. The water-impregnated pulp was preoxidized with 2% NO_2 at 65°C for 60 min with O_2-addition to atmospheric pressure after 1, 10 and 30 min. In the experiments with unsoaked pulp the viscosity dropped from 1238 to 950 dm^3/kg after 2 hours in the oxygen bleaching. The kappa number decreased from 17.5 to 9.0. In the blank without preoxidation the same loss in viscosity was obtained after 30 min. The kappa number was 11.5. Hence, the preoxidation led to a markedly increased protection of the carbohydrates during the oxygen bleaching and to an improved selectivity. The same improvement in selectivity and about the same protection effect were, however, obtained by soaking with hydrochloric acid. Preoxidation of the soaked pulp had only a slight influence on the subsequent oxygen bleaching. Evidently, the main effect of the preoxidation was a removal of catalytically active metal compounds before the oxygen bleaching (See also Fig. 2).

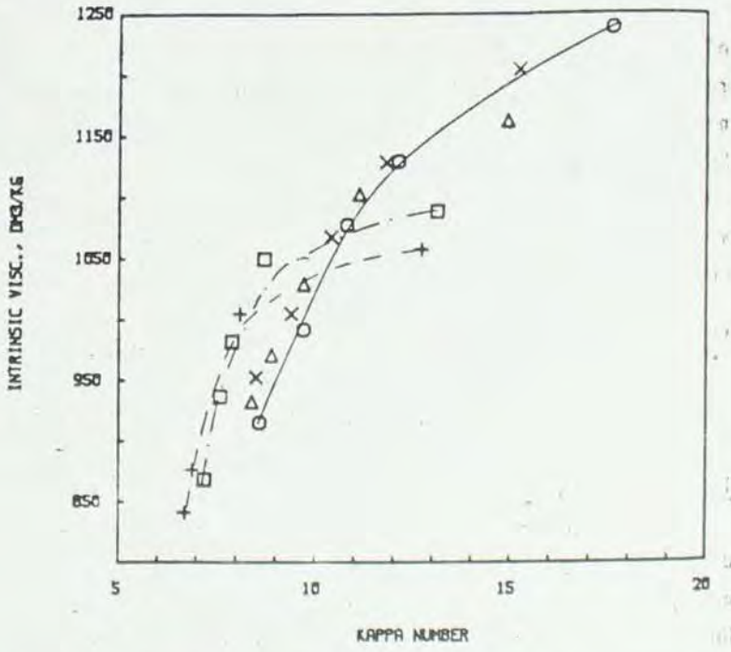

Fig. 2. Oxygen bleaching of birch pulp (Betula verrucosa) following preoxidation under various conditions.
Pulp impregn. with water: x 15%; Δ 27% consistency
Pulp impregn. with 0.3 molal $NaNO_3$ in 0.1 molal HNO_3: □ 15%; Δ 27% consistency. o Blank, no preoxidation

In attempts to improve the effect of the preoxidation, only the acid-soaked pulp was used. In two series of experiments with pulp impregnated with acid nitrate solution included in Fig. 2 the conditions were the same as those used with kraft pulp from softwood with the exception that the final temperature during the preoxidation was

increased from 65 to 72°C. These conditions led to a severe loss in viscosity during the preoxidation, a markedly improved protection during the oxygen bleaching and an improved delignification after the oxygen bleaching. The net result was a significantly improved selectivity for pulps of low kappa number.

Under otherwise unchanged conditions a decreased final temperature to 65°C led to higher viscosities after the preoxidation and an improved selectivity for pulps of comparatively high kappa number (Fig. 3). For pulps of low kappa number the decreased temperature had no significant effect on the selectivity. An experiment in which nitrogen was added instead of air showed that the selectivity was virtually unchanged provided that the addition of NO_2 was increased from 2 to 3%. The results are consistent with the observation (discussed below) that nitrogen dioxide can be generated from nitrate ions even when no oxygen is added. A comparison between the results with birch pulps and those with kraft pulps from softwood shows that under applied conditions the preoxidation has a much larger effect on the selectivity with softwood than with birch pulps.

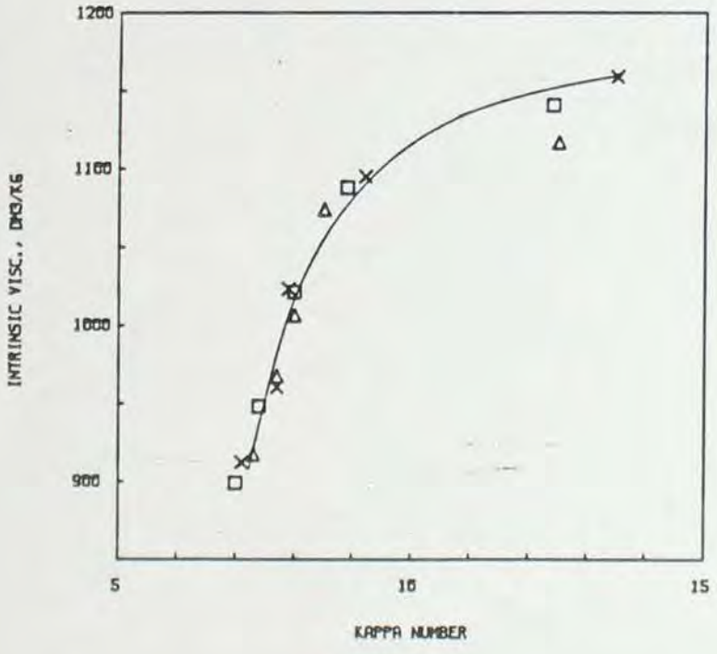

Fig. 3. Oxygen bleaching of birch pulp following preoxidation under various conditions.
Addition of air: x 15%; Δ 27% consistency
Addition of N_2: □ 15% consistency (3% NO_2)

FORMATION OF N_2O AND CO_2
Different pulps (Coworker URBAN ÖJTEG)

Dinitrogen oxide and carbon dioxide are produced in lignin reactions during preoxidation of kraft pulp at high consistency (6). Recent investigations show that for pulps impregnated with nitric acid an improved selectivity can be achieved at medium consistency (7). Figs. 4 and 5 show that with kraft pulp from softwood a decreased consistency from 27 to 15% led to an increased production of both N_2O and CO_2. Independent of the consistency and the type of unbleached pulp the production continued long after the period of a few minutes when the added nitrogen dioxide was consumed virtually completely. The continued production is due to an extensive regeneration of NO_2.

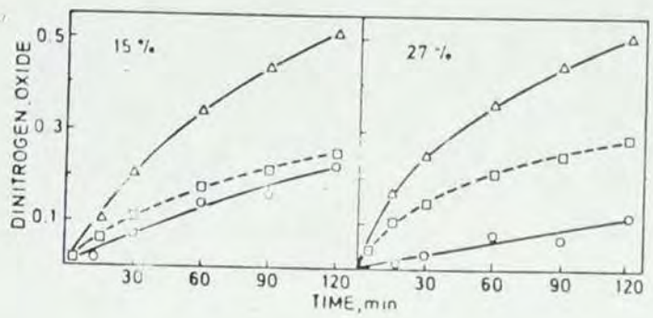

Fig. 4. Production of N_2O (kg per 1000 kg pulp) during preoxidation at 68°C with 2% NO_2 and O_2 of pulps impregnated with 0.3 molal $NaNO_3$ in 0.1 molal HNO_3.
o Kraft pulp, Pinus sylvestris, kappa number 38.7
□ Birch sulphate, Betula verrucosa, kappa number 23.3
Δ Sulphite pulp, Picea abies (Karst.) kappa number 17.5

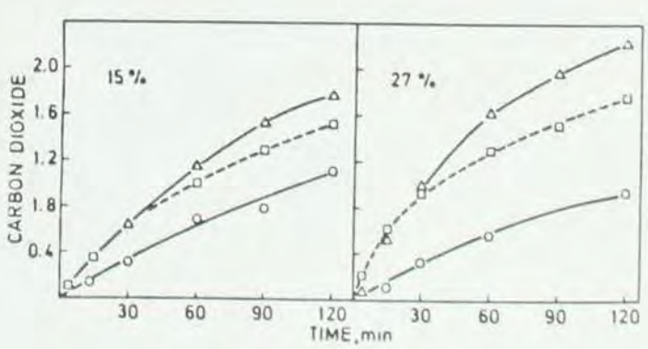

Fig. 5. Production of CO_2 (kg per 1000 kg pulp) during preoxidations referred to in Fig. 4.

Larger amounts of N_2O and CO_2 were produced from sulphite pulp from spruce and a sulphate pulp from birch than from a kraft pulp from softwood. This is noteworthy since the effect of the preoxidation on the selectivity after oxygen bleaching was much larger for the kraft pulp than for the other pulps. These and other results show that there is no generally valid relation-

ship between the oxidation of lignin to CO_2 and the beneficial effects of the preoxidation on the delignification and protection of the carbohydrates. For the birch pulp and the sulphite pulp the decreased consistency led to a decreased production of CO_2, while the production of N_2O was only slightly affected.

The formation of N_2O means that active nitrogen compounds are withdrawn from the regeneration cycle. The conversion of NO_2 to N_2O in these experiments was 5.5% or less calculated as percentage of the added NO_2. The volume of N_2O + CO_2 calculated at 68°C and atmospheric pressure was 0.5 m^3 per 1000 kg kraft pulp after preoxidation for 60 min at 15% consistency. These inert gases will dilute the gas phase. This can affect the chemical reactions in the reactor and the required addition of oxygen. Precautions with regard to the environment may also be justified.

EFFECT OF OXYGEN (Coworker DENNIS RASMUSSON)

In the experiments referred to in Figs. 4 and 5 nitrogen dioxide was evaporated into the evacuated reactor. Oxygen was then added so that atmospheric pressure was approached Experiments in which the initial oxygen concentration was varied from 0 to 100% (of permanent gases) by using pure helium, mixtures of oxygen and nitrogen and pure oxygen are referred to in Tables II and III. In the experiments with oxygen containing gas, helium was added to atmospheric pressure to compensate for the consumed oxygen. In the absence of oxygen superatmospheric pressure was obtained.

Table II. Influence of the initial O_2-concentration on the production of N_2O (kg per 1000 kg pulp) during treatment with 2% NO_2 at 65°C and 10% consistency of kraft pulp (kappa number 39.0) impregnated with 0.3 molal $NaNO_3$ in 0.3 molal HNO_3

Time min	100% O_2	20% O_2	10% O_2	0% O_2
20	0.25	0.23	0.27	0.26
60	0.62	0.55	0.73	0.70
180	1.09	1.00	1.30	1.19
1200	2.58	3.32	3.90	3.45

The results show that very large amounts of N_2O and CO_2 were produced even when no oxygen was present in the added gas. The highest production of both N_2O and CO_2 occurred when the gas contained 10% oxygen. The lowest production of N_2O, which is a reduction product, was obtained with pure oxygen. The oxidation of lignin to CO_2 was somewhat higher with pure oxygen than when pure helium was added. The results suggest that reactions responsible for the formation of N_2O and CO_2 as well as competing reactions are favoured by oxygen.

Table III. Formation of CO_2 (kg per 1000 kg pulp) in the experiments referred to in Table II.

Time min	100% O_2	20% O_2	10% O_2	0% O_2
20	0.93	0.83	1.05	0.91
60	2.51	2.05	2.61	2.21
180	4.15	3.26	4.13	3.59
1200	9.01	8.92	10.0	8.10

Independent of the composition of the gas phase the reactions proceeded over a very long period of time. The results indicate that the autocatalytic regeneration of nitrogen dioxide from nitric acid was very extensive both in the experiments with and without oxygen in the gas introduced into the reactor. The initiation of the regeneration is promoted by oxygen and is one reaction which favours the formation of both N_2O and CO_2. One reaction in the group which tends to suppress their formation is the conversion of NO_2 to HNO_3.

GENERATION OF NO_2 (Coworker LARS ANDERSSON)

NO_2 is produced during heating of dilute HNO_3 with lignin in the presence of oxygen. More than 60 % of the free HNO_3 was under favourable conditions present as NO_2 (including N_2O_4) when an acid nitrate solution was treated with lignin for 20 min at 56°C (8). Only a minor proportion of NO was produced. NO_2 gave rise to nitro groups in the lignin. For this reason the yield of NO_2 decreased on prolonged treatment.

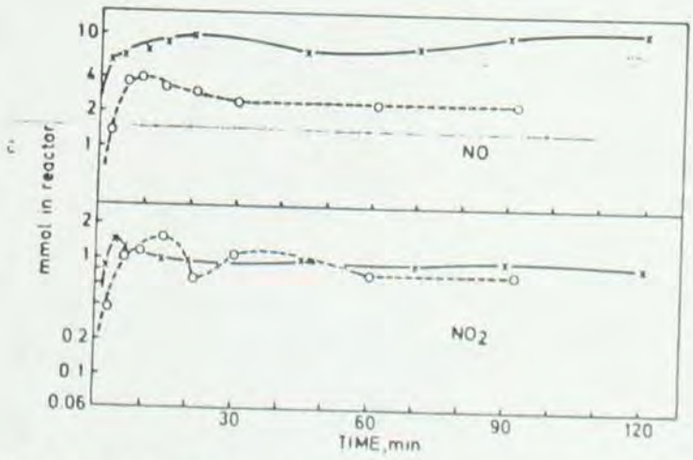

Fig. 6. Treatment of Indulin AT (18.4 g) with 27.6 g of 0.85 molal $NaNO_3$ in 1.05 molal HNO_3 in a 500 ml reactor at 56°C.
x 0.5 % NO_2; o No NO_2

Experiments with addition of nitrogen instead of oxygen showed that a large amount of NO and an appreciable amount of NO_2 were produced already after a few minutes (fig. 6) . The shape of the curves and the striking effect of a very small addition of NO_2 show that the process is autocatalytic.

After 20 min the molar concentration of NO plus NO_2 was approximately the same as in comparable experiments with oxygen addition. On prolonged treatment this concentration was much higher than in experiments with oxygen. This is explained by a less extensive nitration of the lignin reflected in lower nitrogen contents after 120 min (0.38 and 0.32 %) compared to 1.23 and 1.13 % when oxygen was added.

When oxygen was added a decreased lignin addition by 50 % led to an increased maximum concentration of NO + NO_2 (8) while the opposite effect was obtained when nitrogen was added (not shown). It is evident that, like NO_2, oxygen promotes the initiation of the reaction between nitric acid and lignin. Reactions which suppress the yield of NO + NO_2, such as nitration and formation of nitric acid are, however, also favoured by oxygen. This suggests that under conditions which favour the initiation (e.g. high temperature, presence of NO_2) an increased yield of NO + NO_2 should by expected when oxygen is omitted. This was confirmed in experiments at 75°C under otherwise unchanged conditions. The reproducibility was, however, bad and the results are not shown.

All results mentioned above were confirmed in a study with a continuous reactor (Fig. 7) which will be reported elsewhere (Samuelson and Öjteg). It can be mentioned that under favourable conditions (75°C no addition of O_2 and effective removal of the produced gas) approximately 80 % of the added nitric acid was accounted for as NO plus NO_2. The experiments showed that these nitric oxides can be produced from spent liquors from the process. When this technique is used the preoxidation can be carried out under conditions which lead to a lower acid hydrolysis (lower acidity and temperature) than those employed when the consumption of NO_2 is kept at a low level by an effective regeneration during the preoxidation. Compared at the same consumption of NO_2 and degree of delignification after the oxygen bleaching, the new technique gives rise to a higher pulp viscosity, yield and strength of produced paper than a process without production of nitrogen oxides from the spent liquors.

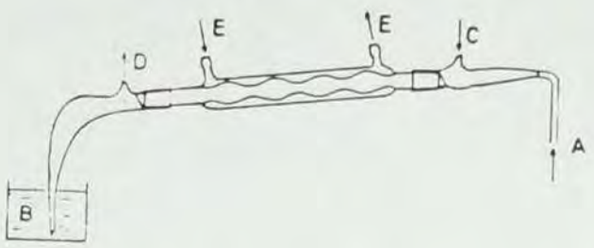

Fig. 7. Reactor for continuous production of NO_x
A. Inlet of lignin slurry from peristaltic pump
B. Receiver for treated slurry.
C. Inlet nitrogen.
D. Outlet of gas.
E. Hot water circulation.

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Investigation on Lignins and Lignin Polymer Models by FTIR Spectroscopy

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In the last two decades it has been often demonstrated that IR spectra of lignins reflect very well their compositon of basic phenylpropane units. Therfore IR spectroscopy has been recommended for lignin classification studies. The main obstacle for a more frequent use of this established routine analysis in lignin chemistry is the interrelation of IR bands, e.g. units containing carbonyl groups and aromatic units with different grades of OMe-substitution may cause response at the same wavelength. Moreover there are no reliable numerical methods to evaluate lignin IR spectra. The purpose of this study was therefore the quantitative evaluation of lignin IR spectra including mathematical/statistical handling of the data. Lingin-like polymer models (DHP's), MWL's, dioxane /HCl, and Willstätter lignins were investigated using the FTIR technic. p-coumaryl-(H), coniferyl-(G) and sinapylalcohol-(S) (separately and in mixtures), isoeugenol and pinoresinol were used for DHP syntheses. Continuous (Zutropf, ZT) and discontinuous (Zulauf, ZL) polymerisation methods were applied. For 30 DHP's peroxidase and for 14 DHP's laccase was used to initiate the random polymerisation process. Most of the DHP's were fractionated according to their solubility or to their molecular size (mol wt) on a Sephadex LH 60 column. Thus lignin-like polymers came into existence having extremely different analytical data with regard to composition of basic units and oxidation levels. Those were appropriate subjects to test the efficiency of IR spectroscopy in lignin chemistry. Lignins of more than 130 plant species were isolated by standard methods. Those species belong to 40 families including the so-called "primitive" dicotyledones and monocotyledones. For all preparates the C_{900} formula were calculated. Their IR spectra were base line corrected and normalized in a way that the absorption of the dominant band was equal to 1. After that spectra were evaluated by the base line technic.

Multiple linear regression analyse were carried out in such a way that each one of the experimental/analytical data was alternatingly considered as dependent variable and 15 IR bands as independent variables. Equations of the type $\hat{y} = b_0+b_1x_1+\ldots+b_nx_n$ were obtained, where $\hat{y}$ = predicted value for an analytical datum; b_0 = constant; $b_1 \ldots b_n$ = coefficients for n IR bands; $x_1 \ldots x_n$ = appropriate numerical values of IR bands at different wavelengths. The ability of the regression equation to predict the response $\hat{y}$ for a certain group of preparates and combinations of them (e.g. laccase or/and peroxidase DHP's, MWL's or/and dioxande/HCl lignins) was calculated by determining the multiple correlation coefficient R and the standard deviation s of calculated and experimentally found values. Results:

- Multiple linear regression analysis of IR spectroscopical and experimental data has been proved an useful data handling method. For calculations it is recommendable to take into account as many IR informations as possible. In this way interactions of IR bands can be mathematically eliminated to some extent.

- For the DHP's it has been demonstrated, that mol% H, mol% G, mol% S, OMe/C_{900}, O/C_{900} values can be calculated independently from each other on the basis of IR spectra. The R values for that kind of calculations were around 0.985 and subsequently the corresponding s values were low.

- The best way to estimate the number of OH groups by IR spectroscopy seems to be the evaluation of difference spectra recorded by substraction of spectra from acetylated and non acetylated lignin.

- IR data of MWL's and dioxande/HCl lignins can be jointly evaluated. OMe/C_{900} values of 36 preparates of these types has been predicted on the basis of IR spectra giving values of R = 0.998 and s $\pm$ 4.

- OMe/C_{900} values of 120 Willstätter lignins has been predicted resulting in R = 0.956 and s $\pm$ 5.

- IR spectroscopy is a good screening method for lignin classification. With this method it can be demonstrated, that some of the dicotyledone plants (e.g. Brachylaena hutchinsii Hutch (Compositae); Tectona grandis L. (Verbenaceae))have guaiacyl lignins. Many dicotyledone species have lignins containing only a few percent of syringyl units demonstrating that boundaries are fluid between typical guaiacyl and guaiacyl/syringyl classification groups.

THE ACTION OF GASEOUS CHEMICALS ON STRUCTURAL TIMBER

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ABSTRACT

Though the resistance of wood against chemicals has been used and proved since long in many fields of industry and craft, wood defects may occur after long-time action of aggressive atmospheres on structural timber. Chemical, microscopical and mechanical investigations on spruce wood exposed to gaseous chemicals of various aggressiveness revealed different degradation effects. However, a general degradation pattern cannot be established as the conditions in the industry halls were very heterogeneous. On the whole the results support the usefulness of wood as a building material in aggressive atmospheres.

KEYWORDS: Spruce timber (Picea abies (L.) Karst.), Gaseous chemicals, Analytical methods.

INTRODUCTION

Defects of structural timber in industrial production and storage halls caused by the action of aggressive atmospheres for long periods gave occasion for studies on the influence of gaseous chemicals on spruce wood.
Analytical methods developed during laboratory experiments with 4 exemplary gases were applied to standard rods attached to the ceilings of halls for 1 year and to bore cores taken from roof beams.

RESULTS

Effects of highly concentrated gases

The action of formaldehyde, ammonia, sulfur dioxide and chlorine on solid spruce wood samples for 28 to 336 days at temperatures of 20 and 40°C (HCHO: 55°C) was investigated by means of chemical, microscopical and mechanical methods (Besold, Fengel 1983; Fengel, Hardell 1983). The amounts and the characterization of the solubles obtained by extraction of the gas-treated wood with water, ethanol-benzene and dilute alkali give important data on chemical changes, which ultimately influence the strength properties.
After treatment with formaldehyde a minute degradation of polyoses was found, while due to a certain network effect the bending strength increased. Ammonia causes the well-known plastification of wood without substantial wood degradation. By sulfur dioxide considerable portions of the polyoses are hydrolyzed, but also cellulose and lignin are degraded to become partly soluble in alkaline solutions and hot water, respectively. The loss of substance of about 10 % leads to a strong decrease in strength, especially in the case of high moisture content of wood. Chlorine has the most degrading effect of all gases applied. Nearly half of the wood dissolved during the extraction steps. In this oxidizing medium particularly lignin is attacked to become soluble to more than 70 %.

Scanning and transmission electron microscopical observations reveal several changes in the cell walls but in all cases the compound middle lamellae and thus the cell tissue structure are remaining (Fig. 1).

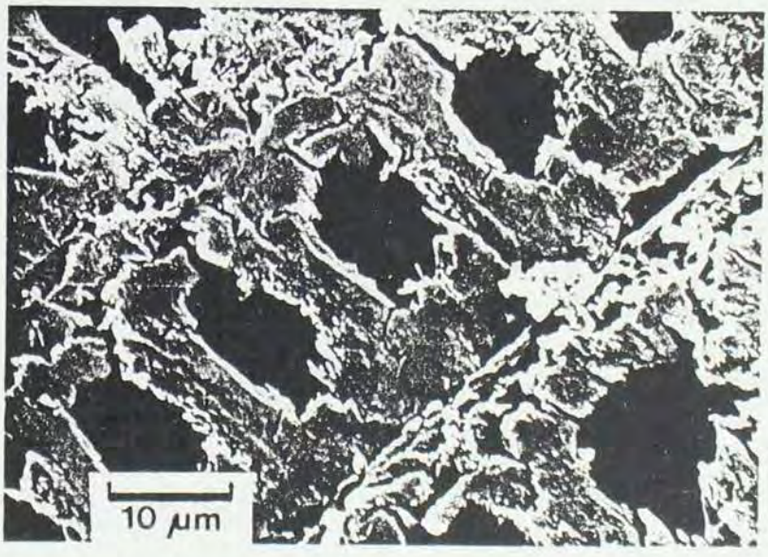

Figure 1. Cross section of a bore core taken from a 70 year old beam exposed to a SO_2 atmosphere. SEM micrograph.

Sorption experiments

In addition to the effects of aggressive gases acting on wood the sorption behaviour with respect to these gases was of interest. Therefore the gas absorption was measured as a function of time at wood moisture contents (u) of 0 %, 11 % and 20 %.
The most significant result is the increase of the maximum absorption of SO_2 at reduced moisture content. In contrast, ammonia and chlorine are much better absorbed at increasing moisture content. The maximum weight of absorbed ammonia amounts to about 7.7 %, related to wood. Cl_2 is absorbed up to 15.5 % at u = 20 % while only about 2 % are absorbed at u = 0 %. A very fast saturation is reached with small amounts of SO_2 (4.3 %) at u = 20 % while the maximum absorption in the dry wood makes up 13 %.

To determine the amounts of fixed gas the samples were flushed with nitrogen for 12 h after having reached saturation. Nearly the whole Cl_2 (90-100 %) is fixed irreversibly while about 40-50 % of SO_2 and only 20-30 % of NH_3 remain in the wood.
If the actual amounts of absorbed gases are considered NH_3 has the highest absorption values of the three gases. The small molecules are able to penetrate into the wood better than the larger molecules of SO_2 and Cl_2, even under absolute dry conditions. In principle the diffusion rate of gases in the presence of water is mainly influenced by the solubility of the gas in water, by possible reactions with cell wall components, and by the swelling behaviour of the cell walls.

Characterization of standard rods and bore cores from industrial halls

For characterizing analytically the state of structural timber exposed to aggressive atmospheres standard rods and bore cores were subjected to the following investigations:

1. pH Value of the cold-water extract
2. Extraction for 1 h with boiling NaOH (1 %) and water, respectively
3. GPC of the extracts
4. GC of chloroform solubles of water extracts
5. Element analysis (EDXA) in bore cores.

Though the pH of samples from 7 halls varied between 3.3 and 6.7 the pH value alone is no significant indicator with respect to wood condition.

The best indication for a weakening of structural timber is the amounts of solubles extractable with dilute alkali and water. While normally about 10 % and 2 %, respectively, of spruce wood are soluble, these values increased in rod samples taken from the halls after 1 year to some 25 and 11 %, respectively. In the outer regions of a bore core from a 70 years old beam the alkali extract reached even 70 %.
From the ratio of the extract amounts ($NaOH:H_2O$) it was found that low values generally indicate severe changes in the cell walls as considerable portions of polysaccharides and lignin become soluble even during water extraction.

The molecular weights of the soluble fragments differ in a wide range between a few hundreds and more than 20,000. The results can be used to argue for a possible degradation pattern but give no hint to the degree of degradation. The same is true for the GC determination of degradation products.

Though it was proved that the chemical cell wall components are affected by aggressive atmospheres the actual wood degradation is restricted to the marginal regions of structural timber. This was cleared up both by the analysis of different layers of bore cores and by means of EDXA.
Figure 2 demonstrates the sulfur distribution of the outermost annual rings of a bore core. There is a high take-up of sulfur in the earlywood regions. Evidently the surface is washed out (left side) and the sulfur concentration decreases to zero after four annual rings (right side).

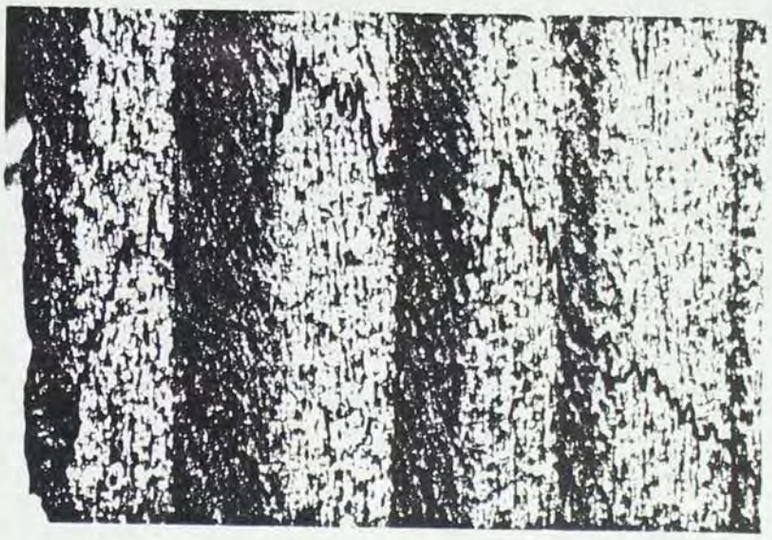

Figure 2. Sulfur distribution in the outermost region of a bore core from a hall in which thiosulfate is produced. EDXA technique.

CONCLUSIONS

Analytical methods are suitable to characterize wood samples with regard to their condition after exposure to aggressive atmospheres. The results give informations about the initiation and progress of degradation effects which are macroscopically invisible, but may cause a fatigue of wood construction elements.
On the other hand it was demonstrated that wood degradation is normally restricted to the outermost regions of structural timber. Additionally the cell tissue structure remains rather stable even if cell wall material is degraded.

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CHEMIMECHANICAL PULP FROM JACK PINE BY SULPHITE/QUINONE PULPING

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ABSTRACT

A satisfactory reinforcement jack pine chemimechanical pulp much stronger than spruce SCMP can be produced by sulphite/quinone pulping process. Within the cooking liquor pH range (6-10) studied, the addition of 0.1% SAQ on dry wood promoted delignification, thereby giving a stronger pulp with less refining energy demands. The efficacy of SAQ increased with increasing liquor pH. The pulp brightness was adversely affected by the use of quinone pulping aid only at the liquor pH of 8 or higher. Dispersed AQ outperformed powder AQ and was quite comparable to SAQ in catalytic action. Alum used for pitch deposition control can cause yellow coloration of the resultant pulp, and more work is needed to better understand the mechanism and to find effective ways for overcoming this problem.

KEYWORDS: Jack Pine, Sulphite, Quinones, Chemimechanical Pulp, pH, Refining Energy, Pulp Strength, Yellow Coloration, Alum.

INTRODUCTION

Jack pine (Pinus banksiana) is well underutilized in Canada as pulpwood for newsprint manufacture, due to it high extractive content and thick-walled tracheids (1). Alkaline sulphonation of chips followed by atmospheric refining produced ultra-high yield pulp with good removal of extractives but the pulp quality was markedly poorer than that from black spruce(2,3). Introduction of quinone pulping aid under alkaline sulphonation conditions accelerated delignification. The chemimechanical pulp produced from sulphite/quinone cook showed a significant improvement in interfibre bonding, and was considered sufficient as reinforcement pulp for newsprint manufacture(3). Nevertheless, the pulp brightness was low, and thus bleaching is required.

Traditionally, sulphite/quinone pulping has been conducted under certain alkalinity either using Na_2SO_3 alone, or in combination with NaOH, Na_2CO_3 or $NaHCO_3$ to produce pulp yield up to about 75%(4-7). Work done by Nomura(8), Fleming(9) and Tay(3) had extended the yield to 80-90% range. In our recent paper(10), it was firstly demonstrated that t quinone pulping aid can be employed in spruce SCMP process at nearly neutral liquor pH of 7. for improved pulp strength properties. At thi liquor pH, the pulp brightness was unaffected the pulping aid. Earlier, Nomura(11) had employed anthraquinone in calcium bisulphite l yield pulping and found that the presence of quinone during sulphonation resulted in higher yield, brighter and stronger pulp. Our furthe investigation revealed that the quinone pulpin aid was effective for preferential delignification of black spruce chips even in the chemimechanical pulp yield range and at sulphite liquor pH of 6 and 7, although its efficacy increased with increasing alkalinity(12).

In order to optimize cooking conditions capable of producing reinforcement quality of chemimechanical pulp from jack pine, the effects of cooking liquor pH ranging from 6 to 10 with and without SAQ (disodium salt of 1,4-dihydro 9,10-dihydroxy anthracene) were investigated. For comparison, dispersed and powder AQ (anthraquinone) were also included in this study. The amounts of residual quinone in the cooking liquors for some cooks were monitored quantitatively. Molecular size distributions of lignosulphonate from some typical cooks were compared. The pulps produced from various cooking liquor pH levels with and without SAQ addition were characterized for pulp strength, refining energy demand and bleachability with both hydrosulphite and hydrogen peroxide. The yellow coloration of jack pine chemimechanical pulps with aluminium ions and methods for reducing this undesirable coloration are also described in this paper.

EXPERIMENTAL

Jack pine trees of 68 years old grown in Thunder Bay area were used for this study. The preparation of pin chips, pilot plant cooking and refining equipments were described before(1). Unless otherwise specified, the pin chips were cooked in the batch digesters using 10 mins presteaming, 10% as Na_2SO_3, liquor to wood ratio of 6:1, 15 mins to and 45 mins at maximum temperature of 170°C and 0.1% quinone based on dry wood if required.

Two series of experiments were run. In the first series only control cooks were made to investigate the effect of cooking liquor pH alone. In the second series, these cooks were repeated and similar cooks with SAQ added were also performed. In both series, duplicate

batches were cooked for each condition to provide sufficient chips for refining. Throughout most cooks liquor samples were periodically withdrawn for TOC determination using an Astro Model 1850 TOC-TC Analyser.

For all cooking conditions, cooked chip yields were determined. A sample of cooked chips from each condition was defiberized in a Waring Blendor to provide an initial cooked brightness, but the Bauer refiner was used to refine the bulk of the material in multiple passes for other characterizations. Klason lignin determinations were made on the first pass pulps after extraction with dichloromethane.

Laboratory bleachings of the first pass pulps with hydrogen peroxide or hydrosulphite were carried out in accordance with our standard procedures(10). All the reflectance curves were obtained on Varian DMS-90 UV/Visble Spectrophotometer with Diffuse Reflectance Accessory. The pulping testings were done based on TAPPI standard methods.

SAQ as 20% active solids was acquired from Kawasaki Chemicals in Japan, whereas both powder AQ and dispersed AQ at 50% solids were obtained from CIL and were used as received without purification. The amounts of residual AQ in the cooking liquors were determined by HPLC using a Varian Model 5000 equipped with Variable Wavelength Detector UV50 and CDS-111 Data Processor. The procedure for extracting quinone compounds from the cooking liquor was the same as that described by Mortimer(13). A gradient elution with acetonitril/water using a reverse phase column MicroPak MCH-5 and 254 nm UV detection and external standard calibration curve. Both peak height and area count showed a straight linear relationship with AQ concentration between 1 to 75 ppm.

Molecular size distributions of lignin dissolved in the cooking liquors were characterized by gel filtration chromatography using the same HPLC with a MicroPak TSK Gel 2000 SW Column and 280 nm UV detection. The column has a molecular exclusion limit of 2×10^4. The samples were filtered through a 0.45u membrane and no further dilution was made prior to the injection.

RESULTS AND DISCUSSION

Liquor pH and Pulping Rate

The effect of cooking liquor pH between 6 to 10 on SAQ performance was investigated and the pertinent data are given in Table I. Cooks 4358 to 4365 were from the first series, while Cooks 4405 to 4420 were from the second series.

Table I

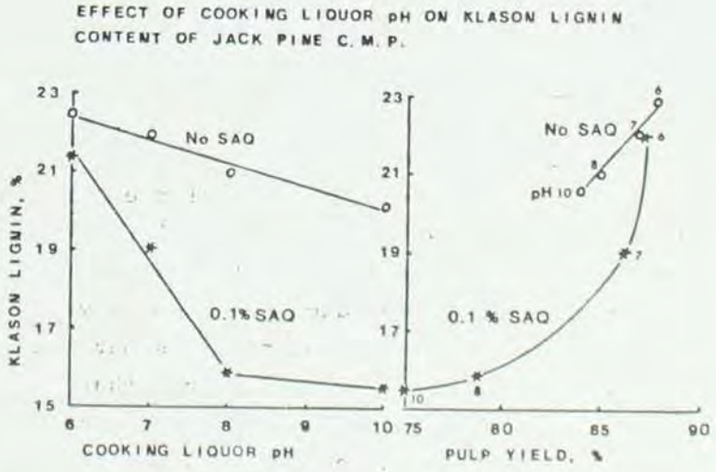
DATA FROM CHEMIMECHANICAL PULPING OF JACK PINE WITH LIQUORS OF VARIOUS pH

Liquor pH	Cook No.	SAQ Add'n.	TOC ppm	Yield %	Lignin Content in Pulp, % Klason	Acid-Soluble	Total
6	4364-65	No	11038	88.7	-	-	-
	4417-18	No	10968	86.8	22.89	5.04	27.93
	4419-20	Yes	11865	87.2	22.00	5.46	27.46
7	4362-63	No	13485	87.0	-	-	-
	4413-14	No	12642	87.1	22.0	5.35	27.35
	4415-16	Yes	14898	86.3	19.05	6.87	25.92
8	4360-61	No	14751	85.0	-	-	-
	4409-10	No	14169	84.5	20.99	5.62	26.61
	4411-12	Yes	18860	78.8	15.84	6.69	22.53
10	4358-59	No	14608	84.8	-	-	-
	4405-06	No	14676	83.1	20.16	6.43	26.59
	4407-08	Yes	21195	74.9	15.49	5.80	21.29

10% as Na_2SO_3, L/W=6:1 15' to and 45' at 170°C
Pin chips
Uncooked chips: 29.52% Klason and 0.04% acid-soluble lignin

It is obvious from this table that the cooked chip yield increased with decreasing liquor pH, but the higher yielding pulp also contained more lignin. This trend became much more pronounced for the cooks with SAQ added. While SAQ addition decreased the cooked chip yield, it did so by preferential delignification as demonstrated in Figure 1. The removal of extractives during chip sulphonation was noticeably poorer at liquor pH 6 than at pH 7 or higher, confirming our earlier finding(2).

Figure 1

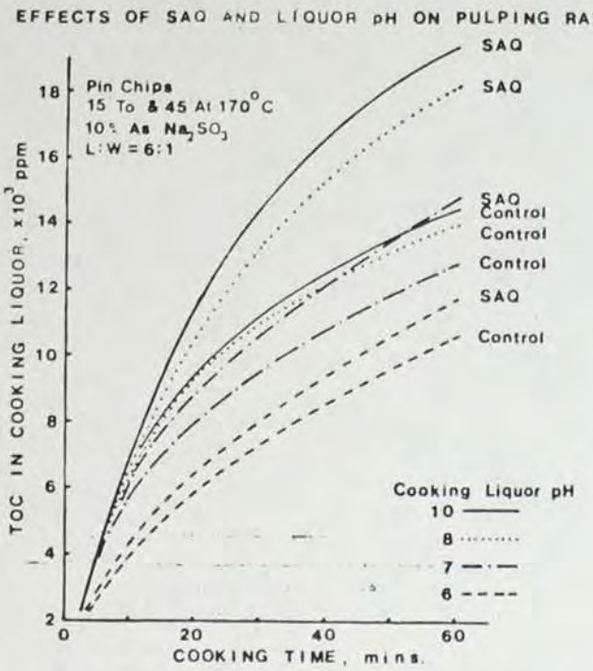


There was a strong relationship between TOC value of the final cooking liquor and cook yield, showing a correlation coefficient of -0.954 for all the cooks listed in Table 1. Knowing this, a plot of cooking TOC as a function of cooking time for the various cooks revealed how readily cooks can be accelerated by increasing liquor pH as depicted in Figure 2. At each pH level tested, the addition of SAQ was shown to further accelerate the cooks.

Liquor pH and Refining Energy Demand

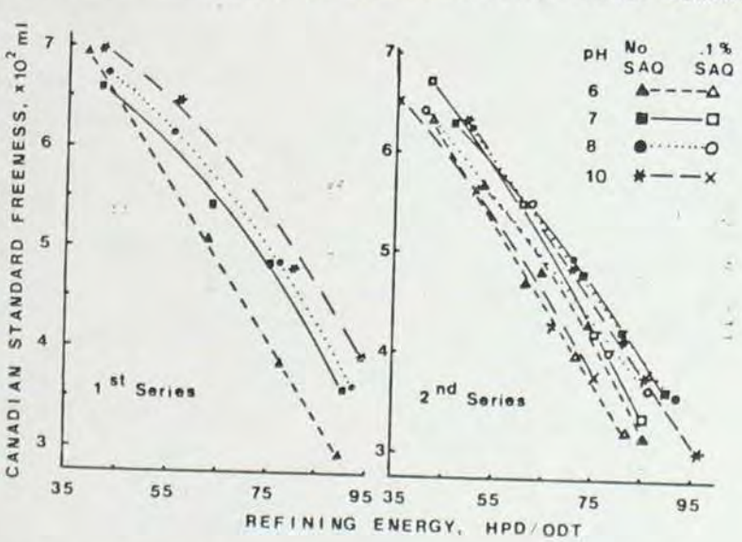
The effect of cooking liquor pH on refining energy required to achieve a given CSF was not

Figure 2



perfectly clear. While chips cooked at pH 6 definitely consumed the least energy during refining, the two series of cooks did not show the same energy consumption trend as liquor pH changed (Figure 3).

Figure 3

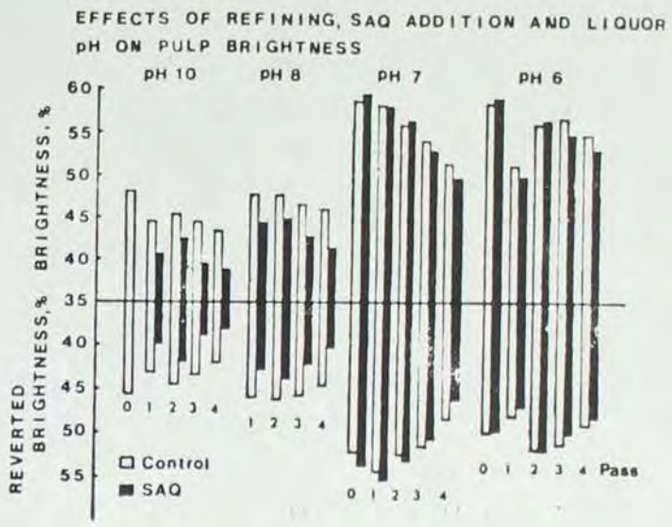


A trend might have been marked by the lack of strict control on horsepower applied at each pass. Nevertheless, the addition of SAQ reduced energy demands for all the cooks with the pH 10 cook having the most dramatic energy reduction over the control. Much more savings in refining energy can be realized by SAQ addition if comparison is made on the basis of interfibre bonding (see Table III).

Liquor pH and Pulp Brightness

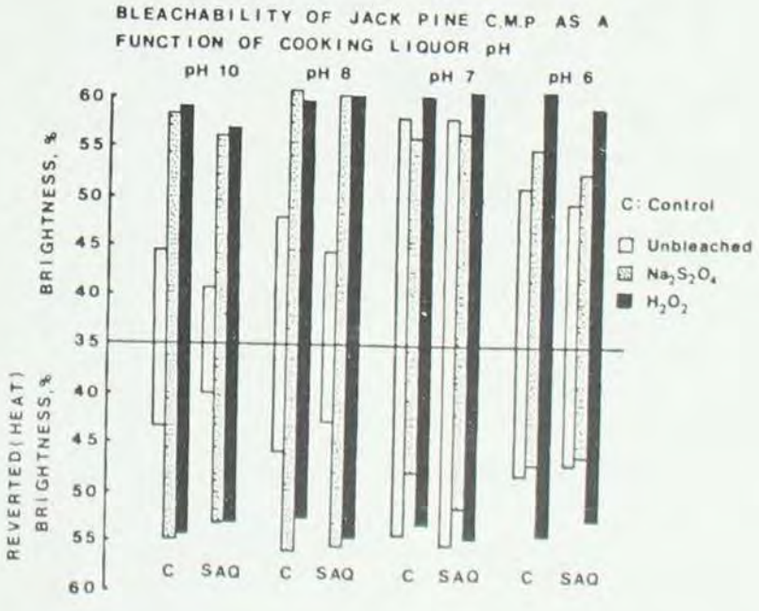
Cooks made at liquor pH 8 and higher lowered the pulp brightness as illustrated in Figure 4. The addition of SAQ at alkaline pH dropped further the brightness. However at pH 6 and 7, SAQ did not harm the brightness.

Figure 4



Given the same bleaching conditions (1% $Na_2S_2O_4$ at 65°C for 15 hrs at 3% consistency or 2.5% H_2O_2 and 2.5% total alkali at 50°C for 2 hrs at 12% consistency) most pulps approached the same bleached brightness, regardless of initial pulp brightness as depicted in Figure 5. Thus the lower initial brightness of the pulps from cooks at pH 8 and 10 is not of immediate concern. While the hydrosulphite was very effective in bleaching the pH 8 and 10 pulps, it did little for the brightness of pH 6 and 7 pulps. Peroxide was more effective here, but again, these pulps were very difficult to bleach. It is obvious that bleaching conditions need to be optimized for individual pulps.

Figure 5



Comparison of Various Quinone Products

In our earlier study, it was pointed out that SAQ was more effective than THAQ and powder AQ as based on TOC in cooking liquor and cooking time relationship(3). Wandelt(14), compared the

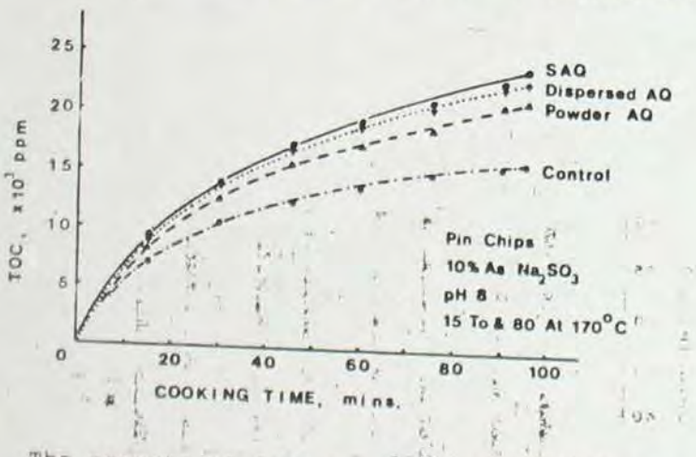
catalytic efficacy of DDA (1,4-dihydro 9,10-dihydroxy anthracene) and powder AQ in both soda and kraft pulping processes using a rotating digester with forced circulation of the liquor and another stationary digester without forced circulation of the liquor, and concluded that DDA was superior to AQ due to its better solubility and lower redox potential.

Catalytic actions of SAQ, dispersed AQ and powder AQ were compared using jack pine pin chips with 10% as Na_2SO_3 at pH 8 for a total cooking time of 95 mins including 15 mins to reach 170°C. The dosage rate of quinone compounds was kept at 0.1% on dry wood. The cooking liquors at certain intervals during the cooking cycle were withdrawn for TOC, residual quinone and gel filtration analyses. The cooked chips from these cooks were not refined.

The TOC values as a function of cooking time are depicted in Figure 6. Apparently the dispersed AQ outperformed powder AQ and became quite comparable to SAQ. All the three pulping aids indeed accelerated the pulping rate markedly. At the cooking liquor pH 8, SAQ was present as slightly yellow fine colloids which were identified as DDA. DDA was readily converted to AQ before reaching the maximum cooking temperature as revealed by HPLC and UV spectrophotometric analyses.

Figure 6

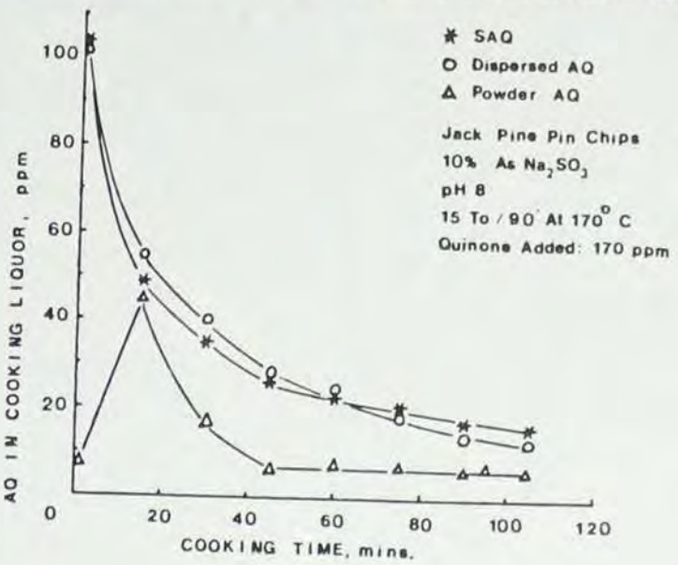
EFFECT OF VARIOUS QUINONE COMPOUNDS ON PULPING RATE



The amounts of free quinone compound present as AQ in the cooking liquors were monitored by HPLC and the results are shown in Figure 7. Note that for the cook with powder AQ added, only 7 ppm free AQ was detected at the first 2 mins, compared with 102-104 ppm for the other two, suggesting that powder AQ was not readily dispersed into the cooking liquor, and this undoubtedly contributed to its relatively poor performance. At total cooking time of 1 hr, the residual amounts of AQ were 14.7%, 14.1% and 4.7% of the initial quinone added for SAQ, dispersed AQ and powder AQ cooks respectively.

Figure 7

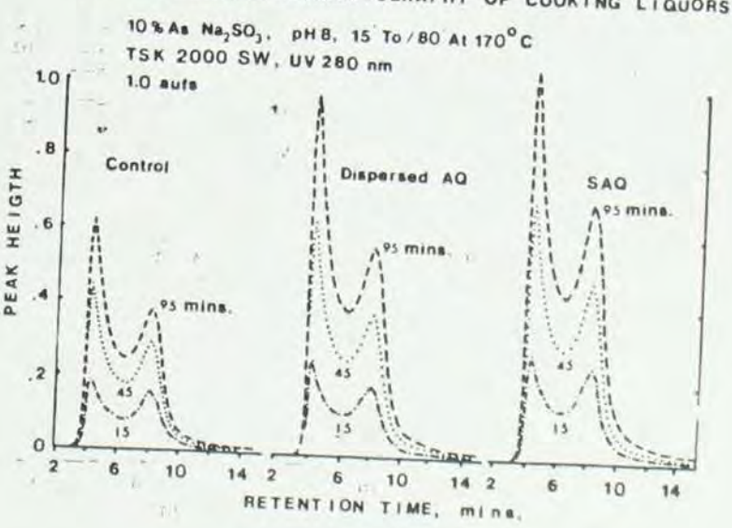
CONCENTRATION OF QUINONE COMPUND IN COOKING LIQUOR



Lignosulphonate present in the cooking liquors for the SAQ, dispersed AQ and control cooks were characterized by gel filtration chromatography. The results as shown in Figure 8 revealed that at a given cooking time, the

Figure 8

GEL FILTRATION CHROMATOGRAPHY OF COOKING LIQUORS



amounts of lignin dissolved in the cooking liquors were much less for the control than for the other two cooks. In all cases, the dissolved lignin showed two dominant peaks. It seemed likely that the presence of quinone pulping aid did little, if any, to reduce the molecular size of lignosulphonate. Obviously, more work is needed to study the mechanism of rapid delignification brought about by anthraquinone under nearly neutral pH and in the chemimechanical pulp yield range.

Cooking Liquor pH and Pulp Strength

All the cooked chips listed in Table 1 were atmospherically refined and the pulps at various

CSF levels were tested for strength properties. Figures 9 and 10 clearly showed that pulp bonding strength and sheet density were affected by the cooking liquor pH. With lower liquor pH, pulp strength was reduced, hence energy savings that were noted during refining may not be savings at all, because the pulp requires more refining to lower freeneses to attain equivalent strengths. While strength and density increased as liquor pH was raised from 6 to 7 to 8, additional increases in liquor pH to about 10 gave no further strength improvement, unless SAQ

Figure 9

EFFECT OF COOKING LIQUOR pH ON BONDING STRENGTH OF JACK PINE C. M. P.

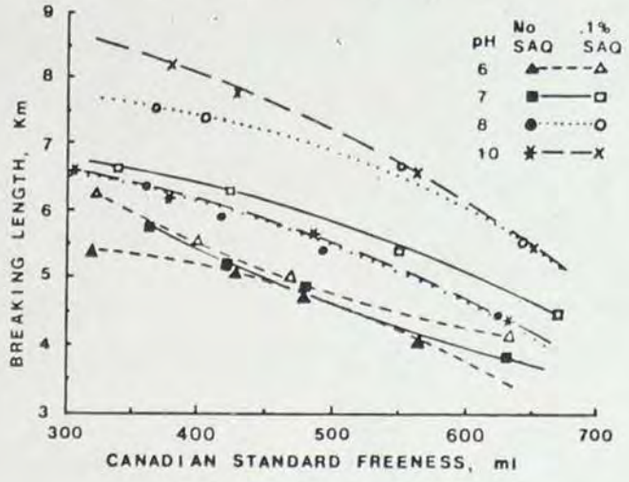
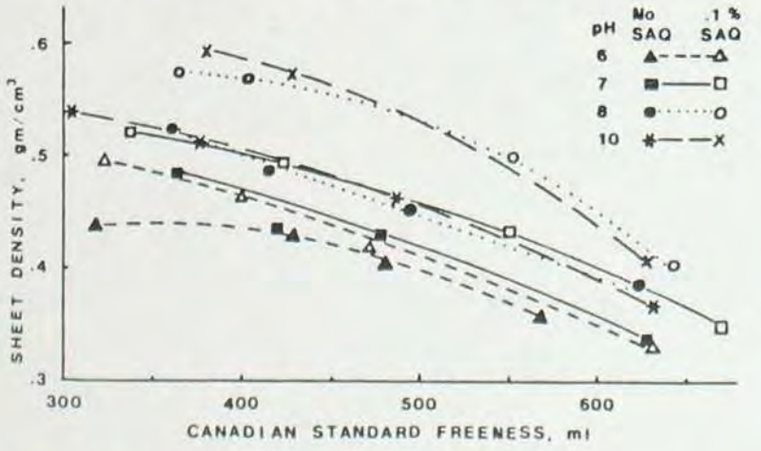


Figure 10

SHEET DENSITY OF JACK PINE C. M. P. AS A FUNCTION OF C.S.F.



was added to the cook. Note that tear strength seemed unaffected by the liquor pH or SAQ addition, and was highly dependent on CSF of the pulp.

Table II and III summarize more clearly the effects of liquor pH and SAQ addition on pulp strength and energy consumption. Based on 400 CSF, the SAQ addition improved burst index by 10-45% and breaking length by 6-29% over the control. The strength gains increased with increasing liquor pH. The pulps from SAQ cooks can have much higher CSF than for the control at a given burst index, and thus a drastic reduction in refining energy demand and higher tear strength are attainable.

Table II

Comparison of Pulps at Constant Freeness (400 ml CSF)

	Power (HPD/ODT)			Burst Index			B.L. (km)			Density		
pH	Control	SAQ	Δ	Control	SAQ	Δ	Control	SAQ	Δ	Control	SAQ	Δ
6	76	71	-6%	3.0	3.3	+10%	5.2	5.5	+6%	.436	.464	+6%
7	84	78	-7%	3.1	3.9	+26%	5.4	6.4	+18%	.464	.504	+9%
8	85	82	-4%	3.7	5.2	+40%	6.0	7.4	+23%	.500	.564	+13%
10	83	72	-13%	3.8	5.5	+45%	6.2	8.0	+29%	.504	.580	+15%

Table III

Comparison of Pulps at Constant Burst Strength (3.5 Mn/kg)

	Control (2nd series)					SAQ				
pH	CSF	B.L.	Tear	Density	Power	CSF	B.L.	Tear	Density	Power
6	<300	<5.5	<6.7	<.460	>87	350	5.9	7.2	.480	78
7	315	6.0	6.9	.494	95	492	5.9	8.5	.460	67
8	450	5.7	8.1	.472	78	625	5.9	9.7	.430	45
10	453	5.9	8.1	.480	75	650	5.5	9.9	.370	36

Yellow Coloration of CMP with Alum

Acid sulphite pulp from jack pine is prone to yellow coloration with aluminIm ions. The formation of galangin from pinobanksin which is present in jack pine heartwood was considered to be the mechanism as illustrated in Figure 11 proposed by Chapman(15). A series of chemi-mechanical pulps from earlier cooks at various liquor pH levels after bleaching with

Figure 11

MECHANISM OF YELLOW COLORATION WITH ALUM

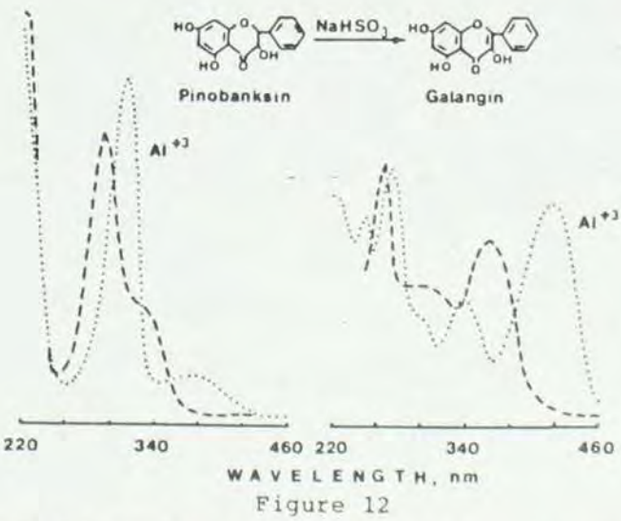
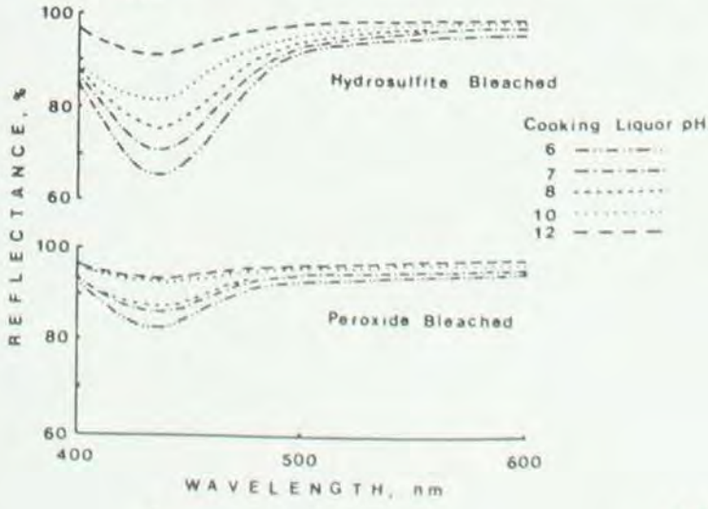


Figure 12

DIFFERENTIAL REFLECTANCE CURVES OF PULPS TREATED WITH ALUM



hydrosulphite or hydrogen peroxide were subjected to alum treatment, and the differential reflectance curves for these pulps are shown in Figure 12. Obviously all these pulps gave similar yellow coloration with alum as bisulphite pulp from the same wood species. However, the extent of the yellow colour formed decreased with increasing alkalinity of the cooking liquor. Alkaline hydrogen peroxide bleaching was of great value for reducing the formation of yellow colour. Pretreatment of the pulp with stannous compounds was also found to be useful for avoiding this undesired coloration(16).

It remains to be learned as to whether or not the formation of galangin would take place at the much higher cooking liquor pH than that for bisulphite. TCMP from jack pine with sulphite treatment was found to give no yellow coloration with alum. Our earlier study(2) suggested that three or more compounds extracted from the cooking liquors exhibited yellowing in thin layer chromatography after spraying with alum. Extraction of pulps with organic solvents did reduce but not eliminate the yellow coloration. These suggest that the formation of galangin during sulphonation may not be the sole mechanism for the yellow coloration. More work is underway to clarify the mechanism, and thus to devise a more effective way for its prevention.

Chemimechanical Pulps from Jack Pine and Black Spruce

Physical strength properties of chemimechanical pulps from jack pine (pin chips) by sulphite/SAQ cooking were compared with those from black spruce (PSF chips) in Figure 13 as a function of cooking liquor pH, and in Figure 14 as a function of cooked chip yield. The data for chemimechanical pulps produced from black spruce were taken from our earlier work(12), using the same cooking conditions (10% as Na_2SO_3, 15 mins to and 45 mins at 170°C).

The beneficial effect of SAQ on interfibre bonding was also realized in black spruce in all liquor pH ranges studied. In Figure 13 it is demonstrated that the jack pine pulps from pH 6 and 7 cooks with SAQ were noticeably weaker than spruce pulps produced without the pulping aid, but the former became stronger than the latter from pH 8 and 10 cooks and were closer to that of black spruce with SAQ addition.

When the comparison was made on the basis of cook yield as depicted in Figure 14, it is very obvious that the cooking liquor pH played a very profound role in affecting both yield and pulp

Figure 13

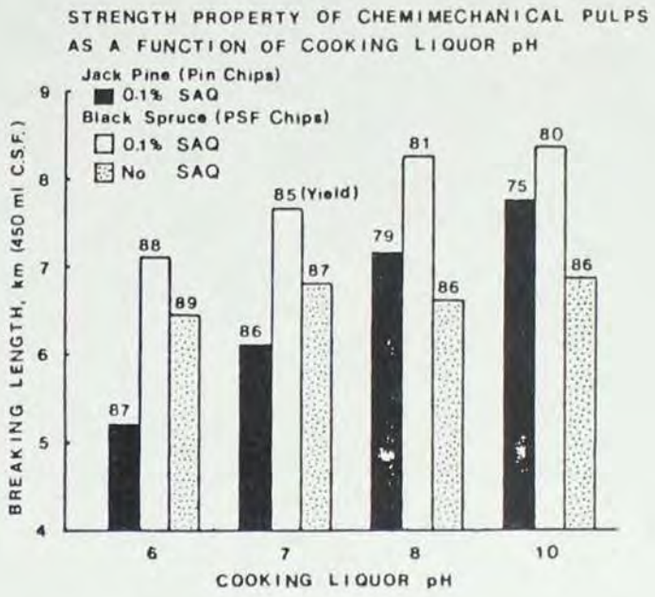
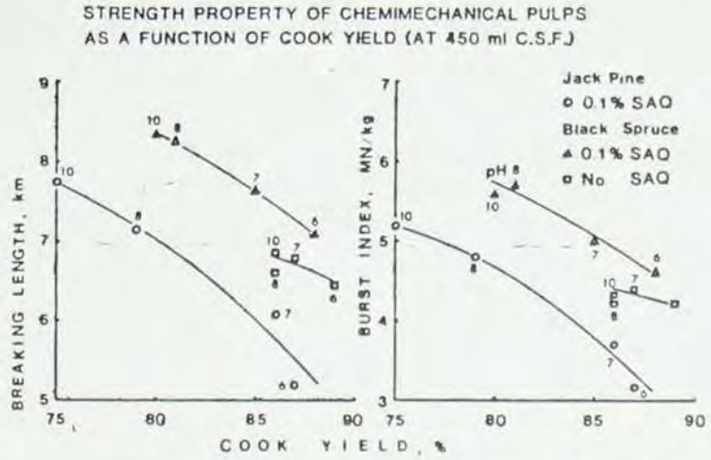


Figure 14



strength characteristics, and the significance was amplified by the addition of quinone pulping aid. Note that for all cooks with SAQ added, chemimechanical pulps from jack pine were always inferior in interfibre bonding to that from black spruce at a given pulp yield. However, the jack pine pulp at a cook yield of about 83% became almost equal to that from spruce cooked to 86% yield without SAQ.

CONCLUSIONS

1. Jack pine pin chips were cooked at 170°C with 10% as Na_2SO_3 for 50 mins including 15 mins to reach the maximum temperature under various liquor pH of 6, 7, 8 and 10. The cook yield decreased from 88% to 84% with increasing liquor pH for the control, and 87% to 75% for the cooks with 0.1% SAQ addition on dry wood.

2. The addition of SAQ accelerated delignification within the pH range studied, but its efficacy increased with increasing liquor alkalinity.

3. Cooking liquor pH was an important parameter affecting yield, quinone performance, pulp brightness, refining energy demand and pulp strength.

4. Pulps from pH 6 cooks were noticeably higher in yield and brightness, but weaker in interfibre bonding regardless of SAQ addition or not.

5. The addition of SAQ improved burst index by 10 to 45% and breaking length by 6 to 29% over the controls, and the improvement increased with increasing liquor alkalinity.

6. Dispersed AQ outperformed powder AQ and was comparable to SAQ in catalytic effect.

7. The quinone consumption during cooking was very rapid. At the 60 mins cooking time (including 15 mins to temperature), only 14.7%, 13.5% and 4.7% of the total quinones added were identified as free AQ for SAQ, dispersed AQ and powder AQ cooks respectively.

8. Molecular size distribution of lignin dissolved in the cooking liquors from the cooks with pulping aids showed no discernible difference from the control.

9. Chemimechanical pulps from jack pine react with alum to form yellow colour, and the mechanism remains to be learned.

10. Jack pine chemimechanical pulp at cook yield of about 83% by sulphite/quinone pulping is comparable to that of spruce at 86% yield from the same sulphite cook without the pulping aid.

11. Sulphite/quinone pulping at pH 7 to 8 is considered a useful process for making a reinforcing quality chemimechanical pulp from jack pine for newsprint manufacture.

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FERMENTATION OF SPENT SULPHITE LIQUOR TO BUTANOL AND ETHANOL

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INTRODUCTION

In the Ontaric Paper Company mill at Thorold, Ontario, spent sulphite liquor (SL) is processed to make alcohol and vanillin (1). Analysis of a recent sample of this liquor is shown in Table 1.

Table 1. Composition of Spent Sulphite Liquor

	g/ℓ
lignosulphonic acids as lignin	67.69
* sugars: mannose	15.61
glucose	5.20
galactose	7.15
xylose	7.80
arabinose	3.25

*In addition to these monomeric sugars, there are oligomeric carbohydrates, which may amount to 30% of total carbohydrate, formic acid, acetic acid, furfural and acid-soluble lignin fragments.

Following a partial removal of free SO_2 by heating, the liquor is brought to pH 4.5 with lime, and fermented to ethanol. The yeast used is Saccharomyces cerevisiae, bakers' yeast. The residue from the alcohol distillation contains lignin and unfermented sugars, and is then processed further, by adding a catalyst and heating under pressure with air to oxidize the lignin to vanillin.

Since the present fermentation to ethanol utilizes only the hexoses, the pentose sugars, which amount to 28% of the monomeric sugars shown in Table 1 remain, and are present in the vanillin reactor, where they are oxidized to organic acids and add to the cost of vanillin production. For this reason a fermentation process for utilization of both hexoses and pentoses is desirable.

In one approach to this problem, we have fermentated SL to butanol by Clostridium acetobutylicum and by Cl. butyricum strains which utilize both hexoses and pentoses. In a previous paper (2), we reported the fermentation of a 5-sugar solution simulating the sugar composition of SL, and identified conditions for producing butanol-acetone-ethanol solvents in yields above 0.36 g solvent/g sugar utilized, and at the same time over 96% sugar utilization. While these substrates did not contain lignin or the other humic substances present in spent sulphite liquor, our success encouraged us to pursue this approach.

In another approach, we fermented SL with the pentose-fermenting, ethanol-producing yeast Candida shehatae (3). With this yeast, we had obtained good xylose utilization at acceptable rates of ethanol production under conditions which appeared to lend themselves to industrial operation, using pure sugars. We now report the application of this fermentation to SL.

Pretreatment of Spent Sulphite Liquor

Since the objective of this study is to effect more complete removal of the sugars from the lignin, while the lignin must remain for conversion to vanillin, we are constrained from removing the lignin prior to fermentation. We report our results in removing the volatile inhibitors.

Samples of SL from Ontario Paper Company were fed to a packed tower, with a countercurrent steam flow. In this way, the pH was raised from 2.6 to 4.5 or 4.7. The concentration of toxic substances, namely formic acid, acetic acid, oxalic acid and furfural, in the liquor was determined by gas chromatography. The total concentration of these was reduced to less than 6% of their original concentration. For butanol fermentation, the SL used was steam stripped to pH 4.7, and for ethanol fermentation, to pH 4.5

Adaptation for Butanol Fermentation

Although pure sugar butanol fermentation has shown excellent results (1) and the concentration of toxic substances had been minimized by steam stripping, SL was still difficult to ferment in the presence of its lignosulphonate and other phenolic substances. Adaptation was carried out following heat shocking and 10 to 16 h incubation in corn steep liquor medium (CL), transferring to

40% SL, 60% CL for 12 to 18 h, then to 70% SL, 30% CL for 16 to 24 h, the resulting cultures being used as inocula. No adaptation to steam stripped SL was required for fermentation to ethanol.

RESULTS AND DISCUSSION

1. Butanol Fermentation

This is the first report of butanol fermentation of undiluted SL containing lignosulphonate. Sugar removal in these fermentations was incomplete, 73.3 to 84.4% of original hexoses plus pentoses being fermented by these bacteria. Total solvent production, butanol plus acetone, was 0.18 to 0.25 g solvent/g initial sugar. This is substantially less than obtained with a pure sugar mixture simulating SL, 0.36 g solvent/g sugar. Growth was vigorous. Various additions to the medium were tried, but none of these improved sugar consumption or solvent yield. Thus only a partial success can be claimed.

2. Ethanol Fermentation

The results of these fermentations showed that C. shehatae is more effective at sugar removal from SL than is S. cerevisiae, the improvement in sugar removal being 58.0%; and also in production of alcohol, the improvement being 32.0%. Sugar fermented by C. shehatae was 88%, while S. cerevisiae fermented only 56%, while ethanol production was 0.37 g/g sugar with C. shehatae and only 0.28 g/g sugar with S. cerevisiae.

CONCLUSIONS

1. Spent sulphite liquor contains many fermentation inhibitors. Most of these are removed by steam stripping, particularly when this raises the pH to 4.3 or higher.

2. Two butanol-producing microorganisms studied here are adaptable to growth on steam-stripped spent sulphite liquor. However, while growth is vigorous, solvent production was well below that experienced with pure sugars (0.25 g solvents/g initial sugar compared to 0.36 with the pure sugar mixture) and sugar removed was less (73.3% compared to 96.6%). This is, however, better sugar removal than experienced with S. cerevisiae (55.7%). If butanol becomes a salable product, for example as cosolvent in gasoline-methanol blends, butanol fermentation of spent sulphite liquor is likely technically feasible.

3. The production of ethanol from spent sulphite liquor by C. shehatae is better than by S. cerevisiae by a significant margin, 32%, and sugar removal is more complete by about 58%. Thus it has the potential for being substituted for S. cerevisiae in industrial ethanol production where pentose sugar concentrations are significant. It can be grown on spent sulphite liquor without adaptation.

ACKNOWLEDGEMENTS

This work was supported in part by the Natural Sciences and Engineering Research Council of Canada.

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3. DU PREEZ, J.C., VAN DER WALT, J.P. Fermentation of d-xylose to ethanol by a strain of Candida shehatae. Biotech. Letters 5: 357-362 (1983).

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FLAVOLOGLYCANS - MAJOR CONSTITUENTS OF FORESTRY MATERIALS?

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ABSTRACT

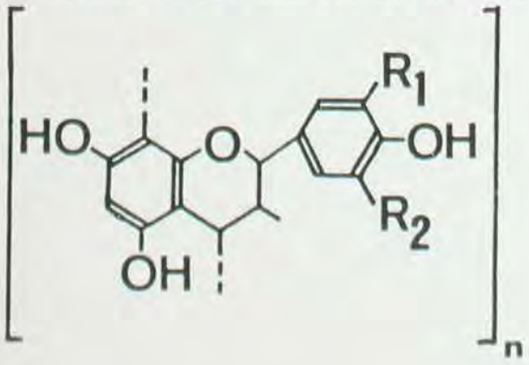
A novel type of natural water-soluble copolymer has been obtained in about 20% yield from mangrove leaves. Evidence has been obtained that the polymers contain covalently bonded flavolan and high molecular weight glycan components, probably in a range of proportions and they are designated as flavologlycans. Fractionation of the polymers has been carried out by lead acetate complexing and by sorption on polyamide and Sepharose. The previous literature on chemical constituents of leaves of other trees and of barks provides evidence that flavologlycans are very probably widespread and abundant in forestry materials.

KEYWORDS: Flavologlycans, Leaves, Bark

INTRODUCTION

The class of natural polymers referred to variously as condensed tannins and flavotannins, or more recently as proanthocyanidins (1,2), or flavolans (3,4) have the general formula 1 with n varying from 2 to approximately 20 (1,2). The polymers are widely distributed, but occur most abundantly in the leaves, fruit, heartwood and bark of woody plants, from which they are normally extracted, in yields of up to approximately 3%, by aqueous methanol, ethanol or acetone (5). However, these conditions of extraction are such that, if any flavolans were covalently linked to polysaccharidic materials, they would remain in the insoluble residue. This possibility was first investigated with mangrove leaves which are known to contain large amounts of tannins.

1



Extraction of fresh mangrove leaves (Rhizophora stylosa) with water or with aqueous ethylenediaminetetra-acetic acid (EDTA), after preliminary extraction of pigments and flavonoid materials with hexane and hot acetone, yields about 20% of polymeric material containing approximately equal amounts of flavolan and galacturonoglycan. The fractionation of this material and the composition and properties of the subfractions have been studied. The results provide reasonable evidence that the major portion of this extract consists of covalently bonded copolymers of the two species (viz. flavolan and glycan).

The only previous report of a flavonoid-polysaccharide compound appears to be by Markham (6) who isolated about 2% yield of what appears to be a related material by water extraction of liverwort. In this case, the molecular weight was about 3200 per flavonoid unit and the polysaccharide was bonded glycosidically via galacturonic acid to positions 7- and 4- (1) of 8-methoxyluteolin. Our polymer appears to be present in the mangrove leaves in much greater amount and the gel chromatography and general viscosity behavior suggest that the glycan component is of much higher molecular weight than the liverwort product. Galacturonic acid, arabinose, galactose, rhamnose, glucose and mannose are the most abundant carbohydrate components. It is possible that the flavologlycans are of wide occurrence in plants, often in high yield.

EVIDENCES FOR INTERPOLYMER LINKAGES

Our evidences for flavolan-glycan linkages may be summarized as follows:

1. Both flavonoid and carbohydrate constituents are retained during dialysis.
2. Both flavonoid and carbohydrate constituents are sorbed by nylon, the major component is completely resistant to prolonged elution with water and both constituents are eluted with formamide.
3. Both flavonoid and carbohydrate constituents are sorbed by Sepharose. The major component is completely resistant to elution with water, but both constituents are eluted with increasing concentrations of urea in water.
4. Treatment of the flavologlycan with chlorite and subsequent dialysis removes the aromatic components and leaves a glycan in the anticipated yield.
5. Treatment with acid removes the glycan and leaves flavolans (now partly soluble in ethyl acetate) in the anticipated yield.
6. Flavolan (non-dialysable) polymer would not

be expected to be readily soluble in water, unlike the isolated flavologlycan, whereas the isolated flavologlycan was totally insoluble in all of the solvents normally used to extract flavolans, such as aqueous methanol or aqueous acetone (5).

FLAVOLOGLYCANS IN BARK?

Bark remains a high-volume, low-value "waste" product of the forest products industry, especially from softwoods. Accordingly, the chemical constituents of barks have been extensively studied with at least 200 research papers and patents published since 1967. The bulk of this research has concentrated on either polysaccharides or polyphenols which are the major constituents of bark by weight and no previous workers in this field appear to have found evidence for covalent linkage of glycans to polymeric aromatic materials. In several instances, however, a reassessment of experimental results from earlier papers reveals that flavologlycans are almost certainly present in several softwood barks. Thus, Pulkkinen and Vaisanen (7) found in hot water extracts of Norway Spruce bark (yield 11%) that polyphenols and carbohydrates both persisted through several molecular weight cuts when fractionated by ultrafiltration. The results would be compatible with presence of flavologlycan and pectin. Pulkkinen and Peltonen (8) also studied hot water extracts of Scots Pine bark (yield 16%) by gel chromatography and observed behavior which was probably similar to our observations with flavologlycans, although they did not monitor columns for carbohydrate. Bailey and Pickmere (9) have extracted "hemicelluloses" from several barks without delignification and noted that all such "polysaccharide" fractions yielded only 25-35% carbohydrate on hydrolysis. It is very probable that their fractions all contained major aromatic constituents and that they include flavologlycans. Laver and coworkers (10) have found protein, tannin, starch and other polysaccharides in hot water extracts of the inner bark of Douglas Fir and these observations would be compatible with presence of flavologlycans. The polyflavonoids extracted by Hemingway and McGraw (11) from southern pine barks probably contain flavologlycans and these copolymers are probably largely responsible for the high viscosity of many bark extracts which causes major problems in the use of such extracts as adhesives.

There are many such pointers to presence of flavologlycans in barks as well as leaves of trees and we have begun a major research effort at the Wood Chemistry Laboratory to seek such compounds. Our work will concentrate initially on softwood barks of commercial importance.

ACKNOWLEDGEMENTS

The discovery of the presence and chemical nature of flavologlycans in mangrove leaves was made at James Cook University of North Queensland in collaboration with M.J. Neilson and T.J. Painter as part of a study of diagenesis of the leaves. The detail of the mangrove studies will be published in collaboration with these authors.

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THE REACTIONS OF ALKALINE HYDROGEN PEROXIDE WITH 1,2-DIARYL-1,3-PROPANEDIOLS

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ABSTRACT

Two 1,2-diaryl-1,3-propanediols were reacted with stabilized and unstabilized alkaline hydrogen peroxide and molecular oxygen under simulated technical bleaching conditions. Product identification revealed the occurrence of reactions in which the n-propyl side chain was fragmented at various locations generating chromophoric and leucochromophoric systems potentially capable of influencing brightness in mechanical pulp bleaching systems.

KEY WORDS: 1,2-Diaryl-1,3-Propanediols, Alkaline Hydrogen Peroxide, Oxygen

INTRODUCTION

In a continuation of previous studies (1-4) of the reactions of lignin model compounds with alkaline hydrogen peroxide, two propanediols, 1-(3-ethoxy-4-hydroxyphenyl)-2-(4-hydroxy-3-methoxyphenyl)-1,3-propanediol (I) and 1,2-bis (4-hydroxy-3-methoxyphenyl)-1,3-propanediol (II) were reacted with stabilized (Na_5DTPA) and unstabilized peroxide and molecular oxygen under conditions simulating those used in technical bleaching. Using a combination of GC, GC/MS and UV techniques, the principal products in the reaction mixtures were identified and their yields quantified. Prior to examining the effect of alkaline peroxide solutions and oxygen on the β-1 diols, the effect of alkali alone was assessed.

The Effect of Dilute Alkali on 1,2-Diaryl-1,3-Propanediols

In the absence or near absence of dissolved oxygen (i.e. when the treatment was performed *in vacuo*), the major effect of the alkali was to convert the β-1 diols to stilbenes IV and V *via* a quinonemethide (III) from β-1 diol I as shown in Figure 1. These two stilbenes, together with the starting compound, accounted for ~95% of the original material and only trace amounts of other products were detected. When the alkaline treatment was performed in the presence of air or even when the system was sparged with nitrogen, neither stilbene IV or V was detected thereby suggesting that these intermediates are extremely sensitive to autoxidation.

Reactions of Stabilized Hydrogen Peroxide with β-1 Diol (I)

In this section and in the following sections, discussion is restricted to results pertaining to β-1 diol I for the sake of brevity; the results of the treatment of β-1 diol II with peroxide are similar and are reported in detail elsewhere (5).

Under the imposed reaction conditions, ~30% of β-1 diol I was consumed, presumably through conversion to and subsequent oxidation of stilbenes IV and V by peroxide and a small amount (1-2%) of oxygen arising from peroxide decomposition. Only trace amounts of the intermediate stilbenes were detected and the main products consisted of ethyl vanillin (VI), guaiacylglycol (VII), ethanol and methanol (Table 1). The low product yields suggest that β-1 diol I is less reactive toward peroxide than its initial oxidation products.

Based on the types of products identified, it appears that the main reactions of the β-1 diol with stabilized hydrogen peroxide (i.e. where the presence of O_2 is minimized) involve a nucleophilic attack of OOH^- on quinonemethide III and the oxidation of stilbene IV. In the former reaction ethoxyhydroquinone (VIII) and guaiacylglycol are postulated as arising *via* the sequence shown in Figure 1. The transformation giving rise to guaiacylglycol is visualized as the alkaline analog of a Baeyer-Villiger reaction (6).

The oxidation of stilbene IV and V by alkaline peroxide in the absence or near absence of oxygen is rationalized as occurring by a nucleophilic displacement on oxygen in the *undissociated* hydrogen peroxide by the stilbene. This concept is supported by the results of experiments in which various stilbenes and isoeugenol were reacted with peroxide at alkalinities corresponding to the pH range 9-13. In such cases the residual stilbene, isoeugenol and peroxide contents were lower at the lower end of the pH range where the fraction of undissociated hydrogen peroxide was higher (Table 2).

Reaction of Non-Stabilized Hydrogen Peroxide with β-1 Diol I (Fixed pH)

As compared to the situation where a peroxide stabilizer (Na_5DTPA) was employed and care was taken to minimize the air (oxygen) content in the reaction mixture, omission of the stabilization system resulted in a substantially higher consumption of β-1 diol I and in the formation of greater amounts of the oxidation products ethyl vanillin (VI), ω-hydroxyacetoguaiacone (IX) and ethoxyhydroquinone (VII) (Table 1). The yields of methanol and ethanol were also substantially increased. These differences are attributed to the more extensive decomposition of peroxide giving rise to oxidants such as O_2, $OH\cdot$ and $O_2^{\cdot-}$. Thus, the electrophilic attack of oxygen on the olefinic group of stilbenes IV and V (i.e. oxygenation) and the autoxidation of the β-1 diol I resulted in the formation of peroxide-labile stuctures in addition to those generated by the initial oxidation of quinonemethide III and the stilbenes by OOH^- and H_2O_2, respectively.

Reaction of β-1 Diol I with Molecular Oxygen

The β-1 diol was reacted with molecular oxygen in order to identify with greater certainty those reactions and products attributable to this oxidant when it arises from the decomposition of hydrogen peroxide. The products and product yields corresponding to this treatment are listed in Table 1 and indicate the major contribution of ethyl vanillin and the dominance of the methanol content over ethanol content as noteworthy features. Several possible routes can be envisaged to account for the above findings and it is likely that the overall result stems from a composite of several competing processes in which extensive breakdown of the B ring (methanol formation) and splitting of the α, β-bond (ethyl vanillin formation) predominate.

SUMMARY AND CONCLUSIONS

The results of the study reveal that unetherified 1,2-diaryl-1,3-propanediols are oxidized by alkaline hydrogen peroxide and its decomposition product, oxygen, in a variety of ways. The initial reactions result in the rupture of the side chain of the β-1 diol at various sites thereby forming monomeric phenols having side chains ranging from 0 to 3 carbon atoms in size.

One important pathway in the overall sequence consists of the initial alkali-mediated conversion of the diol to a stilbene derivative which then may react with oxygen and/or undissociated hydrogen peroxide. The latter reaction is important since technical peroxide bleaching is conventionally performed in a pH range where a considerable fraction of the peroxide is undissociated.

Several of the initially-formed products in the reaction of the β-1 diol with peroxide are either colored or capable of being converted to chromophores through various combinations of autoxidation, oxygenation and other reactions (e.g., Dakin and "Dakin-like"). As applied to the peroxide bleaching of mechanical pulps, such reactions could have an adverse effect on brightness response. However, the potential for β-1 dilignols in lignin to have such an effect on brightness would require that at least one of the rings in the dilignol be phenolic.

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Functional group	Kraft lignin	Oxygen lignin	Note
Aromatic rings	1.0	0.56	per phenylpropane unit
COOH	0.13[1]	0.50[1]	-"-
Ketone	not found	0.02	-"-
Aldehyde	0.03	0.05	-"-
Double bond	0.18	0.29	-"-
Aliph. CH > 57 ppm	0.44	0.61	-"-
Aliph. CH_2 > 57 ppm	0.34	0.45	-"-
Aliph. CH < 56 ppm	0.39	0.25	-"-
Aliph. CH_2 < 56 ppm	0.63	0.55	-"-
Aliph. CH_3 < 56 ppm	0.18	0.19	-"-
OCH_3	0.79[2]	0.85[3]	per aromatic ring
Phenolic OH	0.62[2]	0.58[4]	-"-
Quart. aromatic C	3.42	3.90	-"-

1) Conductometric titration acc. to Ref. 14
2) Value from Ref. 11
3) Assumed value
4) Aminolysis

Table 1. Analytical data calculated from ^{13}C-NMR for kraft lignin and for a lignin obtained after oxygen bleaching to kappa No. 14.8

it can be seen that oxygen bleaching leads to a substantial reduction in the number of aromatic rings. Furthermore, the aromatic rings which remain after bleaching are to a large extent substituted in the 5 and/or the 6 position(s) thus supporting the results obtained from the oxidative degradation analysis. Another important feature concerning the structure of these lignins is the high number of aliphatic carbon atoms with shift values below that of the methoxyl group. Such carbon atoms are substituted only with hydrogens and carbons and thus constitute functional groups which are difficult to modify by chemical reactions.

CONCLUSIONS

In the oxygen bleaching of kraft pulps, a partial lignin dissolution is achieved by the introduction of a large amount of carboxyl groups mainly through oxidative cleavage of aromatic rings. In addition, new phenolic hydroxyl groups seem to be formed, indicating that lignin fragmentation reactions also take place during bleaching. These reactions, facilitating lignin dissolution, are counterbalanced by a certain selectivity in the lignin oxidation and, for example, biphenyl structures are to a large extent left unreacted. The fact that (softwood) lignin seems to contain fairly large amounts of alkyl groups in the side chains may further contribute to a poor solubility of the lignin fragments in aqueous solution.

ACKNOWLEDGEMENTS

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Table 1. Products from the Reaction of β-1 Diol I with Hydrogen Peroxide and Oxygen

Compound	Yield, Mole % H_2O_2 Stabilized[a]	H_2O_2 Unstabilized[b]	Oxygen[c]
Ethoxy β-1 Diol, I	70	31	14-18
Stilbene, IV	16	-	-
Stilbene, V	3-4	-	-
Ethyl vanillin, VI	6-7	15	60
Ethyl vanillic acid or hydroxyl-substituted ethyl vanillin	(Trace)	4	-
ω-Hydroxyacetoguaiacone IX	-	2	(Trace)
Guaiacylglycol, VII	2	4	7-8
Ethoxyhydroquinone, VIII	(Trace)	15	-
Methoxyhydroquinone	-	-	(Trace)
1,2,4-Trihydroxybenzene	-	3-4	-
Ethanol	7	17	4-5
Methanol	15	29	36

Reaction Conditions:

[a] $[H_2O_2]/[\beta\text{-1 diol}] = 3$, $[\beta\text{-1 diol}] = 0.07 \times 10^{-3}$, $[DTPA] = 0.4 \times 10^{-3}$, $[MgSO_4] = 0.16 \times 10^{-3}$, 45°C, 4 h, pH 10.5, in vacuo.

[b] as in "a" except DTPA and $MgSO_4$ were omitted and reaction was performed under N_2

[c] oxygen added continuously for 4 h at 45°C and pH 10.5

Table 2. Reactivity of α, β-Unsaturated Phenols with Alkaline Hydrogen Peroxide[a]

Compound	Initial pH	Atmosphere	Residual H_2O_2 % of Applied	Residual Phenol % of Applied
trans-Stilbene	9.0	in-vacuo	99-100	97
trans-Stilbene	10.5	in-vacuo	97-100	98
p-Methoxystilbene	9.1	in-vacuo	78	85
p-Methoxystilbene	10.5	in-vacuo	87-90	96-97
4,4'-Dihydroxystilbene	10.5	in-vacuo	86	76
4,4'-Dihydroxystilbene	13.0	nitrogen	96	96
4,4'-Dihydroxystilbene	9.0	in-vacuo	74	65
Isoeugenol	10.5	nitrogen	82	83
Isoeugenol	13	nitrogen	90	96

[a] Reaction conditions: $[model] = 5.89 \times 10^{-3}$; $[H_2O_2]/[DTPA] = 0.40 \times 10^{-3}$; $[MgSO_4] = 0.17 \times 10^{-3}$; 45°C, 2 h

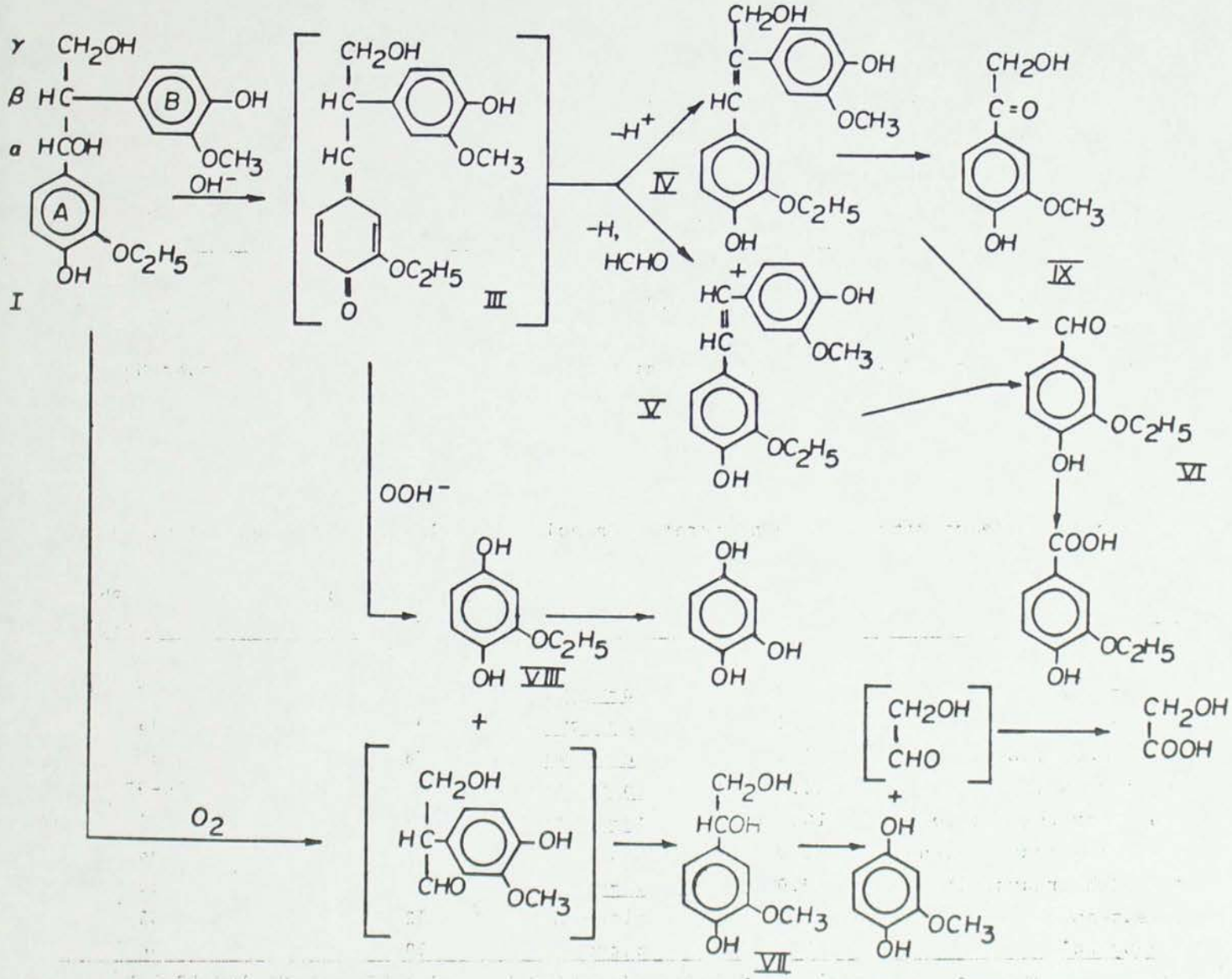

FIGURE I OUTLINE OF PRIMARY REACTIONS IN TREATMENT OF β-I DIOL I WITH ALKALINE HYDROGEN PEROXIDE

CHARACTERIZATION OF WHEAT STRAW LIGNIN

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ABSTRACT

Milled wood lignin(MWL) isolated from wheat straw was characterized by means of GPC,nitrobenzene oxidation,functional groups and other chemical analyses, as well as spectral studies including UV, IR, ^{1}H-NMR and ^{13}C-NMR. As compared with birch MWL, wheat straw MWL is richer in guaiacyl and has more phenolic hydroxyl content. Also wheat straw MWL has a molecular weight much lower than birch MWL.

KEYWORDS: Wheat straw, Milled wood lignin(MWL).

INTRODUCTION

Wheat straw is one of the most major grass materials of paper industry in China. The studies on the pulping mechanism of wheat straw showed that about 60% of the lignin were removed in alkali prior to 100°C, which is much different from wood(1). This difference is probably due to that wheat straw lignin differs from wood lignins in their nature and distribution in cell wall.

This paper concerns studies on MWL isolated from wheat straw by chemical and physical methods, in order to well understand the characteristics and relation with its behavior during pulping.

RESULTS AND DISCUSSION

1.Elemental analyses and functional groups

Sample	% C	% H	% O	% N	% OCH_3
Wheat straw MWL	60.81	5.42	33.60	0.17	16.87
Birch MWL	57.77	6.09	34.05	—	20.13

Table 1. Elemental composition

The C_9 formulas calculated from Table 1 were $C_9H_{7.39}O_{3.0}(OCH_3)_{1.09}$ and $C_9H_{8.70}O_{2.95}(OCH_3)_{1.55}$ for wheat straw and birch MWL,respectively.

Especially noteworthy is the large difference in the phenolic hydroxyl content. The phenolic hydroxyl content of birch MWL was estimated by same method(ΔEi) to be 1.34%, which is 70% less than that of wheat straw MWL. This is probably one of the major causes for wheat straw lignin to be easily removed in alkali.

OCH_3		total OH		phenolic OH	
Zeisel	^{1}H-NMR	Acetylation	^{1}H-NMR	ΔEi	^{1}H-NMR
16.87% 1.09/C_9	1.10/C_9	11.23% 1.33/C_9	1.35/C_9	2.25% 0.27/C_9	0.34/C_9

Table 2. Functional groups of wheat straw MWL

2. Molecular weight and molecular weight distribution

Sample	$\bar{M}n$	$\bar{M}w$	$\bar{M}w$ / $\bar{M}n$
Wheat straw MWL	2,953	8,854	3.0
Birch MWL	7,322	18,[illegible]31	2.5

Table 3. Average molecular weight

It is notable that the average molecular weight of wheat straw MWL is seen to be about one-half as much as of that of birch MWL. This may be considered as one of the major causes for wheat straw lignin to be easily removed during pulping.

3. Ester linkage of wheat straw MWL

Wheat straw MWL was treated with NaOH solution and its alkaline hydrolysis products were determined by HPLC. The most major product was p-coumaric acid and small amount of ferulic acid was found. The amount of p-coumaric acid was 2.08% (based on MWL), whereas the amount of ferulic acid was about one-twentieth of that of p-coumaric acid. The HPLC also showed the presence of traces of p-hydroxybenzoic, vanillic and syringic acid.

The ester linkage is easily saponified in alkali,therefore this portion of the lignin is easily removed during pulping.

4. Alkaline nitrobenzene oxidation

Sample	% V	% S	% H	V : S : H
Wheat straw MWL	14.58	13.59	3.95	1 0.77 0.31
Saponified MWL	14.96	15.11	2.28	1 0.84 0.18
Birch MWL	9.24	16.44	——	1 1.49

Table 4. Nitrobenzene oxidation products

As shown in Table 4, it is obvious that wheat straw lignin is richer in guaiacyl than birch lignin. On the other hand, the amount of p-hydroxybenzaldehyde of saponified wheat straw MWL was 58% of that of unsaponified MWL. This means that this portion of p-hydroxyphenyl is linked via other chemical bonds to the lignin, possibly

phenol ether linkages.

5. Ultraviolet spectra

Wheat straw MWL gave an absorption at 280 nm and its absorption coefficient was 20.4 $l \cdot g^{-1} cm^{-1}$ both similar to softwood lignins. These results are consistent with that wheat straw MWL has a relatively high amount of guaiacyl and some p-hydroxyphenyl units as compared with birch MWL. Also wheat straw MWL gave a shoulder around at 315 nm and after treated with NaOH solution, this peak was almost completely dissappeared indicating that this absorption is duo to the presence of p-coumaric acid esterified to the lignin.

6. Infrared spectra

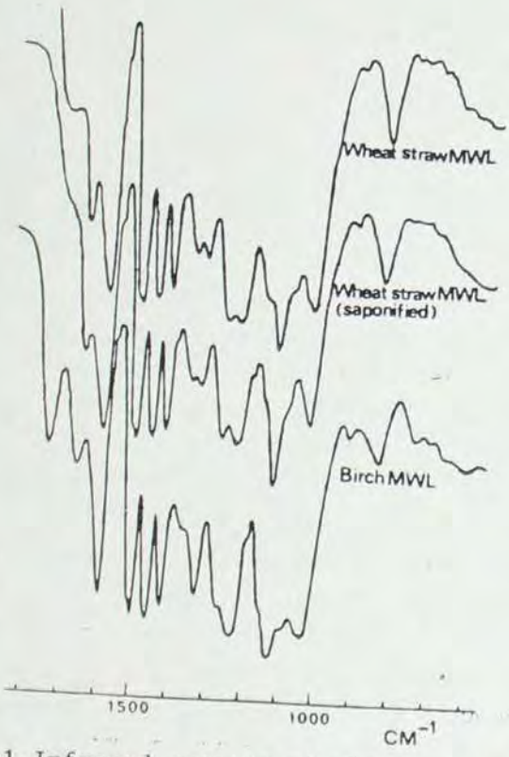

Figure 1. Infrared spectra of wheat straw MWL

As seen in Figure 1, the apparent difference among these three MWLs is the bands at 1715 and 1170 cm^{-1}, which are responsible for the absorption of ester linkage. These absorption were not found in birch MWL, however almost completely dissappeared in wheat straw MWL treated with NaOH solution indicating the ester linkages were saponified. The relatively weak absorption intensity of 1715 and 1170 cm^{-1} also showed that the amount of ester likage of wheat straw MWL is small.

7. ^{13}C-NMR spectra

On the basis of Nimz's studies(2), in the aromatic region(104 – 160ppm) of the spectra the syringyl(S) and guaiacyl(G) residues are indicated. Signals 4,9,17(S) and 5,6,7,8,11,14,15(G). The signals 12,13,16 caused by p-hydroxyphenyl(H) can be taken as characteristic signals for GSH lignin.

In the aliphatic region(50 – 90 ppm), occur three strong signals 19,22 and 25, which can be assigned to carbon atoms β, α and γ in β-o-4 structures, respectively. Also other linkages, such as β-1, β-5, were found in the spectra.

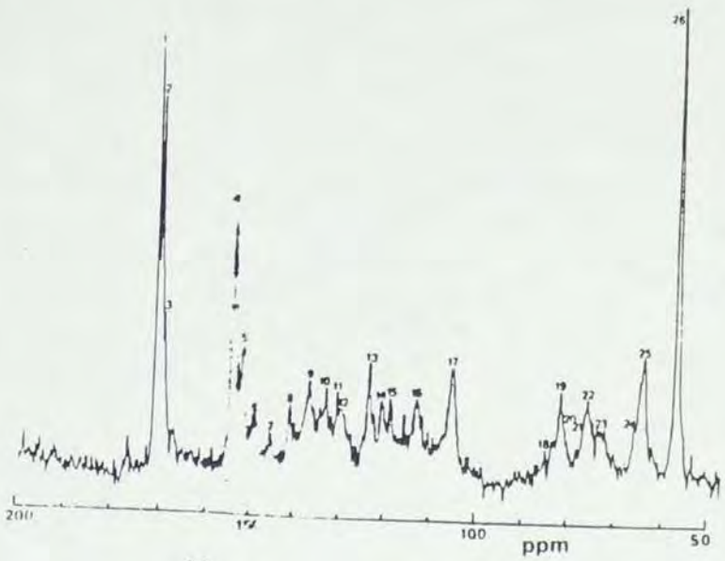

Figure 2. ^{13}C-NMR spectra of wheat straw MWL

CONCLUSION

The characteristics of wheat straw lignin can be summarized as follows:

1. Wheat straw linin is distinguished as GSH lignins and rich in guaiacyl.
2. The phenolic hydroxyl of wheat straw lignin is more than that of birch lignin.
3. Wheat straw lignin has a molecular weight much lower than birch lignin.

EXPERIMENTAL

Wheat straw MWL were prepared by the procedure of Bjorkman(3).

Sephadex LH-60 with 0.1M LiCl in DMF and Waters μ-styragel with THF were used for determination of molecular weight distribution.

^{13}C-NMR spectra were measured by a Varian-FT--80 A NMR spectrometer, solvent: CD_3COCD_3 and reference: TMS.

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AN ELECTRON MICROSCOPE STUDY OF ATTACK ON STRAW BY PANUS CONCHATUS

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ABSTRACT

Using the white-rot fungus Panus conchatus, the growth pattern of the fungus and the changes in microstructure of straws through progressive degradation have been investigated by the aid of electron microscopy. It has been shown that parenchyma are first attacked and destroyed rapidly. Then, the middle lamella between fibers is completely decomposed, the fibers are individually separated, and the secondary wall exposes a macrofibrillar structure indicating that lignin is removed and a cellulose framework is left. The gradual thinning of secondary wall of fiber from lumen, that is normal pattern of wood rotting by white-rot fungi, has generally not been observed in straw rotting. These results further indicate that P. conchatus has considerable potential for biopulping and other delignification processes of straw. In addition, it has been found that epidermis cells of straw are particularly resistant to degrade and the detachment along S_1/S_2 and S_2/S_3 transition layers occurs.

KEYWORDS: White-rot fungus, Straw rotting, Electron microscopy, Lignin bio-degradation.

INTRODUCTION

Panus conchatus is the white-rot fungus which can cause very efficient rotting of both wood and straw. It has been demostrated that 80% Klason lignin in rice straw could be degraded by this fungus for 20 day incubation, and biological pulp with good strength properties was produced after defibering (Bull. Pulp & Paper Res. Inst. Chinese Light Ind. Ministry, 1973). Recent results obtained showed that 24.7% water soluble modified lignin released from wheat straw by P. conchatus in three days following inoculation (1). These results indicated that this fungus has considerable potential for delignification processes.

A large number of data are avilable concerning the micromorphological changes during wood decay by white-rot fungi (2-4, 6-7), but limited information relating to the straw rotting by white-rot fungi has been reported.

In view of these facts, the fungal growth patterns and the micromorphological changes in straw from the fungal attack have been investigated in the present work using scanning electron microscopy.

RESULTS

Changes in tissue construction

The micrograph has clearly shown that parenchyma which mainly exist around the vascular bundles are first attacked on, decomposed in fractions, and then disappear in early decay (Fig. 1). In advanced decay, the middle lamella between fibers is completely decomposed, the fibers in either vascular bundles or epidermis cell layer inward are individually separated and the separation of the fiber closing to parenchyma are always predominant. The epidermis are particularly resistant to degrade even though in advanced decay (Fig. 2). Similar pattern of tissue construction has also been obtained from decomposed wheat straw and reed.

Hyphae distribution

The attack of hyphae on straw not only starts from the ends of straw sticks, but also occurs on straw surface. Then, the hyphae gather at the lumina of parenchyma cells (Fig.3). Simultaneously, hyphae also attack on fibers and penetrate into the lumina of the fibers (Fig. 4). The hyphae propagate and spread mainly utilizing naturally existing connections such as pits and stimata. The spread of hyphae through boring holes on the wall of parenchyma cell or fiber and through the area of middle lamella layer between fibers has also been observed (Fig. 5).

Micromorphological changes

In incipiant decay it has been found that the components between middle lamella and S_2-layer of fibers are degraded and the detachment between S_2-layer and middle lamella take place with the further degradation by the fungal attack, so that fibers can be easily separated from one another (Fig. 6). A macrofibrillar structure appear on the cell wall (Fig. 6). It means that lignin is removed and a cellulose framwork is left. In addition, the detachments along S_1/S_2 and S_2/S_3 transition layers have also been observed (Fig. 7). S_3-layer seems to be resistant to degrade by the fungus. The gradual thinning of secondary wall has generally not been found inthe rotting of rice straw even though the fibers are individually separated in advanced decay by P. conchatus (Fig. 8).

DISCUSSION

The results obtained have offered a better knowledge of the fungal growth pattern and the micromorphological changes in decomposed straw

from the attack by Panus conchatus.

Compared with the pattern of wood degradation by white-rot fungi that have been reported. The following similarities and differences are pointed out:

Similarities

- The fungal hyphae spread through pits and other openings of cell wall and penetrate into the lumina of parenchyma cells and fibers (3).
- The spead of hyphae produces bore holes on the cell wall (3, 7).
- The attack on the fibers closing to parenchyma are always predominat (4).
- S_1 and S_3 layers are resistant to degrade (4).

Differences

It has been reported that white-rot fungi often cause a gradual thinning of the wood cell wall, starting from the lumen continuing towards the middle lamella (3,6,7) and only cell corner with a little secondary wall is left in advanced decay (7). The middle lamella is resistant to degrade (4). The secondary wall of most fibers in rotting sweetgum is earlier destroyed than ray parenchyma cells are (7).

In contrast, a selective degradation of lignin has been observed in straw rotting by P. conchatus. The middle lamella between fibers is completely decomposed and the intact fibers can easily be separated from one another (Fig. 2). The appearance of the macrofibrillar structure on the secondary wall indicates that lignin is removed leaving a cellulose framework . Straw parenchyma are decomposed and disappear rapidly in early decay (Fig. 1).

The results obtained have also offered a tentative explanation in connection with the facts that most of lignin in rice straw could be degraded for limited time incubation and biological pulp with good strength properties could be produced by P. conchatus. That is :

- The middle lamella where the lignin conten. is higher is rapidly decomposed and fibers could easily be separated.
- No obvious thinning of cell wall occurs when the fibers are separated. of course, the separated fibers can be decomposed in highly advanced decay. if suitable control is carried out, the fibers with limited damage can be obtained.
- Parenchyma cells are destroyed in early decay of rice straw. The disappearance of these cells is beneficial to improve the strength properties of pulp and dewatering in the papermaking process.
- Loose tissue construction and low lignified degree are also beneficial to the attack on rice straw by P. conchatus.

Scanning electron microscopy clearly demostrates that the fungal hyphae are not observed in all fibers and any part of cell wall, but almost all fibers are indivioually separated. These observations mean that decomposition should occur at large distances from hyphae and a highly diffusable lignin enzyme system exist during the rotting of rice straw by P. conchatus.

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Figure legends

Fig. 1 Transverse section, rice straw, 9 days, The parenchyma are decomposed. M=220

Fig. 2 Rice straw, 24 days, The fibers are individually separated and the epidermis are particularly resistant to degrade M=330

Fig. 3 Longitudinal section, rice straw, 15 days, The hyphae gather at a lumen of parenchyma cell. M=430

Fig. 4 Transverse section, rice straw, 15 days, Hyphae penetrate the lumina of the fibers. M=880

Fig. 5 Longitudinal section, rice straw, 24 days, The spread of a hypha through area of middle lamella and a boring hole on the fiber wall. M=2200

Fig. 6 Longitudinal section, rice straw, 24 days, Middle lamella are decomposed and a macrofibrillar structure appear on the cell wall. M=2400

Fig. 7 Transverse section, rice straw, 15 days, It snows the detachments along S_1/S_2 and S_2/S_3 Transition layer. M=8300

Fig. 8 Rice straw, 24 days, No obvious thinning occur on the fiber walls even though the fibers are separated. M=1700

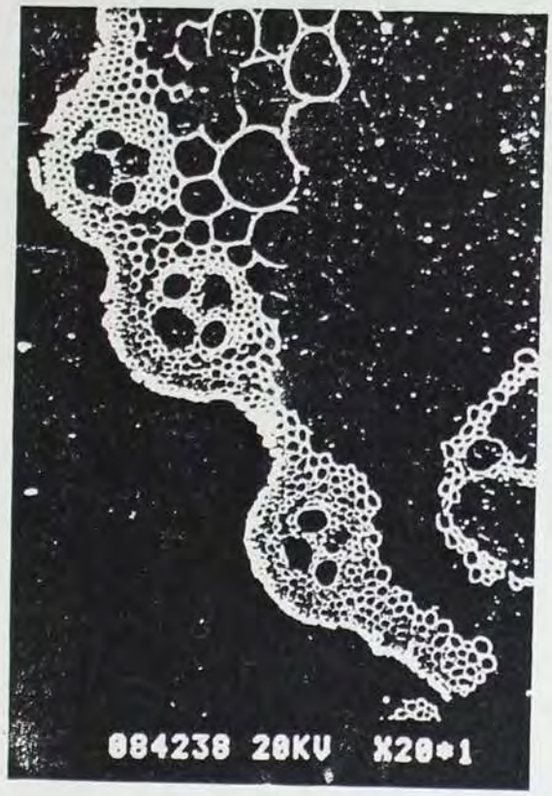

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

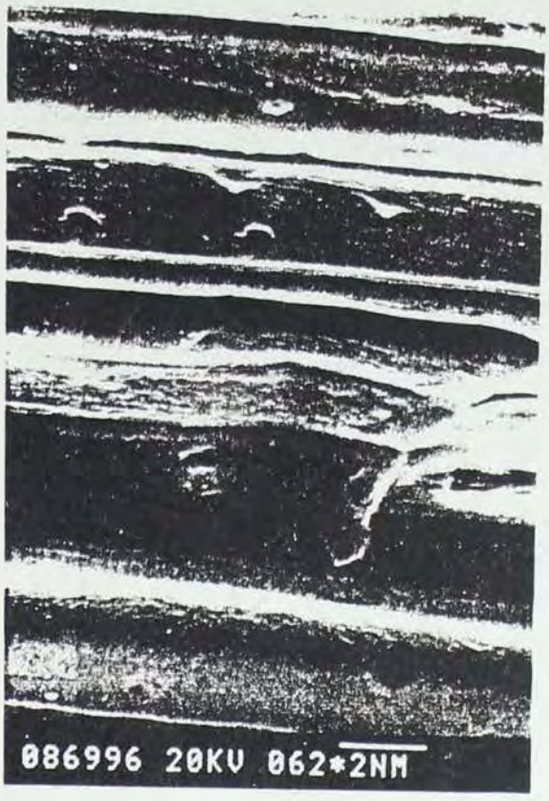

Fig. 6

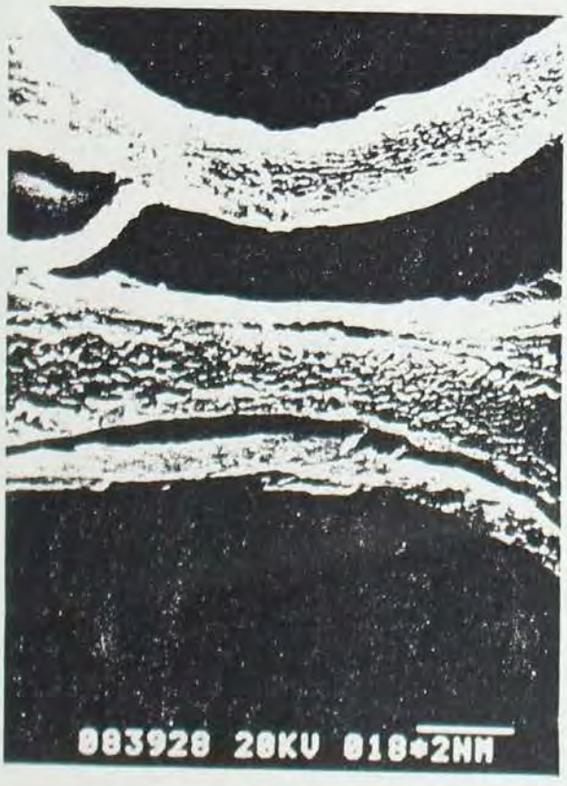

Fig.7

Fig. 8

THE STRUCTURAL MODIFICATION OF LIGNIN DURING OXYGEN BLEACHING

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ABSTRACT

Pulp samples after oxygen bleaching and corresponding lignins precipitated from the bleaching liquors have been subjected to various analytical procedures for lignin, including oxidative degradation, determination of carboxyl and phenolic hydroxyl groups, ^{13}C-NMR analysis and size exclusion chromatography. The results obtained reveal that lignin dissolution during oxygen bleaching is accompanied by a partial oxidative degradation of aromatic rings with the formation of carboxylic acid groups. At the same time, guaiacyl end-groups in lignin are preferentially oxidized, leading to an accumulation of lignin structures with more than one carbon substituent attached to the same aromatic ring. The former reaction type facilitates lignin dissolution whereas the latter can be expected to render this dissolution more difficult.

KEYWORDS: Structural analysis, Lignins, Bleached pulps, Oxygen, Kraft pulps.

INTRODUCTION

Oxygen bleaching of kraft pulps was introduced on a commercial scale 15 years ago. Since then, oxygen bleaching has been adopted, mainly in Sweden, as a way of decreasing the amount of chlorine-containing chemicals used in bleaching. At the same time, the environmental load from the bleaching plant, measured as BOD, COD, color and TOCl (total organic chlorine), can be reduced to a considerable extent since the effluent from the oxygen stage can be incorporated into the chemical recovery system of the pulp mill.

It is possible, in oxygen bleaching, to decrease the lignin content of the kraft pulp by approximately 50 % without affecting the pulp properties to any noticeable extent. Beyond this degree of delignification, oxidative degradation of polysaccharides starts to become more and more pronounced and to lead to a gradual decrease in pulp strength. Kinetic studies show that oxygen bleaching involves two different phases with different rates of lignin dissolution. The second (slower) phase is entered at a kappa number of about 20, and the reaction is normally interrupted at this point (1).

Oxygen oxidation of lignin model compounds in alkaline media has clearly demonstrated that aromatic rings containing free phenolic hydroxyl groups constitute the major sites of reaction. A large variety of oxidation products have been identified from such structures and several routes of reaction have been postulated (2). In addition, lignin structures containing a double bond in conjugation with a free phenolic unit, e.g. stilbenes and enol ethers, have been shown to undergo oxidation reactions including side chain cleavage (3). These reactions render the lignin more hydrophilic and a certain degree of depolymerization of the lignin polymer can be expected to take place. On the other hand, the reactions between lignin structures and oxygen may also involve radical coupling reactions, i.e. a reaction type leading to an increase in molecular weight, and this is often a major reaction route in lignin model systems.

In the present study, attempts have been made to identify those reactions between oxygen and lignin which are quantitatively important for lignin dissolution in the oxygen bleaching of kraft pulps. Pulp samples after oxygen bleaching and corresponding lignin samples precipitated from the oxygen bleaching liquors have been subjected to various analytical procedures for lignin, including oxidative degradation, determination of carboxyl and phenolic hydroxyl groups, ^{13}C-NMR analysis and size exclusion chromatography. The results have been compared with and related to corresponding analytical data obtained from analyses of residual lignin in kraft pulps and dissolved kraft lignins.

THE LIGNIN IN KRAFT PULPS

During the course of a kraft cook, approximately 90 % of the lignin is dissolved in the cooking liquor. The major reaction facilitating this dissolution is a sulfidolytic cleavage of β-aryl ether structures within the lignin macromolecules (4). The lignin is fragmented and at the same time new free phenolic hydroxyl groups are created in the lignin. These groups, which are ionized in the alkaline cooking liquor, constitute the major hydrophilic group and in a particular lignin fragment the number of these seems to be decisive for dissolution (5). Towards the end of the kraft cook, the majority of the β-aryl ether structures in the

lignin have been cleaved, so that the possibility of creating new phenolic sites gradually decreases (6), and the lignin is consequently rendered more resistant to dissolution.

The degree of branching in the lignin also seems to change towards the end of the cook. Around and above 90 % delignification, the lignin fragments which are dissolved have been found to contain a higher amount of biphenyl and biphenyl ether structures than the lignin dissolved earlier in the cook (7). This indicates that a certain accumulation of branched structures takes place during the course of the cook. Alternatively, certain parts of the fibres may contain a lignin which is more difficult to dissolve due to a more "condensed" structure (cf. Ref. 8).

THE STRUCTURE OF LIGNIN AFTER OXYGEN BLEACHING

Starting from the same unbleached kraft pulp from pine, a series of four oxygen-bleached pulps were prepared by variation of the charge of alkali. The kappa numbers of these pulps ranged from 22 to 11. The pulps were purified and the dissolved lignins were precipitated according to the scheme outlined in Fig. 1. The substitution pattern of the aromatic rings in the lignin samples was analysed by oxidative degradation (cf. Ref. 9).

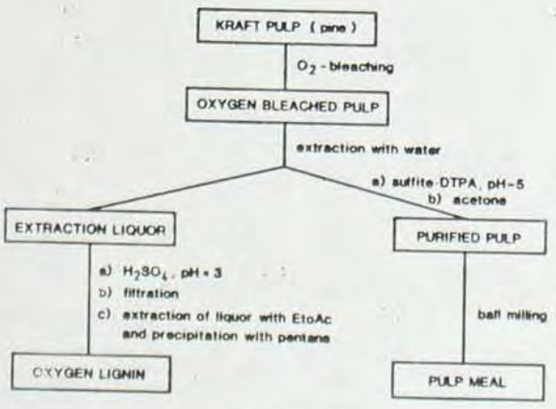

Figure 1. Preparation of pulp and lignin samples for analysis

In this method, the lignin is alkylated to protect free phenolic hydroxyl groups and subsequently oxidized in two stages employing potassium permanganate and hydrogen peroxide. After esterifiction of the low molecular weight carboxylic acids formed, the mixture can be quantitatively analysed by gas chromatography. A total of approximately 40 different degradation products can be obtained from lignin samples. Of these, however, the acids depicted in Fig. 2 constitute more than 95 % of the total mixture on a molar basis.

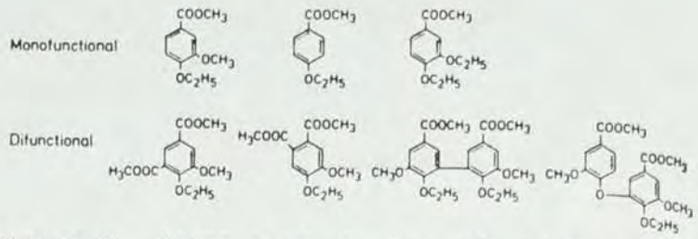

Figure 2. Major products from the oxidative degradation of softwood lignins

The amounts of difunctional and monofunctional acids formed in the analytical procedure provide an indication of the degree of branching in the lignin. The lignin samples obtained after oxygen bleaching are significantly different in this respect from those taken out after a kraft cook. This is illustrated in Fig. 3 where it can be seen in

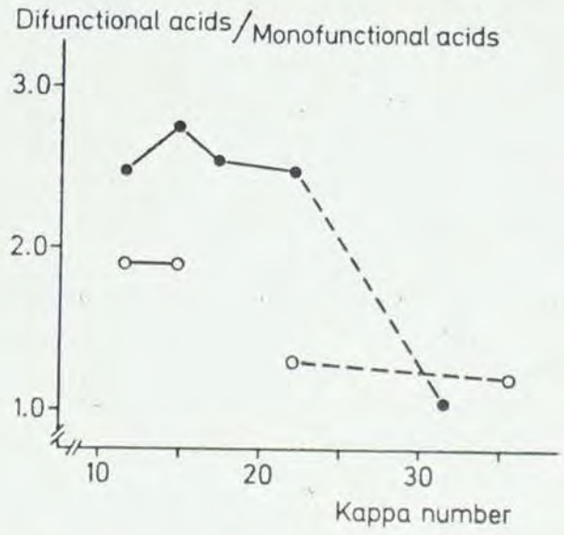

Figure 3. Ratio of acids formed in the oxidative degradation of lignin after oxygen bleaching. Residual lignin in the pulp = o, dissolved lignin = •. (Right hand values = values after kraft cooking).

particular that the lignin which has gone into solution in the oxygen bleaching stage contains a high amount of difunctional acids, acids derived from biphenyl structures being particularly abundant. The same result, although less pronounced, was observed in the residual lignin in the pulp fibres provided that the delignification in the oxygen stage was carried out to low kappa numbers. These results imply that in oxygen bleaching a preferential oxidation of guaiacyl end groups takes place leading to a certain accumulation of biphenyl and other "condensed" lignin structures. This conclusion is in accordance with observations on lignin model compounds. It has been found that biphenyl structures in their ionized form are remarkably stable towards degradation by

oxygen, probably due to the formation of a hydrogen bonded ring structure (10).

The dissolution of lignin in oxygen bleaching is also accompanied by pronounced changes in the number of hydrophilic groups within the lignin, i.e. carboxyl groups and phenolic hydroxyl groups. In unbleached kraft pulps, the amount of phenolic hydroxyl groups is of the order of 1.1-1.5 mekv/g of residual lignin, corrresponding to 20-27 such groups per 100 phenylpropane units (5). After bleaching, the residual lignin gives much lower figures, as shown in Fig. 4. For the corresponding

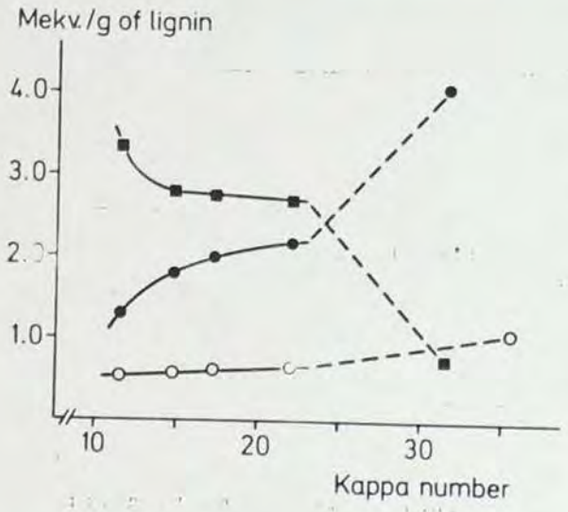

Figure 4. Amounts of phenolic hydroxyl groups and carboxyl groups in lignin after oxygen bleaching. Phenolic hydroxyl groups in pulp lignin = o, phenolic hydroxyl groups in dissolved lignin = •, carboxyl groups in dissolved lignin = ■. (Right hand values = values after kraft cooking)

dissolved lignins, however, fairly high values for the amount of phenolic hydroxyl groups were obtained. These figures are somewhat surprising. They indicate that a certain net formation of new phenolic hydroxyl groups has taken place during the bleaching operation. This conclusion is based upon the fact that the dissolved lignins also contained large amounts of carboxyl groups, the majority of which originate from aromatic rings. Analysis by ^{13}C-NMR also supports this conclusion (see below).

Fig. 4 also shows that when the oxygen bleaching is carried out to very low kappa numbers, the lignin which goes into solution has undergone a more comprehensive oxidative modification. Compared with lignins dissolved at higher kappa numbers, there was a noticeable decrease in the content of phenolic hydroxyl groups accompanied by a corresponding increase in the content of carboxyl groups.

The profound chemical changes taking place in the lignin structure during oxygen bleaching are not reflected in the size exclusion chromatography curves shown in Fig. 5. Lignin samples

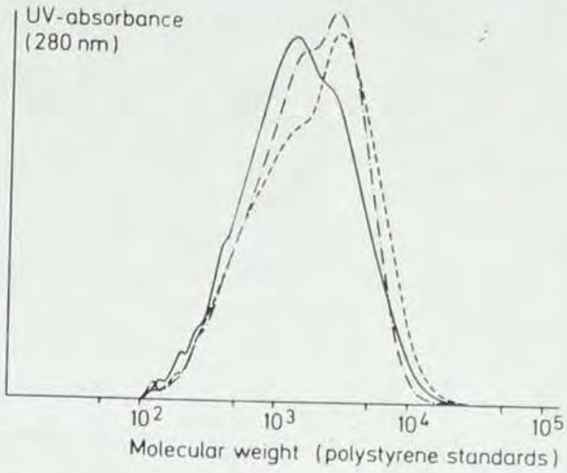

Figure 5. Size exclusion chromatography of lignin samples methylated with diazomethane. (—— = kraft lignin, ---, -·-·- lignin after oxygen bleaching to kappa Nos. 22.0 and 14.8 respectively)

extracted after oxygen bleaching seem to have a molecular weight distribution which is very similar to that of normal kraft lignin. For both types of lignin, bimodal curves are obtained although there is a shift in the position of the most intense peak. The curves shown in Fig. 5 are very similar in shape and position to those obtained earlier from various kraft lignins, including kraft lignins from a flow-through cook carried out to a low kappa number (9, 11). The results may therefore reflect a distribution of pore sizes in the fibre wall of the kraft pulp fibres (cf. Ref. 12).

The structural modification of lignin in oxygen bleaching is further illustrated by the data obtained from ^{13}C-NMR analysis. Dissolved lignin samples from both kraft cooking and oxygen bleaching have been subjected both to a complete quantitative ^{13}C-NMR analysis and to quantitative analysis by the DEPT (Distortionless Enhancement by Polarization Transfer) technique. By combining the information obtained from these spectra with elemental and methoxyl analysis, a comprehensive structural description of the lignins was obtained. The data are given in Table 1, where

Functional group	Kraft lignin	Oxygen lignin	Note
Aromatic rings	1.0	0.56	per phenylpropane unit
COOH	0.13[1]	0.50[1]	-"-
Ketone	not found	0.02	-"-
Aldehyde	0.03	0.05	-"-
Double bond	0.18	0.29	-"-
Aliph. CH > 57 ppm	0.44	0.61	-"-
Aliph. CH_2 > 57 ppm	0.34	0.45	-"-
Aliph. CH < 56 ppm	0.39	0.25	-"-
Aliph. CH_2 < 56 ppm	0.63	0.55	-"-
Aliph. CH_3 < 56 ppm	0.18	0.19	-"-
OCH_3	0.79[2]	0.85[3]	per aromatic ring
Phenolic OH	0.62[2]	0.58[4]	-"-
Quart. aromatic C	3.42	3.90	-"-

1) Conductometric titration acc. to Ref. 14
2) Value from Ref. 11
3) Assumed value
4) Aminolysis

Table 1. Analytical data calculated from ^{13}C-NMR for kraft lignin and for a lignin obtained after oxygen bleaching to kappa No. 14.8

it can be seen that oxygen bleaching leads to a substantial reduction in the number of aromatic rings. Furthermore, the aromatic rings which remain after bleaching are to a large extent substituted in the 5 and/or the 6 position(s) thus supporting the results obtained from the oxidative degradation analysis. Another important feature concerning the structure of these lignins is the high number of aliphatic carbon atoms with shift values below that of the methoxyl group. Such carbon atoms are substituted only with hydrogens and carbons and thus constitute functional groups which are difficult to modify by chemical reactions.

CONCLUSIONS

In the oxygen bleaching of kraft pulps, a partial lignin dissolution is achieved by the introduction of a large amount of carboxyl groups mainly through oxidative cleavage of aromatic rings. In addition, new phenolic hydroxyl groups seem to be formed, indicating that lignin fragmentation reactions also take place during bleaching. These reactions, facilitating lignin dissolution, are counterbalanced by a certain selectivity in the lignin oxidation and, for example, biphenyl structures are to a large extent left unreacted. The fact that (softwood) lignin seems to contain fairly large amounts of alkyl groups in the side chains may further contribute to a poor solubility of the lignin fragments in aqueous solution.

ACKNOWLEDGEMENTS

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ON THE REACTION OF SOFTWOOD TYPE- AND HARDWOOD TYPE-LIGNIN MODEL COMPOUNDS-DURING ALKALINE PULPING

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ABSTRACT

In order to investigate the effect of fundamental lignin structures on the cleavage of β-aryl ether linkages during alkaline pulping, softwood and hardwood lignin model compounds were synthesized and treated under soda and kraft pulping conditions. The cleavage of β-aryl ether linkages was analysed kinetically and the comparison of the reaction of softwood lignin and hardwood lignin was discussed.

KEYWORDS: Alkaline Pulping, Lignin model compound, Kinetics.

INTRODUCTION

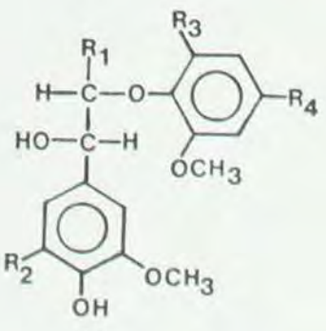
It is well known that hardwoods are pulped more easily than softwoods due both to the different chemical nature of the two lignins and the lower lignin content of hardwoods. Hardwood lignins differ from conifer lignin by the presence of syringylpropane in addition to guaiacylpropane units. Fergus and Goring observed the topochemical removal of lignins from the fibres and vessels in birch wood[1] and spruce wood[2] by sulfate and sulfite pulping with UV microscopy. In these pulping processes, the syringyl-lignified fibres generally pulped faster than the guaiacyl-lignified vessels. They concluded that the rate of delignification in woods did not depend on the accessibility of the lignin but rather on the chemical structure of the lignin gel in woods. However, to what extent this difference may be attributed to the delignification of softwoods and hardwoods has not yet been demonstrated. In this study, in order to investigate the effect of the difference of principal chemical structures between softwood and hardwood lignin on the delignification rate of these woods, the typical softwood and hardwood lignin model compounds were synthesized and treated under alkaline pulping conditions. The results were analysed based on studies of the kinetics of the reactions involved.

EXPERIMENTAL

Materials: Six kinds of β-O-4 model compounds were synthesized and are shown in Figure 1. In the case of GG-II, SG-II and SS-II, the threo-steroisomers were used.

Method of treatments: The model compounds were dissolved (5m mol/l) in the soda (OH^-, 0.1 mol/l) and kraft cooking liquor (OH^-, 0.1 mol/l, SH^- 0.015 mol/l) in an atmosphere of nitrogen. The substrate solution was treated at 4 temperatures ranging from 110 °C to 140 °C. The course of the reactions was followed by taking about 10 samples over a period which covered at least two thirds of the total reaction time after the desired temperature had been reached in 5 minutes.

Method of analysis: After cooling the sample to room temperature, an aliquot (3.0 ml) was withdrawn and transferred into a 10 ml volumetric flask, followed by the addition of 0.5 M phosphate buffer (PH=3) 2.0 ml and 4-methylguaiacol acetonitrile solution 5 ml as an internal standard. An aliquot (5μl) of the reaction products solution was injected directly into HPLC to determine the amounts of the starting materials and the β-O-4 cleavage products such as guaiacol and 4-methyl-syringol quantitatively. The areas of the peak were measured by means of a computing integrator and converted into amounts using calibration cures which in all cases were linear. The amounts of substrate and products are expressed in the figures in mole % of the theoretical. The reactions were studied under pseudo first-order conditions using excess of $[OH^-]$ and $[SH^-]$ over [substrate]. Integration of the rate equation gives the expressions ln b and ln a/a-x, where b refers to concentration of starting material, and a refers to the theoretical and x to the actual concentration of the product formed.



GG-I : $R_1=R_2=R_3=R_4=H$
GG-II: $R_1=CH_2OH$, $R_2=R_3=R_4=H$
SG-I : $R_1=R_3=R_4=H$, $R_2=OCH_3$
SG-II: $R_1=CH_2OH$, $R_2=OCH_3$, $R_3=R_4=H$
SS-I : $R_1=H$, $R_2=R_3=OCH_3$, $R_4=CH_3$
SS-II: $R_1=CH_2OH$, $R_2=R_3=OCH_3$, $R_4=CH_3$

Fig.1. Model compounds

RESULTS AND DISCUSSION

Six compounds were treated with soda and white liquor. The reactions were followed by a decrease in the amount of starting compounds and the increase in the amounts of the ether cleavege products such as guaiacol and 4-methylsyringol. Some parts of the results are illusrated in Figures 2 and 3. Figure 2 shows the plots for a pseudo first-order reaction of the cleavage of GG-I, SG-I and SS-I by white liquor at 120 °C. All reactions followed a pseudo first-order reaction and the rate of cleavage reaction is in the order of SS-I> SG-I> GG-I. Figure 3 shows the reaction of GG-II, SG-II and SS-II as a function of time for the treatment with soda liquor at 120 °C. The reaction of GG-II and SG-II followed pseudo first -order reactions. However, it is immediately obvious that the reaction of SS-II cannot possibly be approximated as a single pseudo first-order process. Rather, it appears to consist of two distinguishable phases; a rapid phase of indeterminate kinetic order for about 40 minutes at 120 °C, and a subsequent slower phase, conforming with first-order kinetics.

In Table 1 all the kinetic data are summarized. Syringyl type model compounds react faster than guaiacyl types in both soda and kraft treatments. For comparison, the ratio of rate constants was calculated. In soda treatment, SG-I/GG-I for k^1=2.7 and SG-II/GG-II for k^1 was 1.7. In kraft treatment, SG-I/GG-I for k^1= 1.8-2.8, for k^2=1.6-2.3 ; SS-I/GG-I for k^1=4.4-6.3, for k^2=4.2-5.0; SG-II/GG-II for k^1=1.7-1.8, for k^2=1.1-1.3; SS-II/GG-II for k^1=1.7-2.9, for k^2=1.8-2.0.

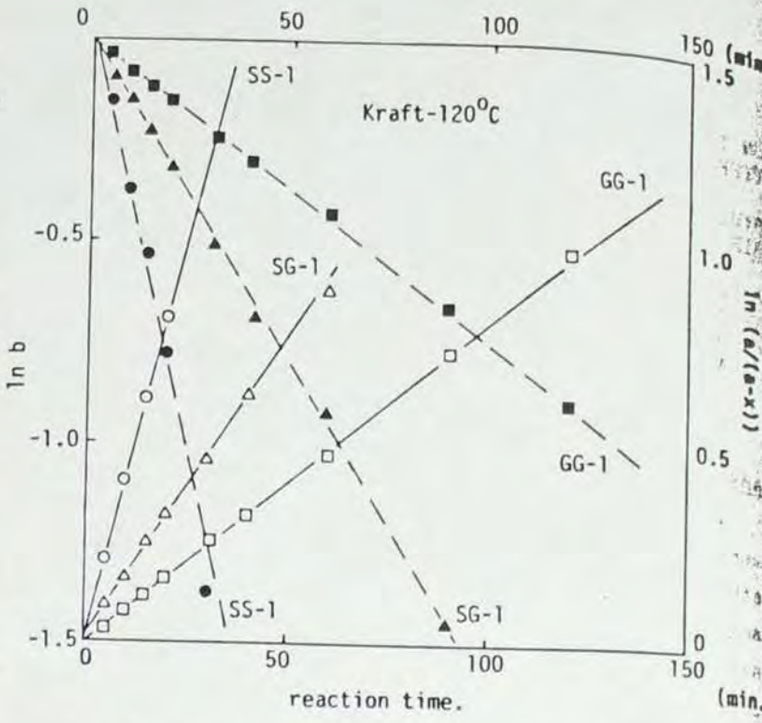


Fig.2. Reactions of GG-I, SG-I and SS-I on treatment with kraft liquor at 120 °C.

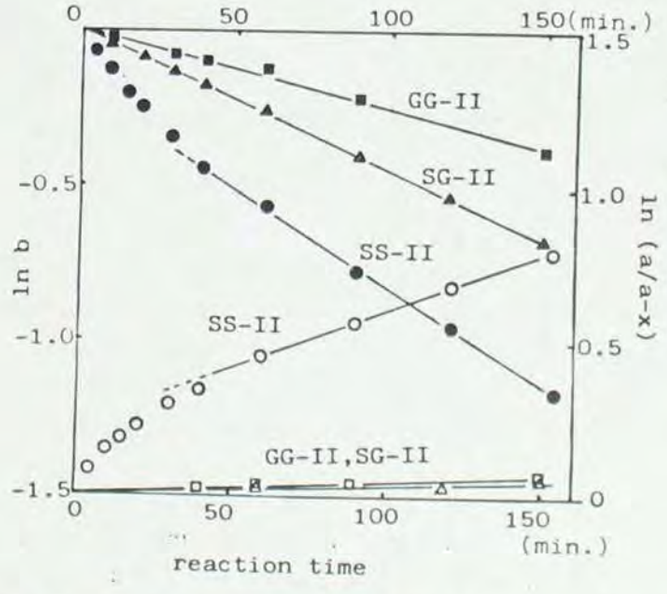


Fig.3. Reactions of GG-II, SG-II and SS-II on treatment with soda liquor at 120 °C.

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Table 1. Observed pseudo first-order rate constants $\times 10^{-3}$ .min^{-1}

	Temp. °C	GG-I k^1	GG-I k^2	SG-I k^1	SG-I k^2	SS-I k^1	SS-I k^2	GG-II k^1	GG-II k^2	SG-II k^1	SG-II k^2	SS-II k^1	SS-II k^2
Soda	110					9.0							
	120					22.5		2.6	0.5	4.3	0.3		
	130	4.0	0.5	10.6	4.5	56.4		6.7	0.7	11.3	0.5		
	140							17.4	1.4	30.1	1.5		
Kraft	110	2.8	3.1	7.8	7.0	17.5	13.1	1.0	1.0	1.8	1.3	2.9	2.0
	120	7.4	8.1	16.8	14.5	44.6	37.9	2.4	2.5	4.4	3.2	5.6	4.7
	130	23.6	20.6	41.7	33.2	105	102	6.7	6.6	11.4	7.3	11.1	12 1

k^1 refers to comsumption of starting material

k^2 refers to formation of guaiacol or 4-methylsyringol

THE EFFECT OF COBALT COMPLEXES ON OXYGEN-ALKALI DELIGNIFICATION OF ASPLUND PULP

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ABSTRACT

Factors affecting the catalytic activity of cobalt complexes for an oxygen-alkali oxidation of guaiacol and oxidative delignification of white birch Asplund pulp were investigated. The cobalt complex which had a formal potential in an amphoteric region from approximately +0.3 to -0.3 V vs. the standard electrode had an ability to catalyze the guaiacol oxidation. If the cobalt complex could form a complex with the substrate, it could catalyze the guaiacol oxidation even when it did not have a formal potential in that region. Only the cobalt complex with both higher catalytic activity for the guaiacol oxidation and higher stability increases the delignification rate significantly.

KEYWORD: Oxygen-alkali pulping, Asplund pulp, Cobalt complexes, Catalytic activity, Phenol oxidation.

INTRODUCTION

Various investigation have been made to develop the most suitable catalysts for oxygen-alkali delignification using some cobalt complexes. The addition of a small amount of Co-salen to a single-stage oxygen pulping of white birch Asplund pulp caused a significant increase in the delignification rate as compared with the control(1). The factors affecting catalytic activity of Co-salen were investigated under guaiacol oxidation. The coordination of guaiacolate anion with Co-salen was necessary for the catalytic oxidation of guaiacol(2). The stability of cobalt complexes was correlated closely with their ability to catalyze an oxidative delignification(3).

Landucci(4) demonstrated that the catalytic behavior of metals in phenoxy radical formation from lignin model phenol and in catalysis of oxidative delignification correlated with the respective electrochemical behavior of the metals as determined by cyclic voltammetry.

In the present work, the electrochemical behavior of cobalt complexes and their ability to form a complex with the substrate were investigated and correlated to their catalytic activity for oxidative delignification of white birch Asplund pulp.

EXPERIMENTAL

Cobalt comple; Eight cobalt complexes shown in Table 1 were used. The concentration of cobal complex was 1.5 mmol/l.

Pulping studies; White birch (*Betula Platyphylla var.japonica*) Asplund pulp (kappa no. = 140) was cooked with 20% $NaHCO_3$, based on Asplund pulp as NaOH, at 130 C for 2 hours at a liquor-to-pulp ratio 50 to 1 in a 4-liter stainless-steel rotary autoclave. Oxygen was introduced to 1.0 MPa at room temperature.

Guaiacol oxidation; Guaiacol was treated in 100 mmol/l $NaHCO_3$ solution with oxygen at 50 C for 3 hours using a 100-ml stainless-steel autoclave. The concentration of guaiacol was 40 mmol/l. Oxygen partial pressure was maintained at 1.0 MP during oxidation. The concentration of unreacted guaiacol was determined by GLC as reported previously(2).

Electrochemistry; Cyclic voltammograms of cobalt complexes were determined with a New Cyclic Voltammetric Analyzer VAM-10 (YANAGIMOTO MFC Co., LTD.). A three- electrode system was used, consisting of a glassy carbon working electrode, a platinum-wire counter electrode and a silver-silver chloride standard electrode.

Visible absorption spectra; Visible absorption spectra of cobalt complexes in a 100 mmol/l $NaHCO_3$ solution were determined with a spectrophotometer. Visible absorption spectrum of the mixture was measured in a glass-cell fitted with plug immediately after guaiacol was added to the $NaHCO_3$ soluton containing a cobalt complex under nitrogen bubbling.

Stability measurement; The $NaHCO_3$ solution containing the cobalt complex was heated at 100 C for 30 min. and filtered by membrane filter (0.1 μm) after cooling. The concentration of soluble cobalt in the filtrate was determined by photometric method using nitoroso R salt. The stability of the cobalt was expressed by the ratio of soluble cobalt in filtrate to added cobalt.

RESULT AND DISCUSSION

The cyclic voltammograms of cobalt complexes were determined in 100 mmol/l $NaHCO_3$ solution. By the addition of Co-salen, Co-acacen and Co-salpr, which had a formal potential in a narrow amphoteric region, the guaiacol oxidation was accelerated significantly as shown in Table 1. On the other hand, Co-acac, Co-GL and Co-EDTE did not have it in that region, and their effects on the guaiacol oxidation were small. Therefore, it

Table 1 Factors affecting the catalytic activity of cobalt complexes for guaiacol oxidation in a 100 mmol/l $NaHCO_3$ solution.

Complexes*1	Electrochemical behavior*2	Complex formation with guaiacol*3	Catalytic activity(%)*4
Co-salen	yes	yes	69.7
Co-acacen	yes	yes	28.6
Co-salpr	yes	no	29.6
Co-TEA	no	yes	37.3
Co-EDTE	no	yes	36.5
Co-acac	no	no	1.2
Co-GL	no	no	8.9
Co-EDTA	no	no	2.8

*1 Ligand: salen; bis-(salicylidene)-ethylenediamine, acacen; bis-(acetylacetonato)-ethylenediamine, salpr; bis-(3-salicylidene-aminopropyl)-amine, TEA; triethanolamine, EDTE; ethylenediamine-tetraethanol, acac; acetylacetone, GL; gluconate, EDTA; ethylenediaminetetraacetic acid.
*2 "yes" shows that the cobalt complex has a formal potential in a region from approximately +0.3 to -0.3 V, as determined by CV.
*3 "yes" shows that the cobalt complex has an ability to form a complex with guaiacol.
*4 Differential percentage of residual guaiacol between non-additive and additive oxidation.

seemed that all cobalt complexes which had a formal potential in an amphoteric region approximated by ± 0.3 V vs. the standard electrode exhibited some catalytic activity for the guaiacol oxidation,in a similar manner as metals investigated by Landucci(4). But CO-TEA and Co-EDTE catalyzed the guaiacol oxidation effectively without having a formal potential in an amphoteric region. This result showed that the potential catalytic activity of cobalt complexes on the guaiacol oxidation could not be postulated only from their electrochemical behavior as determined by cyclic voltammetry (CV). Co-salen, Co-acacen, Co-TEA and Co-EDTE formed a complex with guaiacol as their visible absorption spectra changed significantly by addition of guaiacol.It seemed that Co-TEA and Co-EDTE were activated by forming a complex with substrate, similar to Co-salen in our previous work(2). Accordingly, when screening potential catalysts for phenol oxidation, the ability to form a complex with substrate must be one of the most important factors besides the electrochemical behavior.

In order to catalyze the oxidative de-lignification of white birch Asplund pulp, the stability of the cobalt complex becomes another important factor. As shown in Fig.1, only the cobalt complex with both higher catalytic activity for guaiacol oxidation and higher stability in alkali solution increased the delignification rate significantly under the applied condition. Of the cobalt complexes investigated, Co-salen was the most effective and decreased the kappa no. about 100 points as compared with control.

From these results, the potential catalytic activity of cobalt complex for oxidative delignification of Asplund pulp could be postulated reasonably by checking the electrochemical behavior as determined by CV, the ability to complex with substrate as determined by visible absorption spectra and the stability as determined by concentration of soluble cobalt in filtrate after heating at 100 C for 30 min..

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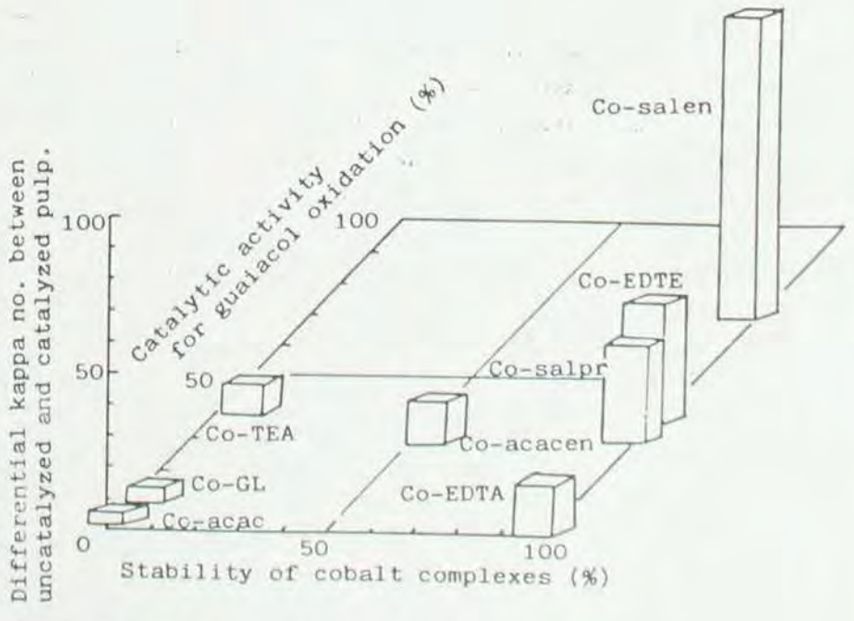

Fig. 1 Factors affecting the catalytic activity of cobalt complexes for oxygen-alkali pulping of white birch Asplund pulp.

ORGANIC ACID PULPING OF WOOD. PART I. AN OVERVIEW OF APPLICATIONS

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ABSTRACT

The use of organic acids in pulping is briefly reviewed. Laboratory scale cooking of aspen and spruce chips demonstrated that good delignification can be achieved with aqueous acetic acid (50-95%) at 175-220°C for 30-60 minutes. The stronger reaction conditions are necessary for softwoods. Acetic acid can be recovered from waste liquors by liquid-liquid extraction with ethyl acetate. A revolutionary new pulping process based on ethyl acetate/acetic acid/water is also described. Chemical recovery costs are greatly reduced because a two-phase liquid-liquid system results after proper adjustment of the solvent ratios.

INTRODUCTION

There are a variety of serious problems associated with conventional pulping processes, such as kraft and sulfite. The predominant kraft process is malodorous, energy intensive, gives low pulp yields and requires very high capital expenditures. The latter requirement will limit future investment in kraft pulping. Conventional acid sulfite pulping is plagued by pollution problems. To circumvent these difficulties, organic acid pulping of wood has been investigated as an alternative method.

Alternate Pulping Systems

During the past 20 years, a variety of non-conventional solvent pulping methods have been explored. Solvents such as glycols, amines, ketones, dimethylsulfoxide, dioxane, phenol, nitric acid, and aliphatic alcohols, have been evaluated as pulping media. Poor pulp quality, chemical losses and recovery, and environmental problems have plagued the further development of most of these processes.

Aqueous ethanol pulping has been recently promoted for delignification of hardwoods. However, catalysts such as mineral acids, Lewis acids or magnesium chloride, are necessary to pulp softwoods. Pulp strength is generally comparable to sulfite pulps. Although the aqueous ethanol organosolv process has reached the pilot plant stage, energy requirements for ethanol recovery and the need for total byproduct utilization may limit further development (1-4).

Less attention has been paid to the use of organic acids as pulping agents. Buchholtz and Jordan (5) described a pulping process in which hardwood or softwood chips were boiled in an 80% formic acid solution containing a catalyst (not identified). Hardwood chips were reportedly pulped to a Kappa number of 60-65 (i.e., lignin content of 9-10%) in 45 minutes with a yield of 59%. However, acetic acid shows much greater promise as a pulping agent.

ACETIC ACID PULPING

It has been known for a long time that acetic acid acts as a solvent for lignin. However, there are few published investigations on the use of acetic acid for pulp production. In 1944, Wiltshire (6) boiled wood chips in glacial acetic acid at atmospheric pressure and was able, by the addition of a small amount of sulfuric acid, to produce satisfactory pulp. Herdle et al. (7) also conducted pulping experiments using strong acid catalysts in acetic acid media. Their work focused on the production of dissolving pulp for conversion to cellulose acetate, but some of their results have a wider significance.

DeHaas and Lang (8) were able to eliminate the need for a strong acid catalyst by increasing the temperature at which the pulping was carried out. They obtained pulps with good strength properties from hardwood and softwood chips by using a solution of 85-96% acetic acid at a temperature in the range 150-205°C for 2-5 hours. They asserted that water content in excess of 15% (of the cooking liquor) reduced the pulp yield as a result of polysaccharide hydrolysis, slowed the delignification process, and caused precipitation of the lignin.

Recent work in our laboratory has convincingly demonstrated that a pulp with a satisfactory Kappa number (10-40) may be obtained with an excellent yield (50-60%) by cooking chips in a liquor composed entirely of acetic acid and water at a liquor-to-wood ratio of 4:1 to 8:1. The maximum degree of delignification at the lowest reaction temperature was observed for aspen when the cooking liquor contained 75% acetic acid by volume. An increase in the acetic acid concentration from 75% to 87.5% by volume improved the selectivity of the process for lignin dissolution (Figure 1) and increased the pulp yield for a fixed Kappa number. However, the delignification rate was lower in the 87.5% solution, and it was necessary to increase the reaction temperature or to extend the reaction time in order to obtain

the desired Kappa number. For every reaction temperature and liquor composition, there existed an optimum cooking time, at which delignification reached a maximum value. Cooking beyond that point led to further lignin condensation and an increase in the pulp Kappa number (9). The activation energy for delignification of aspen in 50-87.5% acetic acid ranged from 38 to 46 kcal/mole.

The importance of washing the cooked chips with solutions that are good lignin solvents was demonstrated for the small batch cooks. Washing with fresh cooking liquor and acetone proved to be very effective for removing the lignin fragments created during the cooking step.

Aqueous acetic acid pulping of softwoods proved characteristically more difficult. Stronger conditions were necessary to obtain spruce pulps with lignin contents comparable to aspen pulps. For example, to obtain a Kappa number in the range of 20-40, the acetic acid concentration must be 75-87% by volume, the temperature 185-215°C, with a total cooking time of 1-2 hours. The effect of reaction time and temperature on delignification of spruce is shown in Figure 2.

Satisfactory strength properties were obtained for both aspen and spruce pulps at optimum cooking conditions. The highest strength properties and yields and the lowest lignin contents were obtained with the cooking conditions shown in Table 1.

Species	Acetic Acid Concentration	Maximum Temperature	Time	Liquor-to-Wood Ratio	Kappa Number	Pulp Yield
Aspen	87%	185°C	60 min.	4/1	10	55
Spruce	87%	220°C	45 min.	8/1	16	46

Table 1. Optimum Acetic Acid Cooking Conditions

Acetic Acid Recovery

An important consideration with any pulping process is chemical recovery, both for economic and environmental reasons. There are a number of possible alternatives for recovery of acetic acid from waste streams. The most viable and proven method is liquid-liquid extraction. A variety of solvents are available for organic acid extraction including 2-butanone, trioctylphosphine and several amines (4). Ethyl acetate is also effective for liquid-liquid extraction of acetic acid from aqueous solutions and has a low cost. This ester has a high distribution coefficient (D_a = 1.11) indicating that it will strip acetic acid with ease, requiring only small volumes. Since ethyl acetate could also be produced at the mill site from acetic acid and ethanol, this ester is the solvent of choice for recovery of acetic acid by liquid-liquid extraction. A computer model of acetic acid pulping and recovery based on ASPEN software (PDP-1134 Computer) is under development in the Department of Forestry.

Overview of Acetic Acid Pulping

Satisfactory pulps can be produced with aqueous acetic acid cooking liquor. From a recovery standpoint, it would be desirable to have a low concentration of acetic acid in the fresh liquor. However, a high concentration of acetic acid (> 75%) must be maintained in the liquor to retain the desired pulp properties and cooking conditions. As the water content of the cooking liquor is increased, the delignification selectivity is decreased and pulp strength properties suffer due to increased hydrolysis of polysaccharide components.

A high concentration of acetic acid is necessary in the pulping liquor because the acetic acid is thought to perform two roles. It is a source of the hydronium ions for acceleration of the acid hydrolysis of lignin and a solvent for the lignin fragments produced by the hydrolysis reaction. Only a small amount of water is necessary for dissociation of the acetic acid. What is needed, then, is a substitute solvent for water that is also miscible with both acetic acid and water.

AN ETHYL ACETATE/ACETIC ACID/WATER PULPING SYSTEM

It is proposed that ethyl acetate serve as the substitute solvent for water in acetic acid pulping to give a new solvent based pulping process comprised of ethyl acetate, acetic acid and water (acetate pulping). The positive implications of the addition of ethyl acetate to the pulping medium are profound and include:

1. A reduction in the amount of water required in the system.
2. Reduced cooking time.
3. Lower pulping temperatures for given cooking pressures.
4. Higher strength pulps.
5. Higher yields.
6. Enhanced solubility of lignin in the pulping solvent.
7. Simplified recovery of organic chemicals.

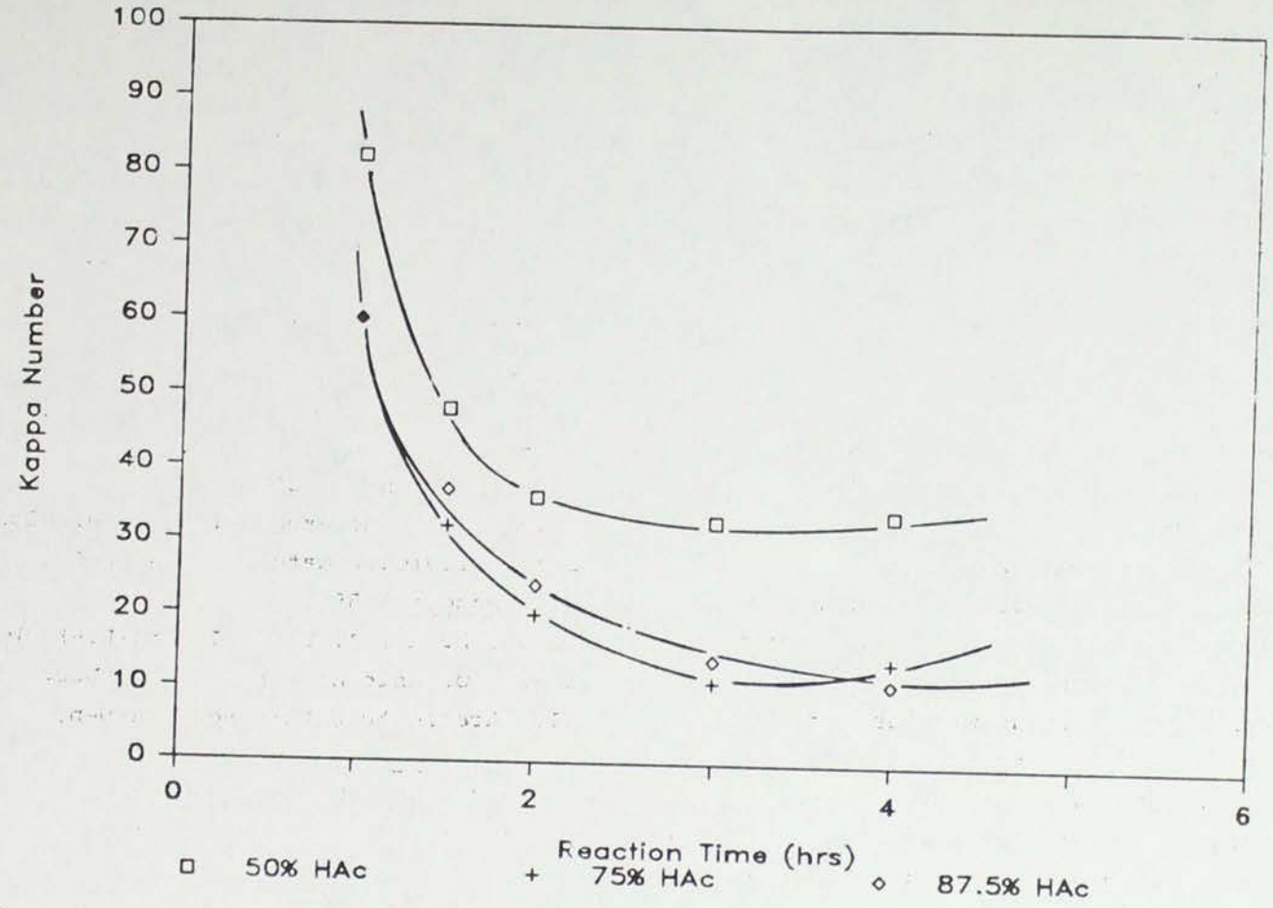

Figure 1. Effect of acetic acid concentration and cooking time on delignification of aspen chips.

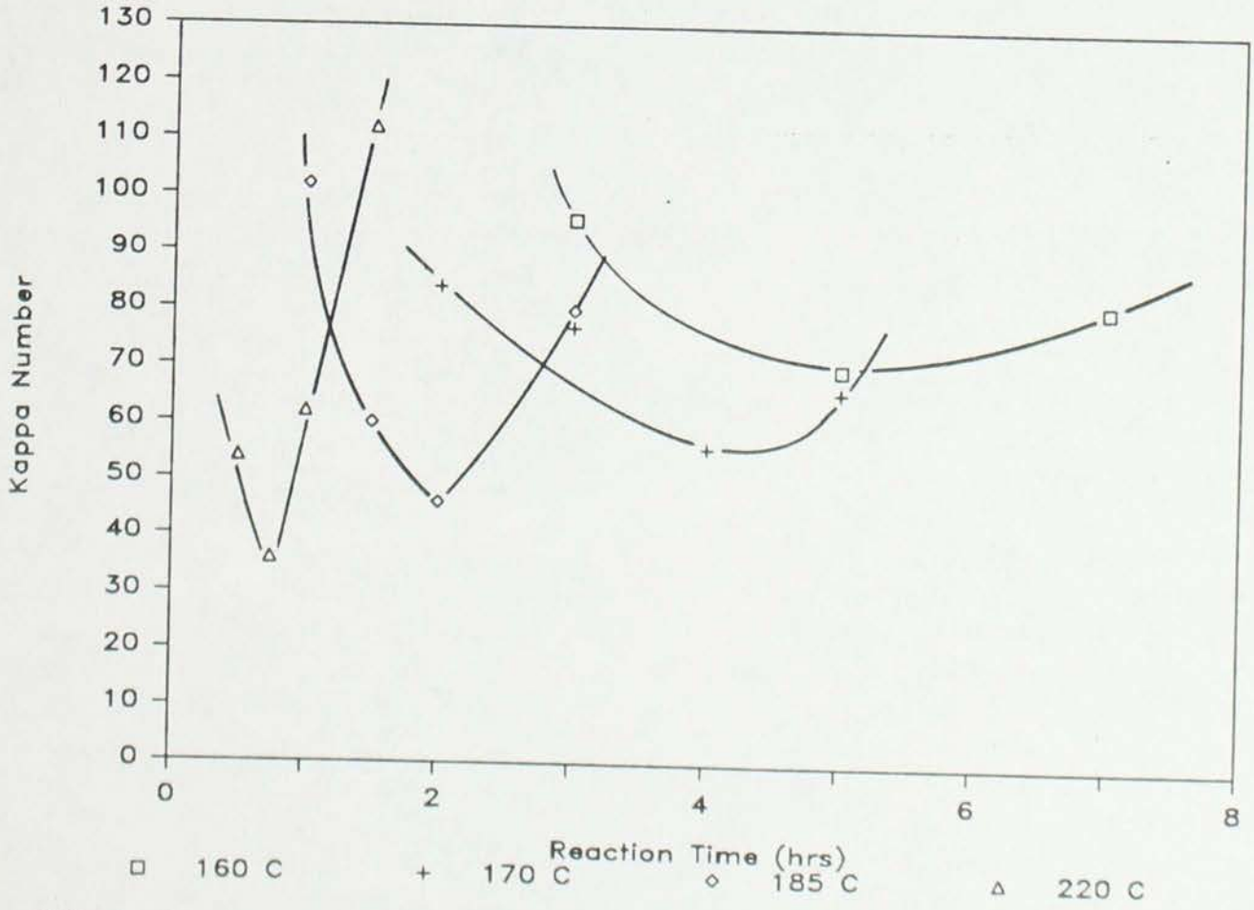

Figure 2. Effect of temperature and cooking time on delignification of spruce chips.

Ethyl acetate is entirely miscible with acetic acid and water, however, by proper adjustment of the solvent ratios, a two-phase system results; an organic phase composed of ethyl acetate and acetic acid, and an aqueous phase. This facile separation (decantation) drastically reduces energy requirements for chemical recovery. Sugars are obtained from the aqueous phase for fermentation and a pristine lignin can be easily precipitated from the organic phase. The lignin properties are characteristic of other organosolv lignins which are uncondensed and contain no sulfur. Thus, possible byproduct utilization of lignin is a distinct possibility.

Another less obvious benefit of acetate pulping is that much less acetic acid is necessary in the pulping liquor. Since ethyl acetate has good lignin solvent properties, it can be substituted for acetic acid as well as water. This is demonstrated in the preliminary results shown in Table 2. As low as 26% acetic acid, with ethyl acetate and water, gives a good yield and a very low lignin content. Further reductions are probably possible. The recovery schemes would be greatly simplified at lower acetic acid concentrations.

Acetic acid, %	Ethyl acetate, %	Yield, %	Kappa No.
50%	--	55%	30
75%	--	52%	10
33%	33%	48%	8
26%	49%	48%	11

Table 2. Acetic Acid and Ethyl Acetate Pulping of Aspen[1]

[1] 165-170°C, 3 hours total cooking time, remainder of liquor is water.

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STUDIES ON WOOD FIBRE STRUCTURE USING BIOLOGICAL DECAY ORGANISMS

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ABSTRACT

Despite considerable research involving the use of both physical and a wide range of chemical techniques, the distribution of the major cellular components (lignin, cellulose, hemicelluloses) within the S_2 cell wall of wood fibres remains a controversial issue. Apart from examples which show distinct polylaminate walls, the S_2 layer of wood fibres is generally considered to be a rather homogeneous entity which is composed ultrastructurally of an array of lamellae. Reports are available however, particularly in the older literature which refer to the occurrence of concentric layers within the S_2 of fibres which may represent variations in structure and/or component distribution. However, since the majority of these observations were made on samples after the application of various swelling agents, the authenticity of the layers has not been fully accepted. To add further suspicion the apparent difficulties in demonstrating such layers using UV or electron microscopy, particularly in softwoods has lead to further sceptism.

In the present study, biological decay organisms have been used as "tools" to select and partially degrade the S_2 wall layer of fibres in order to obtain further evidence for the distribution of the major cellular components. The study involved a correlated light and electron microscopic investigation of fibre walls at various stages of decay caused by a range of fungal (white, brown and soft rot species) and to a lesser extent bacterial and actinomycete types. For a comparison, both delignified (acid chlorite), hydrofluoric acid treated and chemically pulped (sulfate, sulfite) fibres were compared with the decay patterns produced in fibre cell walls by the microorganisms.

The characteristic, preferential and mild manner of the decay process by the white rot fungus Schizophyllum commune gave strong evidence for a concentric and non-homogeneous distribution of S_2 wood components. Decay by S. commune caused the development of pronounced concentric "slits" within the S_2 layer of fibres the location of which showed a close similarity to previously reported concentric layers, as well as indicating the existence of "weak regions". A similar form of S_2 delamination was recognised in chemically pulped, delignified and acid treated fibres. S_2 delamination was also recognised but less frequently with cellulase-less Phlebia mutants during progressive cell wall delignification. Degradation by brown rot fungi caused an enhancement of concentric layers within the S_2 of softwood fibres during early stages before lignin skeletons were produced. Further evidence for non-homogeneity was suggested by the frequent concentric localization of soft rot cavities within the S_2 of wood fibres and by the enzymic diffusion from bore hyphae produced by white rot fungi during penetration of wood fibre walls.

The results which give strong evidence to support a non-homogeneous and concentric distribution of S_2 fibre wall components will be discussed in relation to current ideas on fibre structure and component degradation by decay organisms.

ELECTRON TRANSFER REACTIONS IN PULPING SYSTEMS

DONALD R. DIMMEL AND LOIS F. PERRY

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ABSTRACT

Lignin model compounds containing a phenolic "A" ring, α-OH, and β-aryl (ring "B") ether, with different substituents located on rings A and B, have been synthesized and degraded under a variety of conditions. Substituent changes on ring B had a large effect on fragmentation reactions of the models under "soda" conditions but no effect under "soda/AQ" or "kraft" conditions. Substituent changes on ring A had large effects under soda/AQ and kraft conditions for model degradations. These substituent-reactivity relationships indicate that the slow step in the mechanism for model fragmentation under soda conditions is cleavage of the β-aryl ether bond and under soda/AQ and kraft conditions is quinonemethide formation.

KEYWORDS: Delignification, Mechanisms, Lignin Models, Fragmentation, Synthesis

INTRODUCTION

Single electron transfer (SET) reactions offer a way to remove lignin from wood (1). Scheme I presents a mechanism by which SET reactions from anhydroquinone (AHQ) species to lignin quinonemethide (QM) species can lead to lignin bond ruptures (and thus delignification). The reactions outlined in Scheme I have been verified by room temperature electrochemical studies of lignin QMs in organic solvents (2).

In contrast to this "radical" view of AHQ induced delignification chemistry, Scheme II offers a generally more accepted "ionic" mechanism. Here AHQ^{-2} adds to the α-carbon of a lignin QM to give an "adduct"; in a subsequent step, the adduct fragments to AQ and two phenolate ions (3-6). This chemistry is analogous to some of the ionic mechanisms proposed for soda and kraft pulping systems (7).

MECHANISM DIFFERENTIATION

A key difference between the pure ionic and SET mechanisms of delignification is that the former produces only phenolate ion fragments, while the latter gives some phenolate radical fragments. If rupture of the β-aryl ether bonds is the slow step in delignification, the SET and adduct mechanisms predict that substituent-types on the aromatic fragments could have large effects on degradation rates. Phenolate ions, as produced in the adduct mechanism, are electron-rich species and thus are stabilized by electron-withdrawing ring substituents (8). Phenolate radicals (SET mechanism) are electron-poor species and are therefore stabilized by electron-releasing ring substituents (8).

Delignification of wood and simple fragmentation of lignin model compounds are, however, multistep reactions, of which the fragmentation steps may not be the slow steps in the mechanisms. In fact, quinonemethide generation is probably the slow step (9). Depending on where they are located, aromatic ring substituents may or may not influence the rates of QM generation.

Substituent effects may, however, still provide information about the mechanism of the fragmentation step, even if QM generation is the slow step. This is possible if certain steps are reversible and interaction between reactive intermediates occurs. Consider, for example, the following SET reactions which might exist during the competitive reactions of in situ generated QMs which contain different substituents:

$$QM + AHQ^{-2} \rightleftharpoons QM^{\cdot-} + AHQ^{\cdot-} \qquad (a)$$

$$QM' + AHQ^{-2} \rightleftharpoons QM'^{\cdot-} + AHQ^{\cdot-} \qquad (b)$$

$$QM^{\cdot-} + QM' \rightleftharpoons QM + QM'^{\cdot-} \qquad (c)$$

$$QM^{\cdot-} \longrightarrow ArO^{-} + Ar'O\cdot \qquad (d)$$

$$QM'^{\cdot-} \longrightarrow ArO^{-} + Ar''O\cdot \qquad (e)$$

If two quinonmethides (QM and QM') were generated simultaneously, AHQ^{-2} could react with either one. If one of the quinonemethides (i.e., QM') forms a more stable radical anion, you would expect AHQ^{-2} to preferentially undergo SET reactions with that quinonemethide, i.e., Eq. (b) preferred to Eq. (a). Many SET reactions are characterized by SET steps between species as part of a chain mechanism (10-12); therefore, the equilibrium indicated by Eq. (c) should occur and should be shifted in the direction of the more stable species. Depending on the stabilities of Ar'O· and Ar"O·, fragmentation steps (d) and (e) would be expected to proceed at different rates.

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WOOD-DEGRADING BACTERIA - NEW MICROBES FOR BIOCONVERSION OF LIGNOCELLULOSE

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ABSTRACT

Recent studies have clearly demonstrated that bacteria are able to degrade wood. Results from earlier studies indicated that lignin protected wood from being degraded by cellulolytic bacteria. This led to the erroneous assumption that bacteria are unable to degrade wood.

Wood-degrading bacteria seem to constitute a very specialised group that are adapted to lignified substrates. These bacteria have recently received considerable attention within the field of wood preservation. This interest has been evoked by the discovery that they may cause significant degradation of preservative treated timber. Their wood-degrading activity indicate that they, in analogy with white rot fungi, may have a potential for bioconversion of lignocellulosic materials.

Wood-degrading bacteria attack lignocellulose fibres basically in two diffrent ways. The first type is a form of erosion starting from the cell lumen (erosion bacteria) and the second is characterised by penetration of the bacteria into the fibre wall where subsequent degradation occurs (cavitation bacteria, tunnelling bacteria). The different forms and patterns of attack on wood substrates indicate that a rather large number of different species exist. However, only one wood-degrading bacterium seems so far to have been isolated into pure culture.

The information on wood-degrading bacteria is still rather limited. Only a few types of attack have been described in any detail. All bacteria attack the carbohydrate fraction in wood and we have observed morphological evidence for lignin degradation. Experiments with wood containing ^{14}C-labelled lignin, ^{13}C-NMR studies, and Klason lignin analyses have shown that tunnelling bacteria cause a substantial degradation of the lignin in wood.

There appears to be a number of advantages in using wood-degrading bacteria for the bioconversion of lignocellulose:

1. No preconditioning of the substrate is required. This is in contrast to ordinary cellulolytic bacteria. High lignin levels do not prevent degradation by wood-degrading bacteria. Substantial attack has been observed in lignocellulosic materials with lignin levels well above 30 percent.
2. Tunnelling bacteria have a remarkable ability to degrade durable timbers. This seems to indicate that they may be employed for bioconversion of substrates which contain extractives that are toxic to other microorganisms.
3. There is no need for cloning "ligninase" genes into these bacteria since they already possess lignolytic activity.
4. A presumably more rapid invasion of the substrate compared with fungi. The view that myceliated organisms, fungi and actinomycetes have a better capacity for invasion seems to a large extent be a misconception.
5. A quicker and larger build up of biomass compared with fungi.
6. Nitrogen fixation has been found to occur in substrates which are being attacked by wood-degrading bacteria. Thus there appears to be a possibility of combining nitrogen fixation with bioconversion of lignocellulosic materials.

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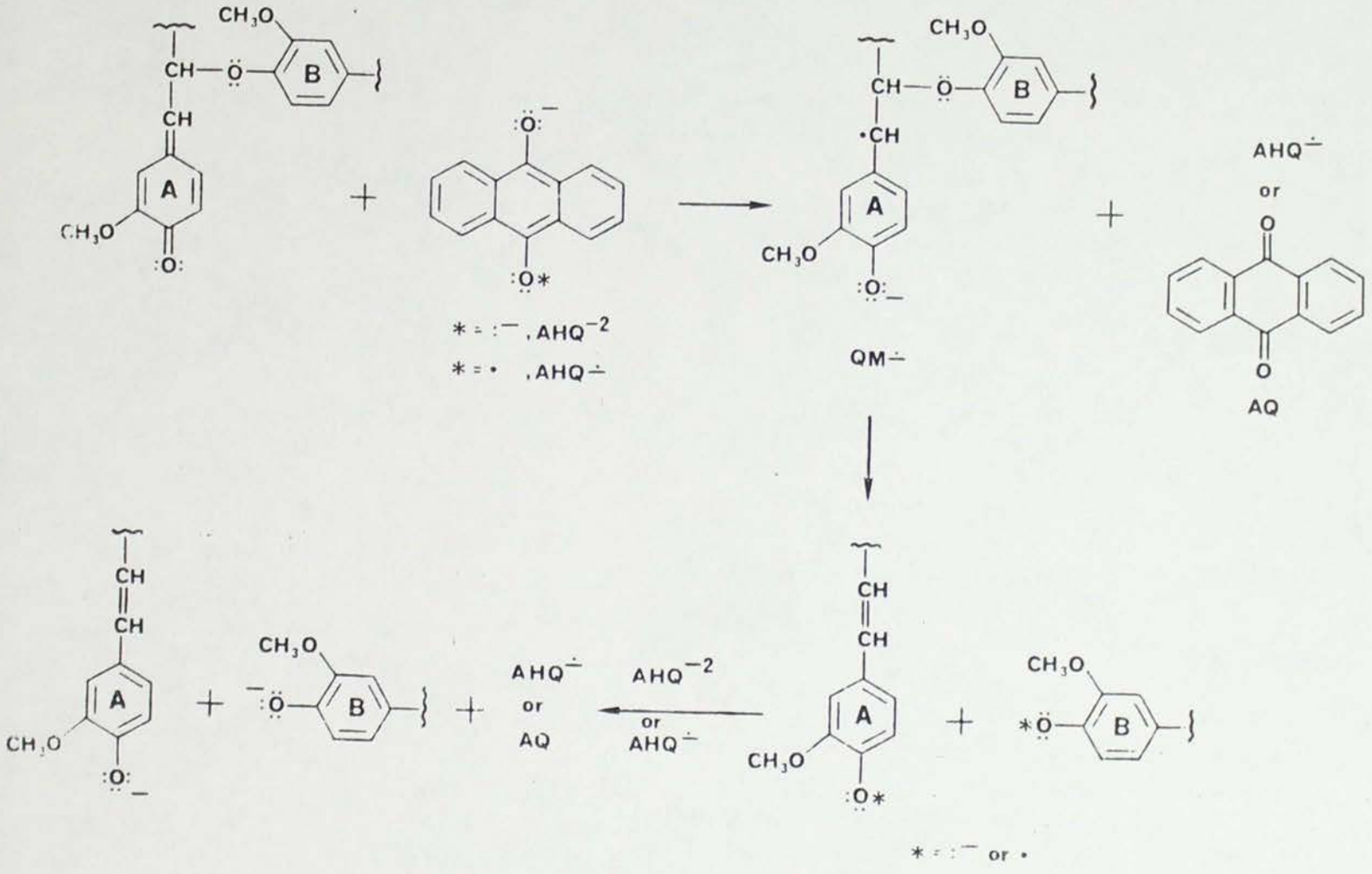
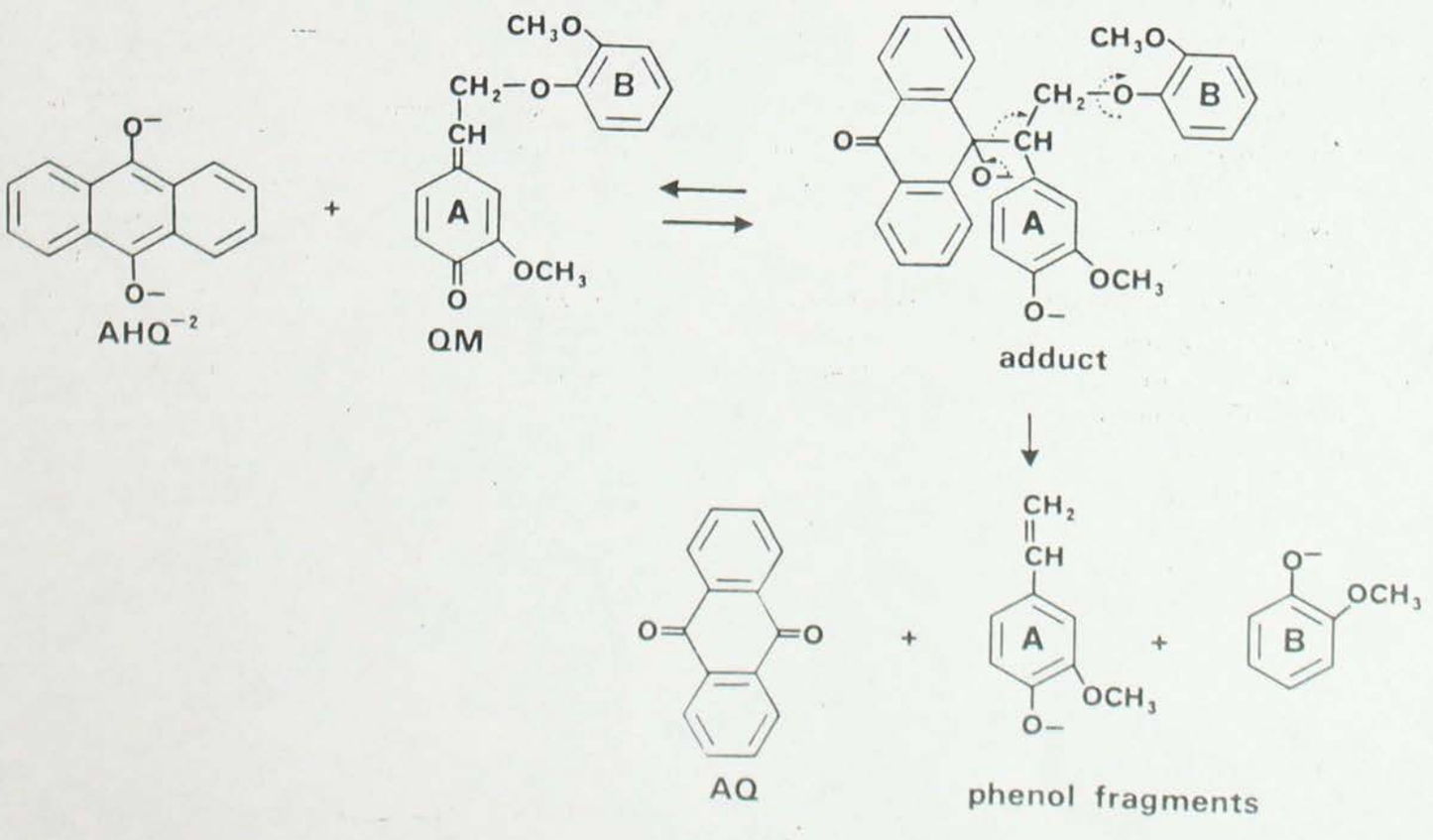
SCHEME I

Delignification via AHQ-induced SET Reactions



SCHEME II

Delignification via AHQ Adduct Reactions



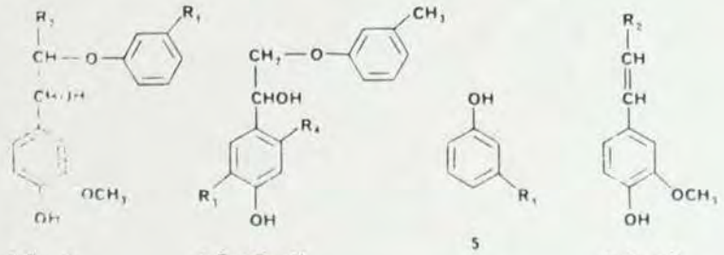
resulting phenolate ion and radical fragments. Since QM-AHQ adduct reactions are reversible (13), similar arguments apply; product distributions from competitive reactions will reflect either the stabilities of the adducts or the stabilities of the resulting phenolate ion fragments.

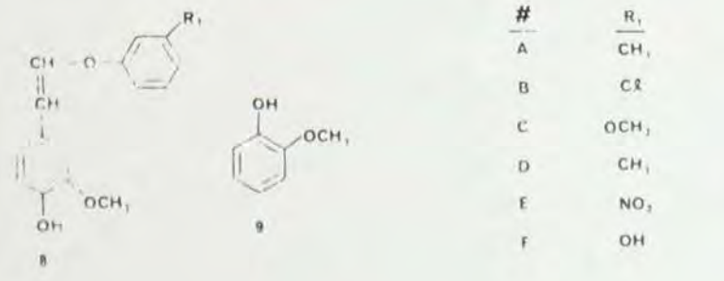
This report covers the synthesis and reactions of lignin model compounds which have different ring A and ring B substituents. Our goal is to detect reactivity differences which will provide information defining specific reaction mechanisms, especially with regard to QM-additive reactions.

RESULTS

Lignin model compounds of the type **1A-F**, **2A-E**, **3A**, and **4A** have been synthesized and subjected to various types of degradation reactions. The quantity of phenols **5A-E** produced was taken as an indication of β-aryl ether fragmentation and, consequently, delignification. Other products observed included vinyl phenols **6** and **7**, vinyl ethers **8A-D**, and guaiacol **9**. The latter, only present in very small amounts, apparently arises from a cleavage reaction of C_α and ring A.

The degradations of the models were performed in the presence of NaOH (soda), NaOH and NaSH (kraft), NaOH and glucose (glucose control), and NaOH, glucose and AQ (soda/AQ). The fragmentation efficiencies followed the order soda/AQ ≥ kraft > glucose control > soda, regardless of the model type which was being degraded.





#	R_1
A	CH_3
B	Cℓ
C	OCH_3
D	CH_3
E	NO_2
F	OH

The ring B substituent (R_1) affected the fragmentation efficiencies under soda conditions but not the other conditions. Variations in ring A substituents had large effects on the degree of fragmentation, with the following order: **4** > **1A** > **3**. Competitive degradation of model pairs, i.e., **1A** and **1D**, in dilute solutions, showed no major differences from degradation performed with single models.

CONCLUSIONS

The results to date are very informative with regard to defining the slow steps in soda and soda/additive degradations, but have not yet allowed distinction between SET and adduct mechanisms. The slow step in the mechanism for model fragmentation under soda conditions is the cleavage of the β-aryl ether bond; the alkalinity of the solution affects the extent of model fragmentation *vs.* vinyl ether by-product formation. The slow step in the mechanism for model fragmentation under soda/AQ, soda/glucose and kraft conditions appears to be quinonemethide formation.

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A COMPARATIVE STUDY OF ORGANOSOLV AND KRAFT PULPS

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ABSTRACT Alcohol pulps produced from aspen wood at the pilot level had higher yields than kraft. When bleached using seven different sequences they consistently produced brighter pulps in fewer stages with lower chemical consumption. Bleached alcohol pulp had strength properties equivalent to kraft at the same brightness. Thus, alcohol pulps are a suitable replacement for kraft in papermaking applications.

INTRODUCTION Previous work (1) has shown the technical feasibility of producing good quality bleachable hardwood pulps using an organosolv pulping technology: the Alcohol Pulping and Recovery (APR) Process. Fibers produced by this low-capital-cost, low-environmental-impact process, have successfully replaced the hardwood chemical pulp component of the furnish in pilot paper machine trials for tissue and writing grades.

Previous reports have compared APR pulps produced at the pilot level with conventional pulps produced on an industrial scale. In this study APR Process alcohol pulps and kraft pulps produced on a pilot scale from a single batch of aspen chips from the state of Wisconsin, USA, were compared for yield, strength, chemical composition and response to bleaching sequences.

RESULTS AND DISCUSSION At equal kappa numbers the APR process produced pulp with a screened yield 1.2 to 1.7 percentage points higher than kraft.

Alcohol pulps were bleached much more readily than kraft pulps in terms of either number of bleaching stages or chemical consumption to achieve an equivalent brightness. The data in Table 1 show that higher brightness levels were reached for alcohol pulps with every sequence studied. In fact, alcohol pulps bleached in three stages as bright (CED) or brighter (C_DED) than kraft by CEDED or C_DEDED. The superiority of alcohol pulp response to bleaching treatments is exemplified by the fact that kappa numbers after first alkaline extraction were 20-50% lower than kraft. This indicates that alcohol pulp residual lignin reacts much more readily with bleach chemicals than kraft. This enhanced reactivity is maintained throughout all subsequent bleaching stages. When pulps with comparable CE- or C_DE- kappa numbers were treated with the same subsequent bleaching conditions, alcohol pulps were always brighter than kraft. Alcohol pulps can thus be bleached to equal brightness at commercial scale with lower capital investment (fewer stages) and lower operating cost (lower chemical consumption).

Table 1

BLEACHED PULP BRIGHTNESS

(Ranges for each pulp type for all initial chemical charges)

Bleach Sequence	Kraft	Alcohol
CEH	75.6 - 78.8	81.6 - 85.5
CEHD	86.0 - 87.0	87.0 - 90.0
CED	83.8 - 85.5	86.5 - 88.5
CEDED	87.5 - 89.0	89.0 - 90.5
C_DED	82.2 - 86.0	88.0 - 89.5
C_DEDED	87.0 - 88.0	87.8 - 90.2
DED	85.0 - 87.8	86.5 - 89.2

Saccharide analyses show that both bleached and unbleached alcohol pulps produced under these conditions contained, on a lignin free basis, 88-89% glucan, as compared with 81-82% for kraft. Xylan was much higher in kraft (16-19%) than in alcohol (8.4-9.4%) pulps, although mannan is slightly higher in alcohol pulps. This difference in carbohydrate

composition can most readily be explained in terms of the difference in the carbohydrate degradation mechanism in kraft (alkaline peeling-off reaction) vs. alcohol (acid hydrolysis) pulping.

Alcohol pulps had strength properties similar to kraft since equivalent tear-tensile relationships were obtained for both processes. Thus, at equal breaking lengths alcohol and kraft pulps had tear indices within 1.0 $mN.m^2/g$ of each other for both bleached and unbleached pulps. Both bleached pulps had higher tear indices than unbleached when compared at the same breaking length.

Strength properties of unbleached alcohol pulp were 62-79% of kraft at 24 mL/g kappa no. and 74-82% at 18 mL/g kappa no. (Table 2) when compared at 1.50 cm^3/g bulk.

Table 2

UNBLEACHED PULP PROPERTIES AT 1.50 cm^3g/gm BULK

	Alcohol		Kraft	
Kappa No., mL/g	24	18	24	18
Tear Index, $mN.m^2/g$	5.7	6.1	7.2	7.8
Burst Index, $kPa.m^2/g$	2.9	3.1	4.7	4.2
Breaking lengths, km	5.6	6.7	8.2	8.2
Viscosity, mPa.s	29.4	29.2	49.0	36.7
Relative refining time	9.0	1.0	3.6	2.6

Once bleached to 88 brightness (by C_DED for alcohol and C_DEDED for kraft), the difference between the two types of pulps was practically eliminated: when samples with the same initial kappa no. were compared, the properties of alcohol pulps were within ± 15% of kraft. (Table 3) Thus alcohol pulps, in spite of having lower unbleached strengths than kraft, produced bleached pulps with comparable physical properties, probably because lower chemical charges and fewer stages were required to achieve the same target brightness.

Table 3

BLEACHED PULP PROPERTIES AT 1.50 cm^3/g BULK

	Alcohol		Kraft	
Original kappa no., mL/g	24	18	24	18
Tear index, $mN.m^2/g$	8.1	7.5	7.0	8.5
Burst index, $kPa.m^2/g$	3.0	2.9	3.0	3.2
Breaking length, km	5.3	5.2	6.1	5.8
Viscosity, mPa.s	30.9	22.8	27.3	23.7
Relative refining time	4.2	1.0	1.8	1.3

Beatability of unbleached pulps, as inferred from relative refining times, followed the order: lower kappa alcohol > lower kappa kraft > higher kappa kraft > higher kappa alcohol. This order remained the same after bleaching.

CONCLUSIONS Alcohol pulps from the APR Process compared favorably with kraft pulps. They were obtained in higher yields and bleached to high brightness levels with less chemicals and in fewer stages than kraft pulps. While unbleached alcohol pulps had strength properties below kraft, bleached samples were comparable and in some instances easier to refine. This study confirmed that alcohol pulps exhibit properties suitable for replacement of kraft pulps in papermaking applications.

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BIOTECHNOLOGICAL METHODS FOR VALORIZATION OF BARK WASTES

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ABSTRACT

Barks and bark wastes may be valorized by several non-biotechnological methods, but are frequently burnt or discarded. Today new processes can be developed using microorganisms to detoxify or convert barks into valuable products. Due to the specific biochemical composition of barks, only selected strains or populations can be used in such processes. Results obtained during personal experiments and found in the literature show that barks should now be considered as valuable lignocellulosic substrates.

KEYWORDS: Bark, Valorization, Biotechnological Processes.

INTRODUCTION

Bark remains today a low-value waste product from the wood and pulping industries in many countries. In France and most parts of Europe the barks are dumped or burnt when possible. Some methods have however been suggested to use part of these barks in different processes. They are used in horticulture to preserve soil or peat moisture or for decoration and also as a substrate to grow orchids. The barks may also be heated and pressed to obtain fuel-grade briquettes with or without a preliminary fermentation. Small amounts of bark are sometimes incorporated into particleboard by some manufacturers, depending on the species of wood utilized. Some recent attempts to incorporate barks in cattle feeding were unsuccessful because of the low proportion of bark allowed in the diet. The main reason why barks are such a problematic substrate is their richness in simple and polymerised phenolic compounds, especially tannins, known for a long time as inhibitors of enzymes and growth for most microorganisms. The phenolics may be easily extracted from barks with hot water or alcohol and could be used in the preparation of adhesives in particleboard manufacture. Some authors report positive result(2) but a controversy remains on this valorization. In addition to the phenolic fraction, barks contain a lot of water-soluble sugars and also typical lignocellulosic polymers (cellulose, hemicelluloses, lignin) but their utilization in biotechnological processes has been neglected because of the antimicrobial components. However some processes have been developed taking into consideration the particular biochemical composition of this substrate.

Enrichment of barks with single-cell proteins:

Some fungi have been known for years to be capable of growth on bark extract or acid hydrolyzed bark, e.g. Phanerochaete chrysosporium, Aspergillus niger and A. fumigatus, Penicillium sp. and Candida tropicalis. These fungi (cited in ref. 1) gave generally poor yields of proteins except for C. tropicalis which was found to degrade pine tannins as well as some of our yeast strains isolated from barks (11). The bioconversion of bark to SCP patented in Canada by Daugulis and Bone (3) needs, before industrial applications, to solve the standard problems associated with lignocellulosics and to use strains adapted to tannins or, preferably, degrading these polyphenolics.

Biodegradation of tannins:

Depending on their variable structure (10) tannins are generally considered as resistant to biodegradation. Hydrolyzable tannins (also named gallotannins) have been known for sixty years to be degradable by fungi and more recently by yeasts (for references see 9). Condensed tannins, which are the most widespread in plants and especially in coniferous barks, are very recalcitrant to biodegradation. We isolated some years ago a collection of bacterial strains able to degrade tannic acid as well as chestnut tannin (9) and produce a tannase activity. These tannins are biodegraded into gallic acid, which accumulates in the cultures before being utilized by the bacteria. This property could be used for the production of gallic acid (5) from tannins or from homogeneous bark extracts containing only gallotannins. We demonstrated also recently the degradation of condensed tannins (wattle and quebracho) by different bacterial strains (4) and also by different species of yeasts (6,11). The bacteria are better degraders but the yeasts could be used at the same time for protein production and enrichment. These original results prove that microorganisms can degrade or convert tannins as well as the other lignocellulosic components.

Biodegradation and bioconversion of bark extracts:

Bark extracts can support the growth of adapted populations of microorganisms (8) such as the tannin-degraders reported above. Tannins in extracts of pure, oak and gaboon-wood barks were degraded as well as commercial or purified tannins (6 and Deschamps and Leulliette, Phytopathol. Z., in press). These bacteria or yeasts can utilize at the same time the other soluble components. Some strains with no particular ability to degrade phenolics, but able to grow in the presence of tannins, have been used to decrease the amount of non-phenolics. Both the increase of the phenolic content and removal of sugars give a more reactive extract for preparation of adhesives (12). Fast growing strains in continuous cultures could be useful for continuous production of such a highly-reactive extract.

Controlled solid-fermentation or composting of bark chips:

Composting of barks has proved to be difficult because of bark antimicrobial compounds such as tannins (13), so barks are frequently mixed (20 to 40% as bark) with different agro-industrial or municipal wastes. This proportion and the long incubation time mean that only a limited fraction of the industrial bark wastes can be used this way. Sometimes tannins must be extracted after or before composting to obtain a non-toxic product for horticultural or agricultural uses (14). We showed some years ago that barks can be degraded by mixed bacterial cultures (7) in a liquid fermentation at controlled temperature to obtain degradation of lignin, cellulose and tannins. Pure cultures degraded tannins and cellulose only. These results were confirmed in solid-state cultures (to be published) carried out in a rotating drum fermentor at 39°C with a high moisture level and neutral pH using mixed cultures of an Aeromonas sp. and Gram-positive bacteria such as Cellulomonas sp., Corynebacterium sp. and Bacillus polymyxa. In such controlled but non-sterile conditions tannins were degraded up to 95% in less than one day, no fungal contamination was observed. After 15 to 20 days depending of the mixed cultures lignin was highly degraded (40 to 55% of the initial content) when cellulose was weakly degraded (10 to 15%). These results showed that bacteria could be used in rapid processers for detoxification or longer processes for delignification of barks with better yields than fungi but in more expansive controlled conditions.

CONCLUSION

Barks may be considered today as a valuable substrate for biotechnological processes. The phenolic compounds can be degraded rapidly by bacteria or converted to useful compounds. Detoxified barks may then be used in conventional processes for biomass bioconversion. The biotechnological processes under investigation in several laboratories must pay attention to the unique composition of bark to obtain particular products such as simple phenolics or adhesives.

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END-WISE DEGRADATION OF HYDROCELLULOSE IN MILDLY ALKALINE SOLUTIONS AND ITS RETARDATION BY AMMONIA

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ABSTRACT

At 140 C and the pH range 11 to 9, the rate of end-wise degradation ("peeling") of hydrocellulose declines by a factor of 0.34 for every pH-unit reduced. The peeling rate, however, is strongly retarded in this pH range by the presence of ammonia. The retardation is believed to be caused by the formation of Schiff's bases during the reaction.

KEYWORDS: End-wise degradation (peeling), Hydrocellulose, Ammonia.

INTRODUCTION

It is well known that the end-wise degradation ("peeling") of polysaccharides proceeds rapidly in alkaline solutions in the temperature range 100 to 130°C. The kinetics of this process have been extensively clarified for hydrocellulose (1), softwood glucomannan (2) and amylose (3) above pH 12, but no systematic studies have been performed at lower alkalinities. Consequently, a study was undertaken to clarify the kinetic pattern of alkaline peeling of hydrocellulose in the pH range 9 to 11. During the course of this study it was found that ammonia exerts retarding influence on the rate of peeling in this pH range. This phenomenon was then subjected to a separate investigation.

MATERIALS AND METHODS

Buffer solutions (4) of pHs 9.2, 10.2, and 11.1 were used without dilution. Hydrocellulose was prepared according to Chiang and Sarkanen (5). All kinetic runs were done in 45-ml autoclaves heated in a rocking aluminum block-heater (5). The rate constant (k_p) of peeling reaction was calculated according to equation 1 (1,3),

$$k_p \times t = X_n \, \mathrm{Ln} \frac{L}{L_\infty - L} \qquad \text{Eq. 1}$$

where X_n is the number average degradable chain length (68 for hydrocellulose (6,7,8)) and L_∞ and L are the percent weight fractions lost due to peeling after prolonged reaction time and time t, respectively.

RESULTS AND DISCUSSION

Effect of pH on the Rate of Peeling

When data from peeling experiments conducted at 140°C in the pH range 9 to 11 were applied to equation 1, it was found that L_∞ values were nearly unaffected by the pH of the experiment and satisfactory straight-line relationships corresponding to equation 1 were obtained (Figure 1).

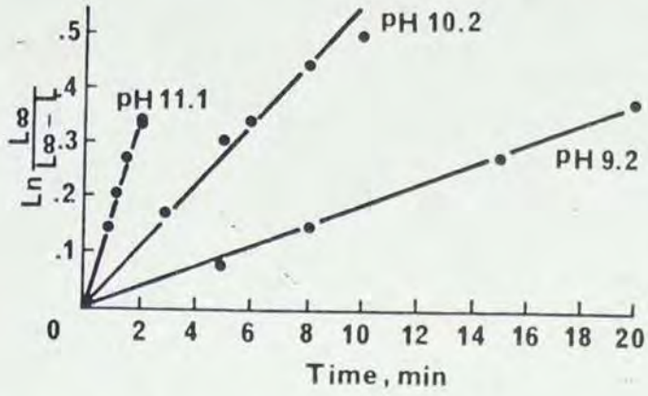

Figure 1. Rate plots, based on equation 1, for the hydrocellulose in three buffer solutions at 140°C.

On this basis, the peeling rate constants were computed. When these values together with those from earlier studies on hydrocellulose (1) and amylose (3) were ploted, as percentages of the calculated peeling rate at pH 14 (1), against pHs, a common sigmoidal curve was obtained (Figure 2, curve 1).

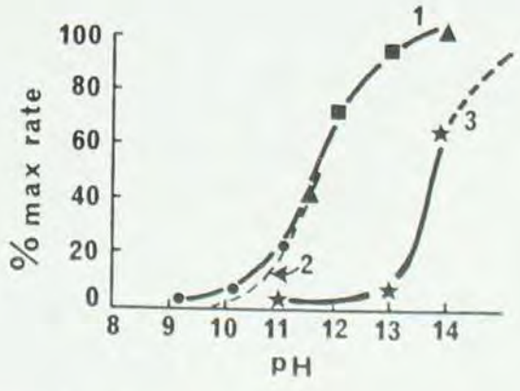

Figure 2. Curve 1: Propagation rate constants, expressed as percentages of the extrapolated constant at pH 14, shown as a function of pH. ■ : Results based on earlier study by Haas et al. (1). ▲ : Present data. ● : Data extrapolated to 140°C for the peeling of amylose (3). Curve 2: Theoretical curve based on the observed inflection point of curve 1. Curve 3: Data for the peeling of hydrocellulose in presence of 0.8M NH_3.

The observed decline in peeling rate at lower pH levels is in conformity with the proposition that the reaction species in peeling is the anion of the reducing end-group, as has been proposed (3). The inflection point in the sigmoidal curve in Figure 2, curve 1 is positioned at pH 11.7

corresponding to the pK-value for the ionization of the reducing end-group. The results suggest that the rate of peeling at lower pH range should be governde by the following expression:

Rate of peeling=k_p x [end-group anion] Eq. 2

If the validity of equation 2 extends to pH values lower than 10, the anticipated rate of peeling can e estimated as a function of pH from the rate observed at pH 11.0 and from the pK-value 11.7. On this basis, expected values for log k_p as a function of pH should conform with the straight line 2 in Figure 3. It can be seen that the experimentally determined log k_p-values are significantly higher than those predicted by line 1.

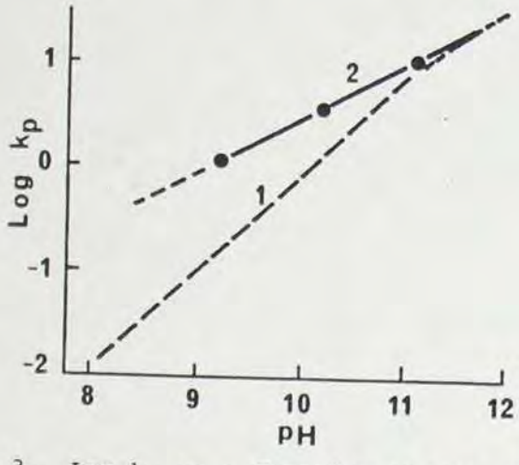

Figure 3. Log k_p as a function of pH. Curve 1: Theoretical curve. Curve 2: Experimental values.

The results indicate that the peeling rate, for some unknown reason, declines less than anticipated with a decrease in alkalinity and may still be significant in a neutral solution.

The possibility prompted us to investigate the peeling process at pH 7. Two runs were conducted in a buffered solution at temperatures 140°and 170°C. The results are illustrated in Figure 4 and demonstrate that the initial rate of the peeling reaction is indeed significant at 140°and

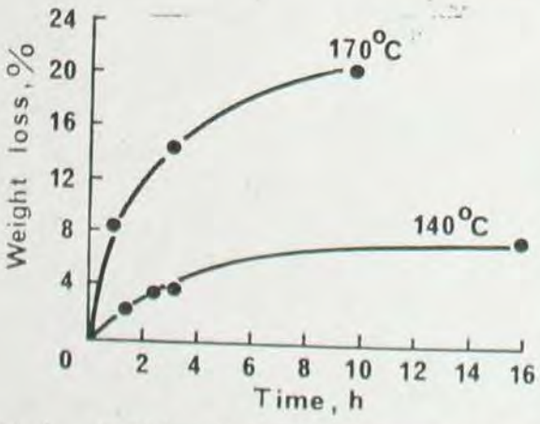

Figure 4. Peeling loss of hydrocellulose as a function of time in a pH 7 buffer at 140° and 170°C.

becomes quite rapid at 170°C. However, the peeling process levels off, in both cases, at lower values than in runs at pH 9 and above, making the comparison of respective peeling rate constants difficult.

Effect of Ammonia on the Rate of Peeling

It was observed that the presence of ammonium salts in mildly alkaline solutions retarded strongly the rate of peeling as illustrated in Figure 5. When partially peeled hydrocellulose

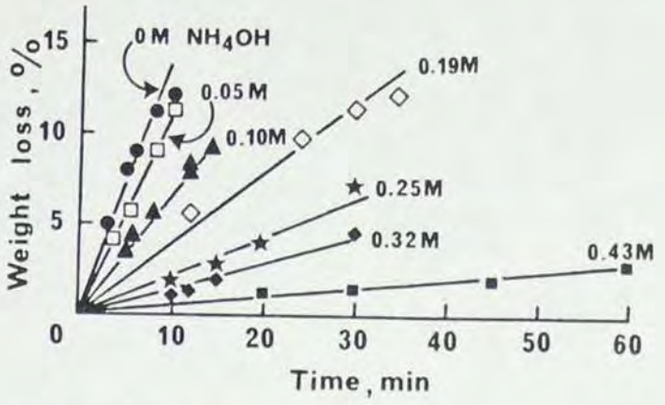

Figure 5. Effect of ammonia on the peeling of hydrocellulose at pH 10.2 and 140°C.

samples were recovered after experiments illustrated in Figure 5 and subjected to a standard alkaline degradation, complete peeling was observed. Consequently, the presence of ammonia does not generate stabilized end-groups but must nevertheless modify them in such a manner as to reduce the rate of peeling.

In the pH range 9 to 13, more than 95 per cent reduction in peeling rate can be achieved by the addition of sufficient amounts of ammonium salts, as shown in Figure 6. In contrast, even large

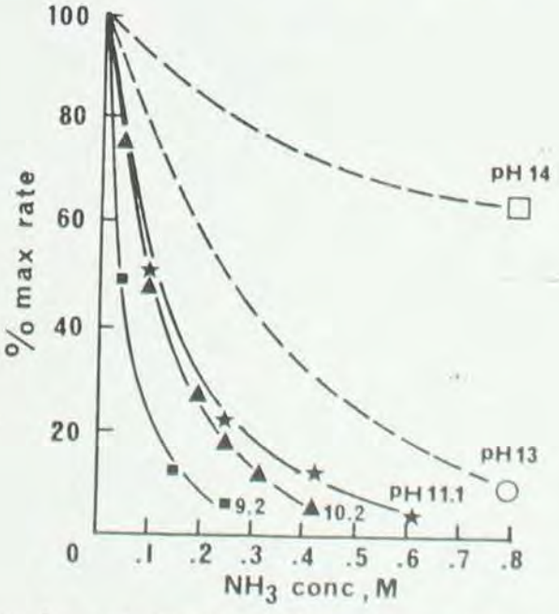

Figure 6. Retardation of peeling of hydrocellulose by ammonia in pH range 9 to 14.

concentrations of NH_4^+ have relatively minor effect at pH 14. The relative peeling rates in solutions (0.8 M in NH_4^+) are shown as a function

of pH in Figure 2 (curve 3). The sigmoidal form of this curve, with an inflection point at 13.7, suggests that the net effect of ammonia is to suppress the ionization of reducing end-groups, shifting the pK-value from 11.7 to approximately 13.7. The underlying chemical reaction is probably the conversion of carbonyl groups in reducing end-groups and in peeling reaction intermediates to the corresponding Schiff's bases (9,10).

Conceivably, the relationship between the rate constant for peeling and the NH_4^+-concentration is complex. However, reasonably good empirical straight-line correlations were found to exist between the logarithm of the ratio of normal over retarded peeling rate constant and ammonia concentration at individual pH levels, as shown in Figure 7. These correlations may be useful in

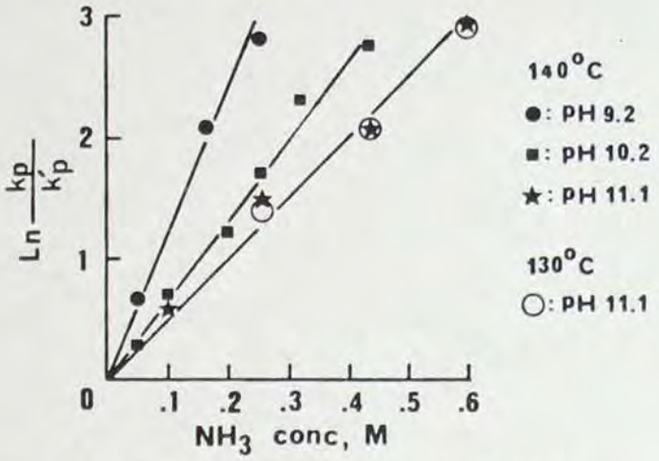

Figure 7. Empirical relationship between Ln k_p/k_p' and the concentration of ammonia. k_p' and k_p are the rate constants of peeling reaction with and without the presence of ammonia, respectively.

predicting the effect of ammonia on peeling especially since data for pH 11 suggest the correlations to reasonably independent of the reaction temperature.

CONCLUSION

Studies carried out by Chiang et al.(11) and Kondo and Sarkanen (12) in this laboratory suggest strongly that the peeling of glucomannans in softwood parallels that of hydrocellulose. Therefore significant hemicellulose losses can be expected to occur whenever wood is pulped under near-neutral conditions. It was also observed that ammonia retarded the peeling of glucomannan as it did that of hydrocellulose.

Some of the observations reported in the literature can probably be credited to these retardation effects. For example, when DeHaas and Lang (13) pulped softwood chips at 200°C, using a combination of ammonia and aqueous acetone, nearly 90 per cent of the original glucomannan was recovered undegraded in the pulp.

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WOOD CHEMISTRY FOR FUN AND PROFIT

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May we begin with a question.

What makes scientists do research?

It is certainly not the thought of getting rich. Neither can it be job security. In North American industry, scientists have been laid off in droves. Government laboratories are being "privatized". Even in the universities, tenure is questioned.

Could it be that research is a cushy job. Hardly. Ashok Vijh (1) points out that a scientist's work life is full of conflicts - "that tend to create deep psychological stresses with profound ramifications". It is a wonder we don't go berserk more often.

Why, then, do we stick with the research game?

Because it is fun!

I believe that we endure the frustration, the conflicts and the basic uncertainties of the scientific life because we enjoy it. It is challenging. It is exciting. And when a scientist finds in all the untidy unknown one clear, small gem of new knowledge, science becomes to her or him completely satisfying.

If research ceases to be fun, it ceases to be research.

By definition, therefore, research in wood chemistry must be fun. Here are some of the fun questions in my own field, which may be loosely described as the molecular architecture of wood:

- Why does the chemical structure of lignin differ in different regions of the wood?
- Are Atalla and Agarwal (2) correct? Is lignin oriented in the cell wall? Does adsorption of the lignin monomers onto the carbohydrate surface contribute to the orientation of the polymer?
- Are the structures of the hemicellulose different in different parts of the cell wall? How are hemicellulose molecules oriented with respect to cellulose microfibrils?
- What is the direction of cellulose chains in the microfibril? Does chain direction affect the properties of pulps?

Of course we may extend this list considerably.

Then there are the bushels of questions on how wood is produced in nature and the way it is degraded. The biochemistry of wood is of great interest these days. A large proportion of the present program falls in this area. Indeed, the prestigous Wallenberg Prize has been awarded this year to two of our leaders in the biodegradation of wood.

Myriads of chemical questions spring up around the processes now current in the pulp and paper industry. In spite of the dedicated work of organic chemists on the chemical pulping of wood and its subsequent bleaching, we have much to learn in these areas. And here may I make a plea. In the introduction to their excellent book, Fengel and Wegener (3) point out that -

> "The chemistry of wood and its components cannot be regarded apart from its structure. Wood is not merely a chemical substance, or an anatomical tissue, or a material - it is a combination of all three. This entirely results from an intimate association of the chemical components which form ultrastructural elements, being combined into higher-order systems which in turn build up the walls of the cells that ultimately compose the wood tissue."

We should bear this in mind whenever we design experiments or interpret data on the chemical reactions in woody materials.

We are now ready for the million dollar question.

Who pays?

The answer, of course, is society. And it pays a lot. It takes at least $100,000 per annum to keep each person in this room going. On a global scale, this could total hundreds of millions of dollars spent on R & D related to wood chemistry. Will society provide this kind of support merely to allow wood chemists to have fun? I think not. There must be profit. The results of our research must have relevance to the short term and long term needs of people.

Here, of course, the forest is very much in the ascendency in people's minds today. The oil is running out - the forests will grow on forever. Let us feed the world, heat the world and transport the world with wood from our forests.

- Can we?
- Can food from wood compete with food from grass, grains, vegetables and fruit? Maybe. But do not forget that nature has designed wood to be very indigestible.
- After oil, will wood be able to compete with coal over the next millenium as the raw material for

bulk chemicals? Perhaps. Although the economics of such usage of wood continues to be negative.

- How about energy? Can we run our automobiles and aircraft on fuels from wood? It is possible. Remember, however, that trees use sunlight very inefficiently. Probably in the lifetime of people in this room, fuels such as methanol or hydrogen will be produced directly by photochemical processes which mimic, but are an order of magnitude more efficient than the photosynthetic pathways in nature.

My own view is that wood is best used for what nature designed it - a structural material. When all the suitable lumber has been extracted from the tree and all the suitable fragments have been made into products such as waferboard, the best use for what is left is paper. Then, for wastes from the forest, the sawmill, the plywood mill, the waferboard mill and the papermill, there may be a hierarchy of uses which include food, chemicals and energy. Note however that, as world demand for wood increases, the use of "wastes" moves higher up the hierarchy. We are now seeing oriented strand board made from poplar (a "weed" species?) competing successfully with plywood. On the horizon are products such as Parallam (TM) parallel strand lumber, a high quality material made from small sticks of wood, coated with glue and pressed together (4). In pulp and paper, the trend world-wide is to make a higher proportion of the wood into usable fibre. And industries based on the exploitation of wastes at the lower end of the hierarchy will gradually have less and less starting material available.

Where does all this leave "wood chemistry for profit"?

I believe that opportunities are greater than ever before. Let me list just a few:

- Can we find new preservatives for wood which are cheaper, effective and benign to humans (unlike the traditionally used compounds such as PCP and creosote)?
- Can we make the superior adhesives required for strength and permanence in the new composite lumber and flakeboard?
- Have researchers on the surface chemistry of wood contributed all they can to paint and adhesive technology?
- Can we synthesize, by conventional chemistry, enzyme-like compounds ("synzymes") which act on wood like enzyme molecules but are smaller, less fragile and much less costly than their naturally occurring counterparts?
- Can we develop methods to bleach chemimechanical pulp to high and permanent brightness?
- Can we mine our process wastes for valuable chemicals (e.g. steroids from the neutral fraction of tall oil (5)).

And then there is what seems to be a rather simplistic project. Zobel (6) estimates that 20-50% of the wood harvested today is used for firewood. Combustion is probably the most efficient way of getting energy from wood. What are we, as wood chemists, doing to increase the efficiency of this current worldwide usage?

May I ask you now to return with me to the beginning.

Fun.

Of course, we must have relevance in mind when we plan our projects. Of course, we must make a strong case for our research to those in our society who hold the purse strings. Of course, we must, more and more, tell the people in simple language what we are doing and why we are doing it. However, at the end of the day, it is the fun that counts. Without the element of joy in research, nothing will make it worthwhile. And (dare I say this!) it has seemed to me after a life of research that if we scientists take care to find fun in our science, the profits take care of themselves.

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SULPHITE TREATMENT OF ASPEN. FACTORS AFFECTING THE FORMATION OF CARBOXYLATE AND SULPHONATE GROUPS

R.P. Beatson, C. Heitner, M. Rivest and D. Atack

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ABSTRACT

Aspen, Populus tremuloides, woodmeal and chips have been treated to high yields, at 120 and 140°C, with sulphite solutions of pH 4 to 10 and total SO_2 concentrations from 0.25 to 1.0 mol L^{-1}. At pH 7, the rate of sulphonation is proportional to the total SO_2 concentration and the sites available for sulphonation; it increases by approximately 60 percent for each 10°C temperature rise. The rate of sulphonation is fastest at high pH.

The sulphonation of aspen lignin displays the same characteristics as the sulphonation of spruce lignin in all respects except one; the maximum extent of sulphonation of aspen lignin is about 50 percent that of spruce. The distribution of sulphur in thin transverse sections of sulphonated aspen, as determined in a transmission electron microscope, matches the previously reported distribution of the guaiacyl units.

These observations imply that only the guaiacyl units of aspen lignin are sulphonated and that the syringyl units bear very few free phenolic hydroxy groups.

Carboxylate formation is promoted by high pH and temperature. It is little affected by total SO_2 concentration. Yield loss increases as pH is increased from 4 to 10 and the effects of changing total SO_2 concentration are small.

High total SO_2 concentration and a pH close to 7 are required for efficient production of high strength sulphite-mechanical pulps from aspen.

INTRODUCTION

Poplar is Canada's most abundant hardwood, representing a volume of 0.79 billion m^3; about 80 percent of this is represented by one species, Populus tremuloides [1]. A strong bright chemimechanical pulp can be produced from aspen chips by treatment with sulphite solution followed by refining [2-9]. In recent work [8] it has been shown that the acid content of these ultra-high yield aspen sulphite-mechanical pulps is a major factor in determining their strength and optical properties. Thus, in order to control the properties of these pulps it is necessary to have a good understanding of the factors controlling the rate and the extent of the formation of carboxylic and sulphonic acid groups during the sulphite pretreatment.

The sulphonation of lignin during treatment of 2.5 mm thick pieces of aspen veneer with sodium sulphite solutions in the pH range 4.2 to 9.0 at 170°C was studied by Marth [10]. However, because of the high temperature, long time to temperature and treatment times of 30 to 600 minutes, little information was obtained on the early stages of sulphonation, so important to chemimechanical pulping. Also, the effects of changes in total SO_2 concentration and temperature on the sulphonation reaction were not investigated. It was apparent, as observed earlier by other researchers [11], that aspen lignin did not sulphonate to as high a degree as spruce lignin.

The generation of carboxylate groups in aspen during sulphite treatment has not been studied owing, in part, to the lack of a convenient method of distinguishing carboxylate groups from sulphonate groups in such pulps. However, a new method based on conductometric titration now provides a convenient way of determining the content of carboxylate and sulphonate groups in pulp [12].

This paper describes a study of the effects of changes in total SO_2 concentration, temperature and pH, on the formation of sulphonate and carboxylate groups in aspen during sulphite treatment and the effects of these changes on the concomitant yield and lignin losses. The degree of sulphonation of lignin in different morphological regions of sulphite treated aspen is also reported.

EXPERIMENTAL

Preparation of Woodmeal

An aspen log from Eastern Ontario was reduced to chips, the chips were dried at room temperature for eight days and then ground to woodmeal in a Wiley mill. The woodmeal was air-dried and screened in a sieve shaker, the fraction passing 40 mesh but retained on the 60 mesh being collected. This woodmeal was allowed to dry further at room temperature to about 95 percent solids.

Preparation of Sulphite Cooking Liquor

Sulphite liquors with pH levels of 4, 6 and 7 were prepared by dissolving the requisite amount of sodium metabisulphite in deionised

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These observations imply that only the guaiacyl units of aspen lignin are sulphonated and that the syringyl units bear very few free phenolic hydroxy groups.

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The generation of carboxylate groups in aspen during sulphite treatment has not been studied owing, in part, to the lack of a convenient method of distinguishing carboxylate groups from sulphonate groups in such pulps. However, a new method based on conductometric titration now provides a convenient way of determining the content of carboxylate and sulphonate groups in pulp [12].

This paper describes a study of the effects of changes in total SO_2 concentration, temperature and pH, on the formation of sulphonate and carboxylate groups in aspen during sulphite treatment and the effects of these changes on the concomitant yield and lignin losses. The degree of sulphonation of lignin in different morphological regions of sulphite treated aspen is also reported.

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Sulphite liquors with pH levels of 4, 6 and 7 were prepared by dissolving the requisite amount of sodium metabisulphite in deionised

water and adjusting the pH with a trace of SO_2 to give pH 4, or with 4 mol L^{-1} sodium hydroxide to give pH 6 and 7. The liquor having pH of 10 was prepared from sodium sulphite and 4 mol L^{-1} sodium hydroxide.

Sulphite Treatment of Aspen Woodmeal

Aspen woodmeal, approximately 10 g o.d., was transferred to a 250 ml stainless steel bomb and soaked for 1 hour at room temperature in 220 ml of cooking liquor. The bomb was immersed in a preheated constant temperature bath. The liquor in the bomb reached temperature in approximately 18 minutes. After treating the aspen at 140°C or 120°C for predetermined times from 0 to 120 minutes the bomb was removed from the bath and rapidly cooled. The treated woodmeal was removed and washed with deionised water until no more sulphite was eluted as determined by a rapid Palmrose titration [13]. The pulp was filtered from the wash water, weighed and part of the pulp was dried at 105°C to obtain the consistency necessary for calculation of the yield. The lignin content, acid insoluble and acid soluble, of the treated wood was determined by CPPA Technical Section standard method G 9 and TAPPI useful method UM 250 respectively.

The carboxylic and sulphonic acid contents of the treated woodmeal were determined by conductometric titration[12].

Sulphite Treatment of Aspen Sticks

Aspen (Populus tremuloides) wood chips were broken into small sticks in a Waring Blendor. About 7.3 g O.D. of the disintegrated chips were fully soaked with water and then immersed for 24 h at room temperature in 220 mL of a pH 7 solution of 104 g L^{-1} of sodium bisulphite and 33.3 g L^{-1} of sodium hydroxide. The impregnated chips and sulphite liquor were placed in a 250 mL stainless steel bomb and immersed in an oil bath heated to 155°C. After 13 minutes the contents of the bomb reached 120°C and cooking was continued at this temperature for known times. The bombs were cooled rapidly and the wood sticks removed. The sticks were washed by repeated soaking in deionized water until no more sulphite was eluted as determined by a permanganate test.

A few sticks were removed for use in preparation of thin sections. The remainder were used for chemical analysis. The acid insoluble and acid soluble lignin were determined by CPPA Technical Section standard method G9 and TAPPI useful method UM250 respectively. The sulphur content was determined by CPPA Technical Section standard method G28. Yields of the treatments were determined by parallel experiments. The results are shown in Table 1.

Preparation of Thin Sections

Small sticks (1.5 x 1.5 x 10 mm, R x T x L) of treated aspen were embedded in Vestopal, a polyester resin. The embedded specimens were sectioned with a Porter-Blum MT2 ultramicrotome to give sections with a thickness of 0.15 µm. The sections were placed on a carbon grid having a single 1 mm hole bearing a collodion film which had been carbon coated. The mounted specimen was again carbon coated to reduce charging.

Microscopic Analysis

Sulphur contents in the middle lamella, fibre and vessel walls were determined with a Philips 400 transmission electron microscope coupled with an EDAX 9100/60 analyser. The system was fitted with an anticontamination trap cooled with liquid nitrogen and a beryllium tipped specimen holder to reduce background noise. The conditions used for analysis were: condenser aperture, 100 µm; no objective aperture; no diffraction aperture; tilt angle of specimen holder towards the detector, 21°; accelerating voltage 100 keV; spot size 0.2 or 0.4 µm, emission current 10-13 µA. Under these conditions, the sulphur K_α X-ray counts during a 50 or 100 s analysis were recorded. The counts for the sulphur K_α line were determined by subtracting the background, as estimated from the counts at 2.12 and 3.16 keV, from the total counts in the window at 2.23 to 2.39 keV. The sulphur K_α counts were taken as the measure of sulphur concentration.

Table 1. Sulphur Content of Aspen Treated at 120°C with pH 7 Sulphite Solution having a Total SO_2 Concentration of 1 mol L^{-1}.

Treatment Time (minutes at 120°C)	Yield (percent)	Lignin Content (percent)	Lignin Losses (percent O.D. wood)	Sulphur Content of Treated Wood
13	94.7	21.8	0.8	0.10
70	88.4	21.3	1.3	0.19
240	85.6	19.1	3.5	0.30

Lignin content of original wood: 22.6 percent

water and adjusting the pH with a trace of SO_2 to give pH 4, or with 4 mol L^{-1} sodium hydroxide to give pH 6 and 7. The liquor having pH of 10 was prepared from sodium sulphite and 4 mol L^{-1} sodium hydroxide.

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13	94.7	21.8	0.8	0.10
70	88.4	21.3	1.3	0.19
240	85.6	19.1	3.5	0.30

Lignin content of original wood: 22.6 percent

The ratio of sulphur concentration in the cell corner to that in the centre of an adjacent cell wall was determined by alternating the measurements between the two regions. Using adjacent areas minimises errors caused by variations in section thickness, alternating the region of analysis reduced errors arising from variations in microscope conditions. The ratio was determined 14 to 16 times to give a reasonable precision of the mean value. It was assumed that any sulphur mass loss occurred to an equal extent in each region and hence the ratio was independent of possible mass loss.

RESULTS AND DISCUSSION

Yield of Treated Woodmeal

As shown in Figure 1, yield decreases rapidly in the initial stages of treatment, especially at high pH. The yield of treated woodmeal increases as pH is decreased from 10 to 4.

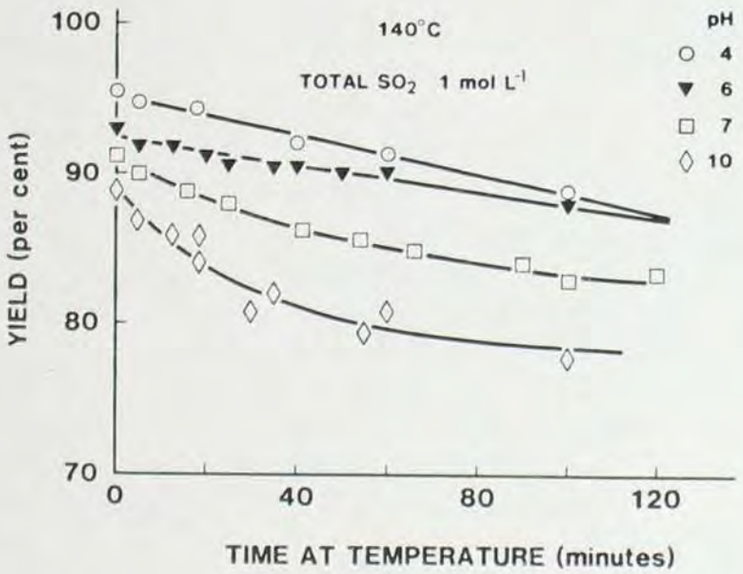

Figure 1. Yield loss increases with increasing pH, for treatments at 140°C with a total SO_2 concentration of 1 mol L^{-1}.

Table 2 shows that the lignin content of the treated woodmeal drops by 1.5 percent during the rise to 140°C. At pH 6 the lignin content of the treated woodmeal remains the same for further time at temperature. At higher and lower pH levels slightly more lignin than hemicellulose is dissolved during the treatment at 140°C. Thus, the more rapid yield loss at higher pH reflects increased removal of both hemicellulose and lignin with increasing alkali concentration. A large portion of the hemicellulose loss is a result of base catalysed hydrolysis of acetates and fatty acid esters [14,15].

Table 2. Lignin Content (soluble + Klason) of Woodmeal Treated at 140°C with Sulphite Solutions 1 mol L^{-1} in Total SO_2

Time at Temp. (minutes)	pH	Lignin Content (percent) 10	7	6	4
0		20.7	20.9	21.1	21.2
18		19.9	19.6	21.2	20.5
30		19.2	-	-	-
40		-	19.0	21.4	21.0
60		18.5	-	20.6	20.0
90		-	18.7	-	-
100		18.2	-	21.0	18.8
120		-	18.0	-	-

Lignin content of untreated woodmeal 22.6 percent

At pH 7 changing the total SO_2 concentration from 1.0 to 0.5 mol L^{-1} had no effect on the rate of yield decrease or the rate of lignin removal, as shown in Figures 2 and 3, but it does affect the rate of sulphonation as shown in Figure 4. Thus, as was observed for spruce [16], the sulphonation reaction does not control the rate of delignification during the early stages of sulphite treatment.

The slightly lower rate of yield and lignin loss as the total SO_2 concentration is lowered to 0.25 mol L^{-1} is probably a result of a drop in the pH of the liquor. The buffering capacity of the 0.25 mol L^{-1} solution was insufficient to maintain constant pH during the initial stages of treatment. The room temperature pH of the liquor dropped from 7 to 6.7 during the first 10 minutes of treatment and as shown in Figure 1, the rate of yield loss is quite sensitive to pH changes in this range.

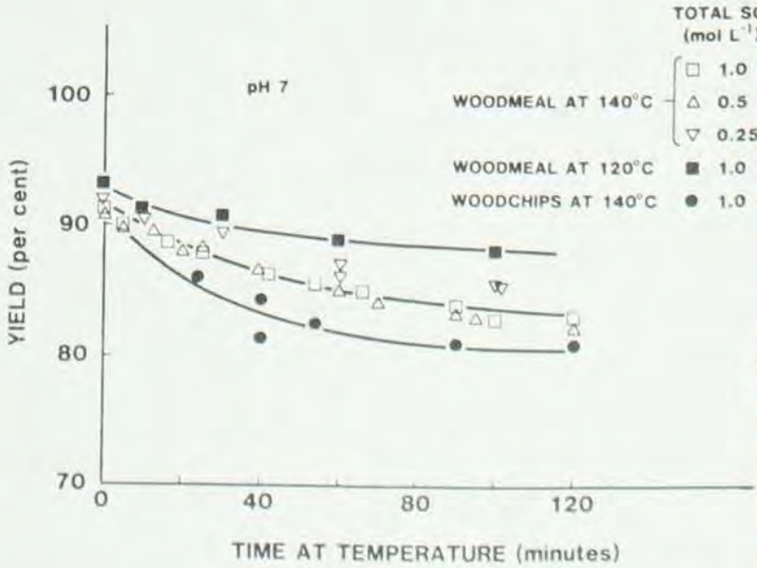

Figure 2. Changing total SO_2 concentration has little effect on yield. Decreasing temperature decreases yield loss and wood chips give slightly lower yields than woodmeal.

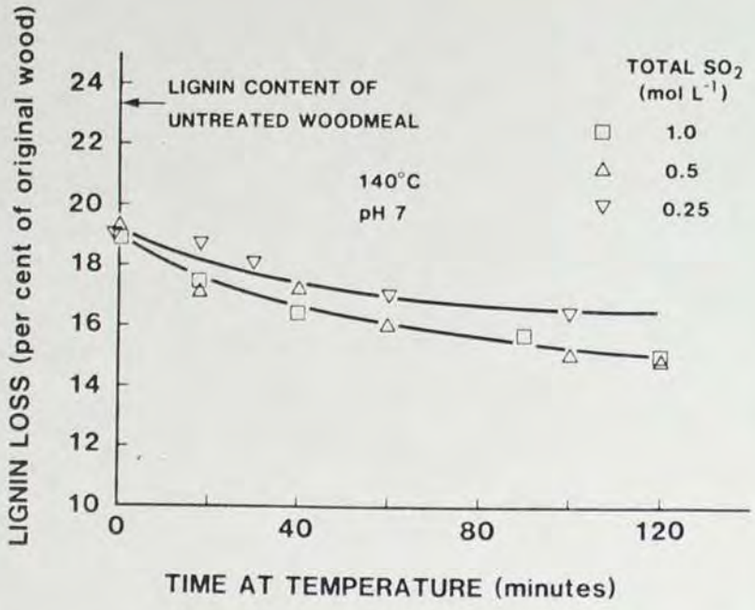

Figure 3. Changing the total SO_2 concentration from 1.0 to 0.5 mol L^{-1} has no effect on lignin losses. Lignin losses are slightly less at 0.25 mol L^{-1}.

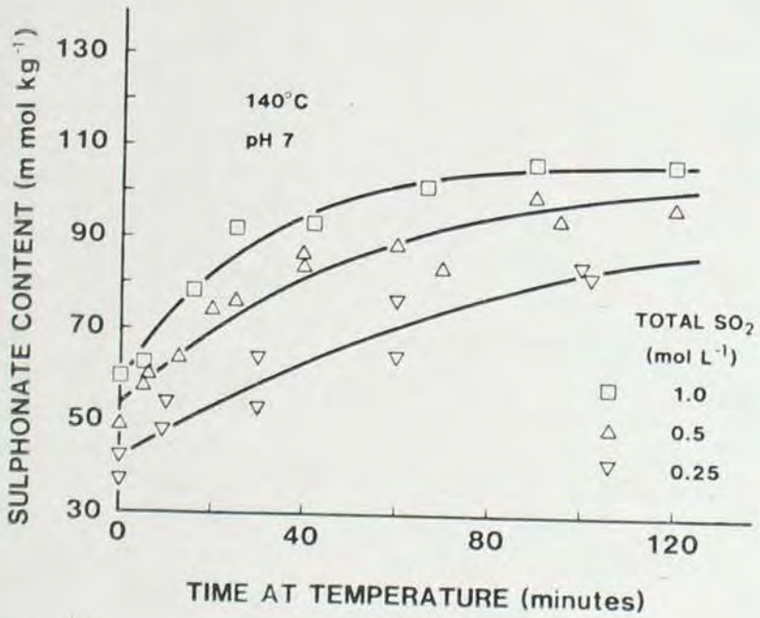

Figure 4. Increasing total SO_2 concentration increases the rate of sulphonation at 140°C and pH 7. The lines are generated from regression fits to the data points.

It is also shown in Figure 2 that yield losses decrease with a decrease in temperature from 140°C to 120°C and wood chips give slightly lower yields than woodmeal.

Sulphonation of Aspen

As shown in Figure 4, for treatment of aspen woodmeal with 1 mol L^{-1} sodium sulphite solution at pH 7 and 140°C, the rate of sulphonation decreases as the reaction proceeds, with a plateau in the sulphonate content of 105 m mol kg^{-1} being achieved within 90 minutes. This plateau corresponds to 0.34 percent sulphur on wood. Under similar conditions black spruce incorporated a maximum of 0.78 percent sulphur on wood [16].

Also, Figure 4 shows that the rate of sulphonation at pH 7 decreases with decreasing total SO_2 concentration. For small yield losses, if the rate of sulphonation at pH 7 is proportional to the number of sites available for sulphonation and the total SO_2 concentration; then the sulphonate content(S) at a given time (t) can be described by the following equation:

$$S = S^{\infty} - (S^{\infty} - S^{O})e^{-kt}$$

where S^{∞} is the sulphonate content at the plateau

S^{O} is the sulphonate content at time $t = 0$

Fitting the data points to this equation by non-linear least squares gives the values of the parameters, incuding the rate constants and the R^2 values, shown in Table 3. The value of S^{∞} was fixed at 107 m mol kg^{-1} for total SO_2 concentrations of 0.5 and 0.25 mol L^{-1}. The rate constant from the data at each total SO_2 concentration is the same within experimental error. Also the rate constant is close to the value of 4.19×10^{-2} L mol^{-1} min^{-1} previously reported for the sulphonation of black spruce under similar conditions [17]. As can be seen from the R^2 values, the data fit the equation quite well. The quality of the fit is illustrated in Figure 4, where the lines calculated from the equation are displayed along with the data points.

Table 3. The Dependence of the Rate of Sulphonation on Total SO_2 Concentration

Total SO_2 mol L^{-1}	S^{∞} m mol kg^{-1}	$S^{\infty}-S^{O}$ m mol kg^{-1}	$k \times 10^2$ L mol^{-1} min^{-1}	R^2
1.0	107 ± 2.7	49.4 ± 3.3	3.60 ± 0.67	0.979
0.5	107	53.5 ± 2.5	3.62 ± 0.38	0.938
0.25	107	64.9 ± 2.6	3.94 ± 0.49	0.919

The effects of pH changes on sulphonation are displayed in Figure 5. For sulphite treatment at 140°C with solutions 1 mol L^{-1} in total SO_2, the rate of sulphonation is the same at pH 7 and pH 10. Below pH 7 decreasing the pH causes a reduction in the rate of sulphonation. Similar observations were made for the sulphonation of black spruce [16] and are related to a lower concentration of the highly nucleophilic sulphite dianion at pH levels below 7.

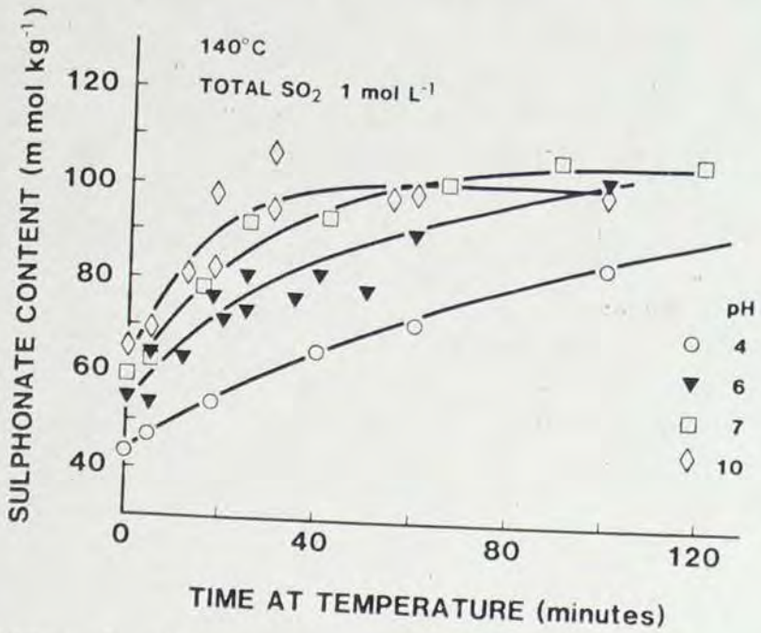

Figure 5. Increasing pH from 4 to 10 increases the rate of sulphonation at 140°C and a total SO_2 concentration of 1 mol L^{-1}.

Figure 6 and Table 4 show that reducing the temperature from 140°C to 120°C causes a reduction in the rate of sulphonation and also that the rates of sulphonation for woodmeal and well impregnated chips are the same. The rate constant for sulphonation increases by 60 percent for each 10 degrees centigrade rise in temperature, corresponding to an activation energy of 63.4 kJ mol^{-1}, a value which is very close to the value of 63 kJ mol^{-1} found for black spruce [17].

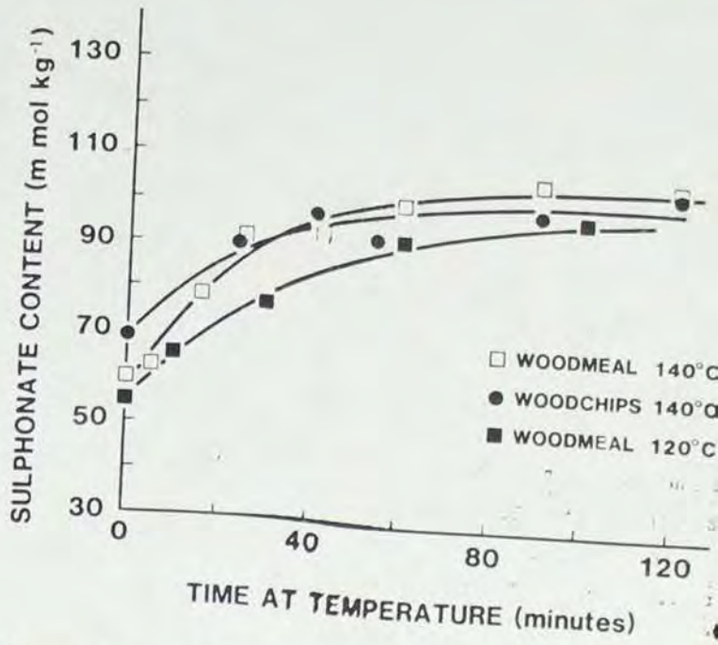

Figure 6. Woodmeal and wood chips sulphonate at the same rates. Reducing the temperature from 140 to 120°C decreases the rate of sulphonation.

The sulphonation of aspen woodmeal displays the same characteristics as the sulphonation of black spruce in all respects except one; the maximum extent of sulphonation of aspen lignin is about 50 percent that of spruce. Since black spruce lignin contains only guaiacyl units, these observations strongly imply that the guaiacyl component of aspen lignin and not the syringyl component is being sulphonated. This is especially so since guaiacyl units constitute about 40 percent of aspen lignin (see appendix) and model compound studies [18] imply that the rate and dependence on pH of sulphonation of syringyl lignin should be somewhat different to that of guaiacyl lignin. Lack of sulphonation of syringyl lignin would also account for the reported low yield of syringaldehyde on the nitrobenzene oxidation of pulp liquors from the early stages of sulphite cooking of aspen [10, 19].

Table 4. The Dependence of the Rate of Sulphonation on Temperature and Wood Form

Form	Temp. °C	S^{∞} m mol kg^{-1}	$S^{\infty}-S^{o}$ m mol kg^{-1}	k x 10^{2} L mol^{-1} min^{-}	R^2
Woodmeal	140	107 ± 2.7	49.4 ± 3.3	3.60 ± 0.5	0.979
Woodmeal	120	103 ± 1.6	48.8 ± 1.8	2.32 ± 0.24	0.997
Wood chips	140	103 ± 4.0	34.1 ± 5.6	3.53 ± 1.3	0.931

The selective sulphonation of the guaiacyl units in aspen lignin is consistent with the results of the microscopic studies of sulphur distribution. Table 5 compares the sulphur concentrations in the middle of the fibre wall, vessel wall and cell corner. Results are given for aspen which had been treated for three different times at 120°C with pH 7 sulphite solutions 1 mol L^{-1} in total SO_2. It is apparent that the sulphur concentration in S_2 layer of the fibre wall is on average about 11 percent of that in the cell corner region of the middle lamella. The value of 11 percent is maximum since up to 50 percent of the low x-ray counts in the fibre wall may arise from background radiation. Thus, the sulphur content of the fibre wall may be as low as 5 percent of that in the cell corner. The sulphur concentration in the vessel wall is much higher being about 33 percent of that in the cell corner.

The distribution of sulphur between the cell corner and fibre wall is markedly different to that found for black spruce sulphonated under similar conditions [20]. In black spruce the concentration of sulphur in the fibre wall was about thirty percent of that in the cell corner.

It is reasonable to assume that the distribution of lignin in aspen is similar to that in birch [21]. Using the data for birch, the relative sulphur contents of the lignin in each region can be calculated as shown in Table 5. The low content of sulphur in the fibre wall lignin relative to that in the cell corner and vessel wall lignin, when combined with the observation that maximum extent of sulphonation of aspen lignin is only 50 percent that of black spruce lignin, indicates that the aspen has less reactive sites in its fibre wall lignin.

It has been demonstrated previously, by u.v. microscopy [22], and fibre fractionation [23] that the syringyl moieties in hardwoods are located mainly in the fibre secondary wall whereas the lignin in the cell corner and vessel walls [24] is composed mostly of guaiacyl units. Thus, the distribution of sulphur in aspen lignin matches the distribution of guaiacyl residues providing further evidence that only the guaiacyl units are sulphonated.

The proposal by Marth [10], that poor penetration of sulphite liquor into the syringyl rich regions is the reason for the low level of syringyl sulphonation seems unlikely since well impregnated wood chips and woodmeal were found to sulphonate to the same degree at the same rate. The lack of sulphonation of the syringyl lignin may result from a low phenolic hydroxy content. If phenolic lignin units are the site of sulphonation at pH levels close to 7, as has been shown for black spruce [17], a low phenolic hydroxy content in the syringyl moieties, which account for about 50 percent of aspen lignin, would explain the observation that the degree of sulphonation of aspen lignin is much lower than that of black spruce. Indeed, it has been shown [25] that lignin isolated from sweetgum has a phenolic hydroxy content about 67 percent lower than that of spruce and recent carbon-13 NMR studies [26] have shown that lignin in the hardwoods beech, maple, oak and cherry also have a lower phenolic hydroxy content than softwood lignin. Thus, it is probable that this is also true of lignin in aspen.

Formation of Carboxylate Groups

As shown in Figure 7, carboxylate groups are formed in aspen woodmeal on treatment at 140°C with sulphite solutions 1 mol L^{-1} in total SO_2 having pH levels in the range of 4 to 10. A maximum carboxylate content of around 160 m mol kg^{-1} is attained very rapidly at pH 10 during warm-up. As the pH is reduced to 4 the rate of carboxylate formation decreases. It is apparent from Figure 8 that for sulphite treatments at pH 7 and 140°C changing the total SO_2 concentration from 1.0 to 0.5 mol L^{-1} has little effect on the generation of carboxylate groups. However the rate of formation of carboxylate groups slows on reducing the total SO_2 concentration to 0.25 mol L^{-1}.

Table 5. Sulphur Content of Lignin in Morphological Regions of Aspen

Morphological Region		Ratio of Sulphur Concentrations	Ratio of Lignin Concentrations	Ratio of Sulphur Contents of Lignin
Fibre	S_2	1	1	1
	ML	9	4.5	2.0
	CC			
Vessel	S_2	3	1.4	2.1

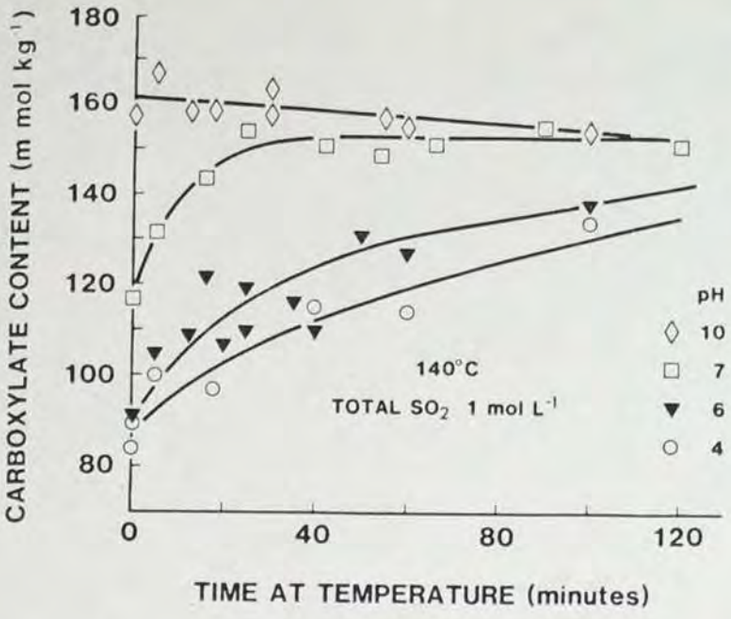

Figure 7. Carboxylate groups are formed most rapidly at pH 10, for treatments at 140°C and a total SO_2 concentration of 1 mol L^{-1}.

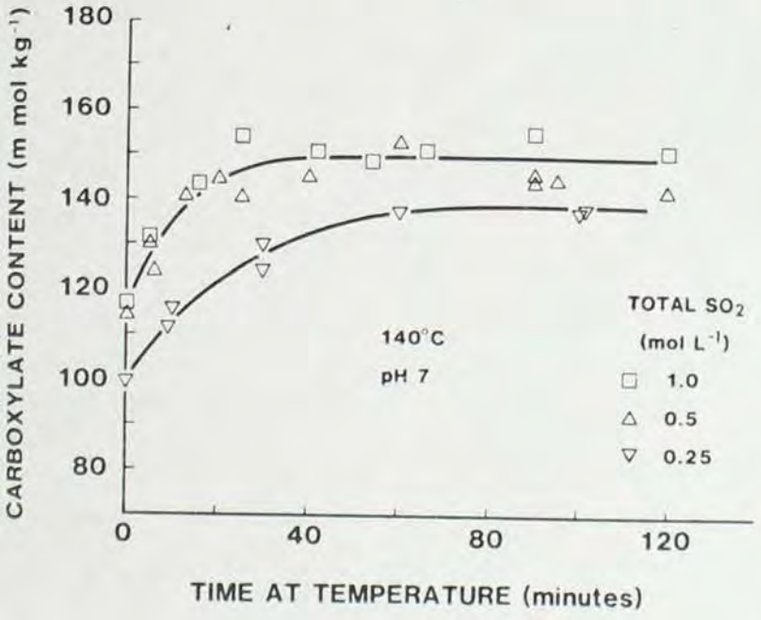

Figure 8. For treatments at 140°C and pH 7 carboxylate groups are formed at the same rate for total SO_2 concentrations of 1.0 and 0.5 mol L^{-1}. Reduction of the total SO_2 concentration to 0.25 mol L^{-1} reduces the rate of carboxylate formation.

The observed lower rate of carboxylate formation as the total SO_2 concentration is lowered to 0.25 mol L^{-1}, like the lower yield loss, is probably a result of a drop in pH of the cooking liquor since, as shown in Figure 7, the rate of formation of carboxylate groups is extremely sensitive to pH changes in this range.

The increasing rate of formation of carboxylate groups with increasing pH and the lack of an effect of decreasing the total SO_2 concentration from 1.0 to 0.5 mol L^{-1} are consistent with the formation of the carboxylate groups by base catalysed hydrolysis of carboxylic esters. Since extraction of the woodmeal with acetone prior to the treatment caused no reduction in the amount of carboxylate groups formed during sulphite treatment, it is apparent that there is no significant contribution to the carboxylate content from hydrolysis of the fatty acid esters. Thus the carboxylates must be formed by the hydrolysis of the esters of 4-O-methyl-D-glucuronic acid which are present in the hemicellulose [27].

The maximum carboxylate content of 160 m mol kg^{-1} corresponds closely to the uronic acid content of aspen which is estimated from data available in the literature to be 148 m mol kg^{-1} (see appendix). The carboxylate content of aspen woodmeal before treatment with sulphite was about 88 m mol kg^{-1}. Thus about 45 per cent of the carboxylic acid groups in the aspen woodmeal were esterified. This is slightly higher than a previously reported value of 36.4 percent [28].

Figure 9 shows that, for treatment of aspen with sulphite solutions having pH 7 and 1 mol L^{-1} in total SO_2, reduction in temperature from 140°C to 120°C reduces the rate of generation of carboxylate groups. Also Figure 9 shows that, at pH 7 and 140°C, carboxylate groups are formed slightly more rapidly in woodmeal than in well impregnated wood chips. Thus the rate of hydrolysis of the esters is influenced to a small extent by penetration or diffusion of the liquor to the reactive site. This is a result

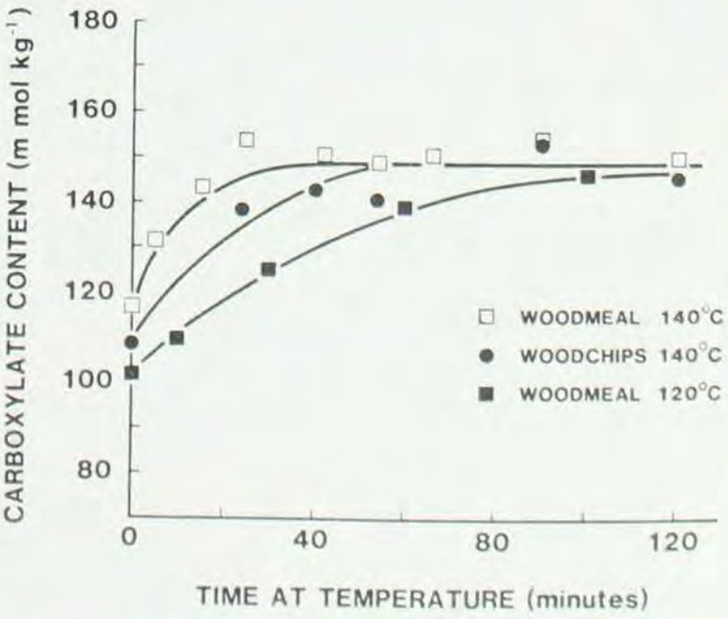

Figure 9. For treatment at pH 7, increasing the temperature increases the rate of carboxylate formation. At 140°C and pH 7 the formation of carboxylate groups is slightly faster for woodmeal than for well impregnated wood chips.

of the fast hydrolysis reaction leading to penetration or diffusion being involved in the rate limiting step.

CONCLUSIONS

Sulphite treatment of aspen sulphonates lignin and hydrolyses ester groups in the hemicellulose to carboxylic acids. The rate of sulphonation of aspen lignin at pH 7 is proportional to total SO_2 concentration and the number of sites available for sulphonation. It has a second order rate constant of $3.7 \pm 0.3 \times 10^{-2}$ L mol^{-1} min^{-1} and an activation energy of 63.4 kJ mol^{-1}. The rate of sulphonation increases with increasing pH. In all these aspects the sulphonation of lignin in aspen behaves in the same manner as the sulphonation of lignin in black spruce. However, the extent of sulphonation of aspen lignin under these conditions is only 50 percent of that of spruce lignin. These observations imply that the guaiacyl and not the syringyl units of aspen lignin are sulphonated due to the fact that syringyl units have a very low phenolic hydroxy content.

For aspen treated with sulphite at pH 7 and 120°C, the sulphur content of the lignin in the fibre wall was found to be about half of both that in the cell corner region of the middle lamella and that in the vessel wall. This distribution of sulphur matches the distribution of guaiacyl units confirming the conclusion that only guaiacyl units sulphonate in aspen lignin.

The low degree of sulphonation of fibre wall lignin indicates that sulphonation at pH 7 is not an effective method of softening fibres. Thus, sulphonation of aspen chips at pH 7 will not increase the bonded area and tensile strength of aspen chemimechanical pulps.

Carboxylate formation is favoured by high pH and arises mainly from hydrolysis of uronic acid esters in the hemicellulose. At pH 10 the maximum carboxylate content of 160 m mol kg^{-1} is achieved during the 18 minutes required to reach 140°C. Total SO_2 concentration has little effect on the generation of carboxylate groups.

Yield losses are lowest at pH 4 and increase with increasing the pH to 10. Total SO_2 concentration has little effect on yield or lignin losses.

At pH 7 and a total SO_2 concentration of 1 mol L^{-1} increasing temperature increases the rates of sulphonation, carboxylate formation and yield losses. The rate of sulphonation increases by 60 percent for each 10 degree centigrade rise in temperature between 120 and 140°C.

The results show that high total SO_2 concentration promotes sulphonation without a detrimental effect on yield. Although increasing temperature increases the rates of sulphonation and carboxylate formation it lowers yield. Carboxylate formation is promoted by high pH but at the expense of much lower yields.

Thus in order to obtain aspen chemimechanical pulps that have high sulphonate and carboxylate contents while maximizing yield, high total SO_2 concentration and a neutral pH should be used. A pH much below 7 will result in slow sulphonation and very slow carboxylate formation, whereas pH 10 causes rapid yield loss.

ACKNOWLEDGEMENTS

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APPENDIX

The methoxyl content of Populus tremuloides lignin is reported to be 1.44 OMe/C_9 unit [29].

The p-hydroxybenzoate content is reported to be 10 percent [30].

Let the number of guaiacyl moieties per C_9 unit be $\underline{a}$ then there are $90-\underline{a}$ syringyl moieties and a methoxyl balance gives;

$$\underline{a} + 2(90-\underline{a}) = 144$$

$$\underline{a} = 36$$

Thus aspen lignin contains about 40 percent of guaiacyl units.

Aspen is reported to contain 23 percent of 4-O-methyl glucuronoxylan in which there are 9 parts of xylan to each part of uronic acid [26].

As the molecular weight of 4-O-methyl glucuronic acid is 208 and that of xylan is 150 there are 1350 g of xylan to 208 g of uronic acid in aspen glucuronoxylan. Thus the uronic acid content of aspen is about 3.1 percent or 148 m mol kg^{-1}.

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LEACHING OF LIGNIN AND CARBOHYDRATE FROM CHEMIMECHANICAL PULPS

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When ultra-high yield chemimechanical sulphite pulp fibres were suspended in water, both lignin and carbohydrate were leached out of the pulp, as shown in Figure 1. The experimental procedure used for this study was based on the method developed by Favis et al. (1). The concentration of lignin in the leachate was measured using ultraviolet spectrophotometry. The carbohydrate content was determined using an orcinol colorimetric technique. The observed rate of leaching for both lignin and carbohydrate fitted a theory developed previously by Choi et al. (2) and Favis et al. (1) for the diffusion of macromolecules through the water-swollen fibre wall. For six hours of leaching, the average intrafibre diffusion coefficents calculated for lignin and carbohydrate were 5.8×10^{-13} and 1.4×10^{-13} cm^2 sec^{-1}, respectively. These values are several orders of magnitude lower than the free diffusion of these macromolecules in solution. This suggests, therefore, that the infrafibre restrictions which hinder the movement of the macromolecules during leaching are an important factor in the diffusion mechanism.

Leaching over a long period indicated a polydispersity of diffusion coefficients, ranging from 1.9×10^{-12} to 5.7×10^{-14} cm^2 sec^{-1} for lignin and 2.8×10^{-13} to 4.4×10^{-14} cm^2 sec^{-1} for carbohydrate. This was related to an increase in the size of the macromolecules removed from the fibre at longer times of leaching. The molecular weights of lignin and carbohydrate leached from the pulp were found to increase from 11430 to 61350 and 6130 to 17400, respectively, as the washing at 20°C progressed. The decrease in the diffusion coefficients during leaching was attributed to larger restrictions imposed on the diffusing macromolecules by the porous matrix of the cell walls of the pulp fibres, as a result of the increasing size of these macromolecules.

The leaching of lignin and carbohydrate from the pulp was also studied as a function of temperature, from 20°C to 90°C. As shown in Figure 2, for both lignin and carbohydrate, the rate of leaching increased markedly with temperature. Removal of lignin and carbohydrate was particularly pronounced at temperatures exceeding 70°C. This effect was attributed to the softening of the pulp as a result of the glass transition of the water saturated hemicelluloses.

For both lignin and carbohydrate, the rate of leaching was found to decrease with an increase in pulp yield, and a decrease in the refining energy used to prepare the pulps. Measurements of the water retention values (WRV) of these pulps were performed since such values give an indication of the pore size of the fibre wall and as a result can be equated with fibre swelling. For both lignin and carbohydrate,

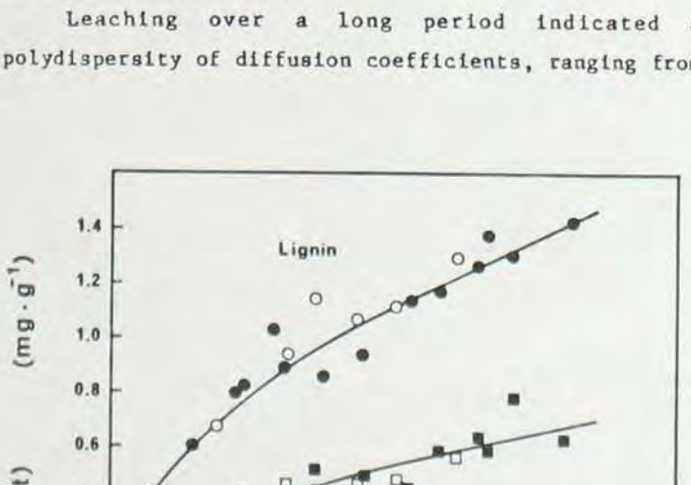

Figure 1. Average quantities of lignin and carbohydrate in the wash liquid, $W_f(t)$, versus time, t, at 20°C.

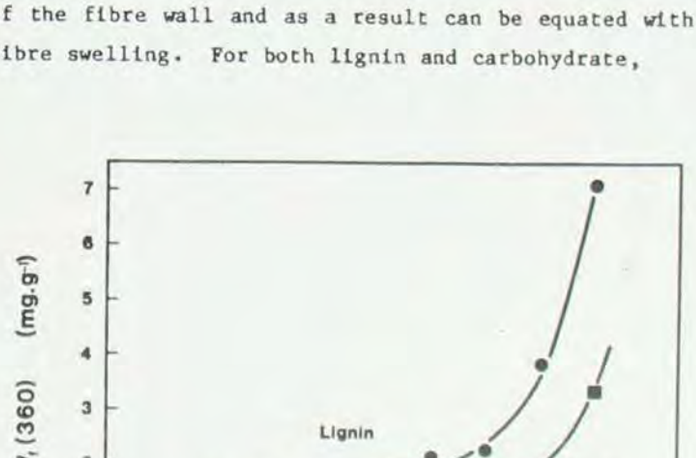

Figure 2. The variation with temperature of the quantities of leached lignin and carbohydrate, W_f (360), after 6 hours of washing chemimechanical pulp.

direct correlation was found between the WRV and the quantity of material leached from the pulps, as shown in Figure 3 for lignin.

The swelling of the cell walls of the pulp fibres was therefore deemed to be a dominant factor in the leaching process. A decrease in leaching was also observed for an increase in the cationic strength of the wash water, probably as a result of fibre deswelling. These observations are in accordance with trends previously found between fibre swelling and cationic strength (3).

Pretreatment of pulp with formaldehyde and increasing the pH of the wash water were both found to decrease the leaching of lignin and carbohydrate, while decreasing the pH of the cooking liquor and the use of anthraquinone in the pulping process increased the leaching of lignin but did not affect the leaching of the carbohydrate. The observed effects could be related either to crosslinking within the fibre or further degradation of the fibre wall. The use of polyethyleneoxide/alum retention aid in the wash water also caused the leaching of lignin and carbohydrate to decrease. In this case, leaching was probably impeded as a result of having the pores on the fibre wall surfaces physically blocked by the polyethyleneoxide macromolecules. Of the methods investigated to reduce leaching, the most effective one was found to be the formaldehyde pretreatment. However, the feasibility of the practical use of this technique has yet to be determined.

The implications of these results are significant with respect to the newsprint industry. The total solids capable of being removed from the pulp, about 1% of the fibre weight, does not represent a large loss in yield. However, when papermachine systems are closed, the build up of these soluble materials in thewhite water could lead to several problems including slower production rates and a poorer quality of newsprint produced. The results obtained indicate that conditions do exist whereby leaching and as a result, material loss in white water systems, can be minimized.

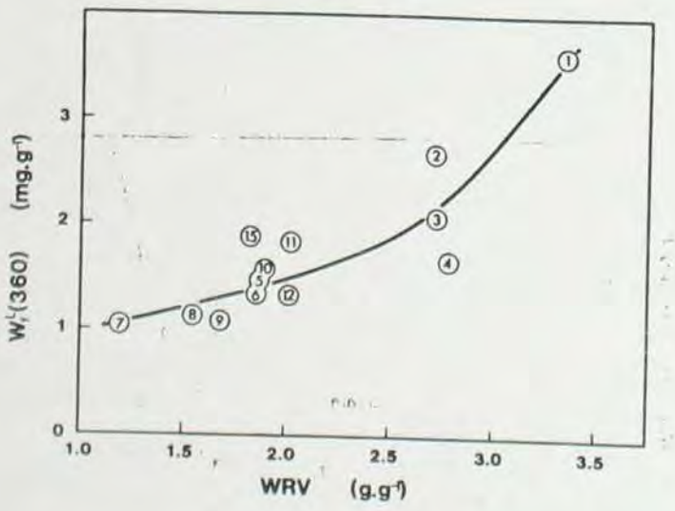

Figure 3. The variation of the quantity of lignin leached after 6 hours, W_f^L (360), with the water retention value of the pulp.

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Biological, Chemical, and Technological Wood Investigations from Pollution-affected Trees

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About 50 % of the forest stands of the Federal Republic of Germany are affected by immission and deposition of toxic substances. The species mostly affected by this phenomenon is spruce (Picea abies) because of its widespread distribution in Germany, although disease had firstly been observed with fir (Abies alba). Recently the damage has been observed on beech trees (Fagus silvatica). The level of damage is classified according to the visible feature of the trees, the basic criterion with softwoods is the extent of needle loss. In addition thinning of the top, shape of the top,discoloration of needles and similar symptons are included in the assessment. The system of classification is as follows: damage class 0 (not affected trees), damage class 1 (mildly affected), damage class 2 (moderately affected), damage class 3 (strongly affected),damage class 4 (dead).

In spite of all scientific doubts whether the vitality of a tree can be estimated by its external appearance this classification seems to be the only practical method of differentiation in the forest.

In forestry and the wood utilizing industry there has been some uncertainty about the quality of wood from trees stressed by pollution. For this reason there exists a big demand for research about consequences of tree disease in relation to wood quality.

Comparative studies on wood from about 100 healthy and diseased spruce trees were carried out to evaluate possible alterations of wood characteristics and wood quality respectively. Alltogether trees from 13 different sites in Germany were selected.

Trees from many polluted sites show a growthring depression. For individual trees no strong relationship between this phenomenon and the severity of disease was observed. However, at some sites these parameters are well correlated for the whole stand.Growthring depression of trees belonging to damage class 3 can be traced back over 20 to 30 years, where a stress situation was not yet visible from needle loss and shape of the top.

Trees from all polluted sites show a decrease of width and proportional amount of sapwood with advanced disease, revealing a limitation of water transport capacity. Furthermore, the inner sapwood of diseased trees contained less water than that of healthy ones. The morphology of the individual tracheids and parenchyma cells appeared unchanged in wood of diseased trees. The physical and technological properties of wood are largely a function of its density, but these show no particlular influence of the disease as yet.

Wood of healthy and diseased trees was characterized by its varying content of free sugars, starch, cellulose, hemicelluloses, and lignin. Free sugars were extracted with cold methanol : water. These extracts, derived from wood of healthy trees, had generally smaller dry matter contents than those derived from wood of diseased trees. In many cases the extract yields, at least for the youngest tree rings, were directly correlated with the classification into damage classes. Dry matter contents of extracts from wood from healthy trees range from 1 to 3 %, whereas extract yields derived from diseased trees ranged from 2 to 10 %. At the same time the outer sapwood of diseased trees showed higher concentrations of free sugars than outer sapwood of healthy trees. This phenomenon was verified with all samples analysed so far. Starch content determinations did not reveal such uniform results. Samples of affected trees often contained less starch than material from healthy ones.

In most cases the composition of the main constituents, cellulose, hemicelluloses, and lignin in wood of diseased and healthy trees was identical. Only in wood of heavily affected trees (damage class 3) were minor shifts detected.

THE ROLE OF SIDE-CHAINS OF XYLAN IN ITS BIOTECHNICAL UTILIZATION

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Pure xylose has often been used as a model substrate for studying the conversion of pentoses to ethanol and other chemicals. Problems arise, however, when practical industrial substrates are employed instead of pure xylose. Inhibitors are formed as degradation products during pulping or pretreatment, although some of these are volatile and can easily be removed. However, the chemical composition of the substrate itself may also cause problems in further processing.

Most of the hemicellulose in hardwoods and agricultural residues is xylan. Besides the β-D-xylopyranosidic backbone the xylans contain various amounts of acetyl groups and 4-O-methylglucuronic and α-L-arabinofuranose residues. Hemicellulose is usually solubilized during pulping or pretreatment processes and can thereafter be separated. A second hydrolysis step, however, is needed in order to achieve fermentable sugars.

In this study hemicellulose was separated from birchwood by steaming and water-extraction. With a steaming time of 10 minutes the optimal temperature for hemicellulose recovery was 190-200°C. After steaming 66 % of the extract dry weight was carbohydrates, 80 % of which were acetyl- and 4-O-methylglucurono-substituted xylo-oligomers and xylose. About 40 % of the O-acetyl groups of xylan were liberated and acted as a catalyst during steaming.

The hydrolysis of the hemicellulose fraction was studied using enzymes of Trichoderma reesei and Aspergillus awamori. Because of the large amount of cellulases, especially cellobiohydrolase produced by T. reesei, the specific xylanase activity of the Trichoderma enzyme mixture was low compared to that of Aspergillus enzyme. With equal xylanase activities the yield using T. reesei enzyme was higher than that obtained using A. awamori enzyme. The maximal xylose yield obtained with T. reesei and A. awamori enzymes after a 24 h hydrolysis were 94 and 73 % of theoretical, respectively.

The difference in xylose yields obtained using the two enzymes could at least partly be explained by their different capabilities of liberating the acidic substituents. As compared to the rapid release of acetic acid in the hydrolysis of xylo-oligomers by T. reesei enzymes, the formation of acetic acid by A. awamori enzymes was slow and its final concentration was only half that produced by T. reesei enzymes. The enzymes of these two organisms also differed from each other in their capability of hydrolysing the 1-2-glycosidic linkage between the 4-O-methyl-glucuronic residue and the xylan backbone. 4-O-methylglucuronic acid was detected in the hydrolyzates produced by T. reesei enzymes but not in those produced by A. awamori enzymes. It is therefore obvious that in addition to the xylanolytic enzymes endo-1,4-β-xylanase (EC 3.2.1.8) and β-xylosidase (EC 3.2.1.37), esterases are also needed for the complete hydrolysis of substituted xylans.

The fermentability of the hemicellulose hydrolyzates was tested using Fusarium oxysporum as a model organism. This organism ferments xylose, galactose, glucose and mannose to ethanol with a good yield but is severely inhibited by acetic acid. In the hydrolyzates obtained using T. reesei enzymes the ratio of sugars to acetic acid was 5:1 (g/g), and at a carbohydrate concentration of 30 gl^{-1} the acetate concentration was 6 $g\ l^{-1}$. The extent of acetate inhibition could be remarkably reduced by carrying out the fermentations at neutral pH, at which the acetic acid was completely dissociated.

To summarize, the acetyl- and 4-O-methylglucuronic side groups of the xylan backbone of birchwood were found to limit the utilization of the raw material in two ways: by affecting the yield in enzymatic hydrolysis and through the inhibitory effect of the released acids.

THE PROSPECT OF ENGINEERING MATERIALS FROM LIGNIN

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The entry of lignin into engineering plastics markets is envisioned on grounds of recent advances in the understanding of the structure-property relationship of lignin-based polyurethane materials. These advances concern improvements in the solubility characteristics of lignin derivatives, in the control over modulus and brittleness, in understanding the effect of molecular weight and molecular weight distributions, and in color.

1. Solubility : The synthesis of lignin derivatives with greatly improved solubility characteristics has been achieved by hydroxyalkylation with a variety of alkylene oxides (1,2). Hydroxyalkyl lignin derivatives are materials with single functionality (primary OH groups in case of ethylene oxide derivatives and secondary OH groups in case higher alkylene oxides are used) and with sharply reduced glass transition temperatures at degrees of substitution ranging between 1 and 2 (3). These derivatives have exhibited solubilities in excess of 20% in numerous solvents ranging from methanol to THF, for lignins including milled wood lignin, kraft lignin, organosolv lignin, and steam explosion lignin. Molecular weights have not been found to be diminished by the chemical modification reaction. The significant improvements in thermal and solubility characteristics have been explained with increased free volume due to the alkylene oxide substituent.

2. Modulus (brittleness) : Although some lignins with low molecular weight, and all hydroxyalkyl lignin derivatives exhibit melt flow characteristics when heated to above their glass transition, they fail collectively to produce acceptable structural materials by extrusion. This is due to their low molecular weights. Chemical crosslinking reactions with diisocyanates produce polyurethane networks the property of which have been studied extensively in relation to chemical and polymer network effects (4-8). Where glass transition temperature was found to vary with NCO:OH ratio (i.e. network density), moduli are constant between 1600 and 2200 MPa (4). Ultimate strain rates of > 10% are difficult to obtain with these network polymers unless strain building (toughening) components are incorporated into the network structure. This has been explored by the addition of polyethylene glycol (PEG) (7) and polybutadiene glycol (PBD) (8). While PEG produces uniform networks up to 18% of total polyol content, PBD addition results in distinct phase separation at glycol contents of > 2%. The PEG miscibility can be explained by considering (a) molecular compatibility between hydroxypropyl lignin and PEG, and (b) the low molecular weight of both components. PBD containing materials can best be described as lignin reinforced rubber polyurethanes (rubber polyurethane as a continuous phase with lignin inclusions) and as rubber toughened lignin polyurethane (lignin polyurethane as continuous phase with rubber inclusions). The two types of products display a wide range of modulus properties and it is seen that different types of glycols added to the hydroxyalkyl lignin derivative afford an excellent control mechanism over modulus, brittleness, rigidity, and toughness.

Other mechanisms of property control of hydroxypropyl lignin based polyurethanes have been explored as well. These include reductions of hydroxyl functionality of lignin prepolymers by chemical modification, and alkylene oxide chain extension.

3. Molecular weight and weight distribution : Lignins from different sources differ distinctly in their molecular weight and weight distribution characteristics (9). Although no systematic studies have yet been completed on this issue, preliminary tests indicate a modest positive effect of molecular weight on Young's modulus and tensile strength. Broad molecular weight distributions were found to contribute to network nonuniformity (5). Low molecular weight lignin fractions unincorporated into the network were found to reinforce the network at low sol contents (< 2%) and to plasticize it at contents of > 2%.

4. Color : The light absorbing properties of nonphenolic hydroxyalkyl lignin derivatives have been improved by an oxidative treatment with chlorine dioxide (10). It appears possible to remove up to 95% of the color of kraft lignin without significant yield loss.

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HYDROXYL RADICALS IN OXYGEN BLEACHING

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ABSTRACT

The selectivity of hydroxyl radicals, generated by radiation, with respect to lignin and carbohydrate degradation is studied using appropriate model compounds.

INTRODUCTION

It was early recognized that radicals play an important rôle in oxygen bleaching reactions. Compared to molecular oxygen these intermediates are less selective, contributing not only to lignin degradation but also to partial degradation of cellulose.

Oxygen bleaching is initiated by an electrophilic attack on structural elements of the phenolic and enolic types by molecular oxygen. However, this initial step, which almost exclusively takes place in the lignin part, is energetically unfavourable and requires a high alkalinity to proceed efficiently. The first reduction product, the superoxide anion, $O_2^{\cdot-}$, is a fairly selective species, capable of acting as a mild oxidizing or reducing agent. By further reduction the superoxide anion yields hydrogen peroxide, which may undergo a metal ion catalyzed decomposition giving rise to the extremely reactive hydroxyl radical, $^{\cdot}OH$.

This species is generally considered to be responsible for the greater part of the chain ruptures taking place in cellulose during oxygen bleaching and thus causing viscosity losses. It should be noted, however, that the hydroxyl radical is a very weak acid which becomes deprotonated above pH 12. As shown in Fig. 1. there are important differences in chemical properties between the hydroxyl radical and its anion.

The complexity of the chemistry involved in the stepwise reduction of oxygen may explain the difficulties encountered in the chemical interpretation of oxygen bleaching processes.

In order to elucidate the rôle of a particular species, e.g. the hydroxyl radical, its behaviour must be studied in the absence of interfering species. This can hardly be achieved in conventional bleaching studies, where several reactive species are simultaneously present.

We try to solve this problem by applying radiation chemical methods (1).

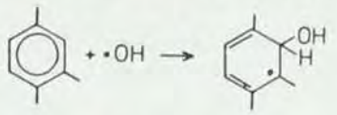
The absorption of ^{60}Co γ-rays or a beam of high energy electrons in water generates approximately equal numbers of powerful oxidizing ($^{\cdot}OH$) and reducing (e^-_{aq}, $^{\cdot}H$) radicals together with smaller yields of the molecular products H_2 and H_2O_2.

CHEMICAL PROPERTIES $^{\cdot}OH/O^{\cdot-}$

$^{\cdot}OH \rightleftarrows H^+ + O^{\cdot-}$
$pK_a = 11.9$

$^{\cdot}OH$: Electrophilic character
$O^{\cdot-}$: Nucleophilic ——"——

1. Only $^{\cdot}OH$ participates in rapid electron transfer reactions with inorganic anions, e.g.:
   $^{\cdot}OH + CO_3^{2-} \rightarrow OH^- + CO_3^{\cdot-}$
   $^{\cdot}OH + 2Cl^- \rightarrow OH^- + Cl_2^{\cdot-}$
   $^{\cdot}OH + SiO_3^{2-} \rightarrow OH^- + SiO_3^{\cdot-}$
2. Only $^{\cdot}OH$ adds to π-electron systems, e.g.:



3. Only $O^{\cdot-}$ reacts with O_2:
   $O^{\cdot-} + O_2 \rightarrow O_3^{\cdot-}$ (ozonidanion)

Figure 1.

The ensuing chemistry is much simplified if essentially only one kind of radical operates in the system. Thus conversion of reducing solvated electrons into oxidizing hydroxyl radicals is crucial. This conversion is accomplished by saturating the solution with dinitrogen oxide (N_2O), according to the reaction:

$N_2O + e^-_{aq} \rightarrow {}^{\cdot}OH + OH^-$

This operation also expels dissolved oxygen. In a N_2O-saturated solution, hydroxyl radicals constitute about 92% of all radicals acting in the system. The remaining fraction of radicals, i.e. hydrogen atoms, can generally be neglected. Thus, radiolysis of dilute aqueous solutions saturated with N_2O closely approximates a monoradical system suitable for $^{\cdot}OH$-radical investigations. Knowledge of the absorbed dose immediately provides a quantitative basis for determination of the products formed.

Our radiation sources are a ^{60}Co-facility and a pulsed electron accelerator. A very short pulse of electrons can deliver enough energy to produce an observable concentration of radicals. By temporal analysis using fast electronics, real time kinetics of the radicals formed may be followed. This pulse radiolysis technique has received wide applications in chemistry and biology and has contributed significantly to the understanding of radical-mediated reactions. The combined use of pulse- and γ-radiolysis to elucidate problems associated with bleaching chemistry is a new approach.

RESULTS AND DISCUSSION

We have started our investigations on reactions induced by radiolytically produced hydroxyl radicals with a few model compounds representing important carbohydrate and lignin structures, Fig. 2.

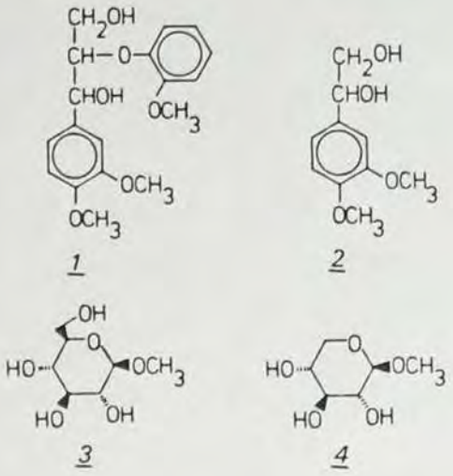


Figure 2.

Research items we are working on are summarized as follows

1. Study of the degradation of model compounds representing important carbohydrate and lignin structures by the action of oxidative radicals, e.g. ·OH, generated by radiation methods. Analysis of the products formed.
2. Determination of the reaction rates of the above models and their dependencies on structural features.
3. Competitive experiments using carbohydrate and lignin model compounds and isolated carbohydrates and lignins to elucidate the limits of selectivity for the action of various radical species.

Our studies on pure lignin model compounds have generated considerable insight into the mechanism of C_α-C_β cleavage and demethoxylation effected by hydroxyl radicals. These results which contribute to the understanding of microbial lignin degradation, will be reported elsewhere.

Selectivity is a key word in bleaching but its quantitative meaning is not well defined. In our opinion selectivity is a kinetic concept, which may be estimated from the relative reaction rate of a particular oxidant, e.g. the ·OH radical, with specific carbohydrate and lignin model compounds.

Two complementary techniques were applied. Most straight forward is a pulse radiolysis measurement which clearly avoids possible secondary reactions obscuring the initial radical attack. The absolute ·OH radical reaction rates with particular model compounds were measured using a competition method. This is based on the measurement of the initial optical density at the end of the pulse due to the transient ·OH-adduct with thiocyanate at 500 nm.

The primary ·OH radical selectivity for a particular pair of carbohydrate and lignin models is given by the ratio of the corresponding absolute rates.

The other technique applied comprised steady state γ-radiolysis of mixtures of one carbohydrate and one lignin model compound and HPLC-analysis of the degree of conversion effected by ·OH radical reactions. By varying the concentration ratio of the models, it is possible to calculate the overall selectivity of the ·OH radical with a particular pair of carbohydrate and lignin models.

Table 1, summarizes some of the results so far obtained.

Table 1.

a. Absolute rate constants determined by pulse radiolysis

Compound	k ($dm^3 mol^{-1} s^{-1}$)
1. Veratrylglycerol-β-guaiacyl ether	$1.7\ 10^{10}$
2. Veratrylglycol	$1.5\ 10^{10}$
3. Me β-D-glucopyranoside	$3.2\ 10^{9}$
4. Me β-D-xylopyranoside	$2.6\ 10^{9}$

b. Overall selectivities determined by γ-radiolysis

Lignin compound	Carbohydrate compound	Selectivity*
Veratrylglycerol-β-guaiacyl ether	Me β-D-glucopyranoside	2.7
Veratrylglycerol-β-guaiacyl ether	Me β-D-xylopyranoside	2.2

* k_L/k_C

The pronounced difference in the rates of the hydroxyl radical reaction with carbohydrate and lignin models reflects the electrophilic nature of the hydroxyl radical, which adds to the aromatic nuclei of lignins in preference of abstracting hydrogen from carbohydrates. The addition reaction is almost diffusion controlled and proceeds via a short lived charge transfer complex. At pH<3 this intermediary complex yields the radical cation of the lignin model which may decompose monomolecularily. Hydrogen abstraction by hydroxyl radicals is a sterically more hindered reaction than addition of hydroxyl radicals to the π-electron cloud of aromatics. This explains the intrinsic selectivity of the hydroxyl radical found in the system investigated. As the hydroxyl radical anion is a nucleophilic species it does not add to aromatic structures faster than it abstracts hydrogen from carbohydrates. Thus at pH>12 the intrinsic selectivity is lost.

The significant difference found between primary and overall selectivities indicates secondary reactions which either restores the lignin model or enhances the conversion of the carbohydrate model. Both possibilities can be formulated by reasonable assumptions. At the present time we are not able to ascribe the secondary effect to a specific reaction.

We have recently found that Mg^{2+} ions have a remarkable retarding effect on the rate of hydrogen abstraction from Me β-D-glucopyranoside by hydroxyl radicals. Our analysis shows that Mg^{2+} ions form surprisingly strong carbohydrate complexes containing one or two ions per glucoside molecule depending on the Mg^{2+}/carbohydrate concentration ratio.

At pH~7 the protective effect of Mg^{2+} ions is rather small but increases strongly with increasing pH up to pH~11.

At pH~10 the hydrogen abstraction rate in the presence of Mg^{2+} ions is only about 5% of that measured in the absence of Mg^{2+} ions. In our opinion the observed kinetic effect due to the formation of Mg^{2+} / carbohydrate complexes explains the increased selectivity obtained by addition of Mg^{2+} ions in oxygen and peroxide bleaching sequences.

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ENZYMATIC DEGRADATION OF CELLULOSE CRYSTALS

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ABSTRACT

Valonia and bacterial cellulose microcrystals were digested with purified components of the cellulase complex from Celluclast®. Four enzymes were considered, namely the exo CBHI and CBHII, together with the endo EGI and EGII. CBHI led to thinning and sub-fibrillation of the crystals whereas CBHII eroded only one of their two tips. With EGI and EGII, the attack was localized at kinks and defects occurring along the microcrystals. Mixture of the purified enzymes (such as CBHII + EGII) gave composite attack together with a synergistic action.

KEYWORDS: Cellulase, Cellulose Microcrystals

INTRODUCTION

The biodegradation of cellulosic material is a complex process which involves the interaction of multi-components enzymes on partially crystalline solid substrates. To date, the mechanism of cellulase attack is only partially understood even though great efforts have been made in purifying the various cellulase components and testing them individually on various substrates. When doing so, it is found that the accessibility and crystallinity of the substrates are two important features which will delay the enzymatic digestion. The authors, however, do not always agree on the relative influenced of these two parameters. The present work is an attempt of simplification by examining how well characterized and dispersed- i.e. highly accessible-cellulose crystals are digested away by the various cellulase components.

EXPERIMENTAL

Microcrystals of Valonia and bacterial cellulose were prepared by acido-mechanical treatment of Valonia cell wall or pre-purified bacterial cellulose pads.

A crude Celluclast® mixture, together with purified 1,4-β-D glucan glucan hydrolase (E.C.3.2.1.4, EG) I and II and 1,4-β-D glucan cellobiohydrolase (E.C.3.2.1.91,CBH) I were kindly provided by M. Schülein from Novo Industri. CBHII was purified by successive chromatography of Celluclast® on DEAE Sephadex, followed by Phenyl Sepharose and Sephadex G50.

Electron microscopy was achieved with a Philips EM400T after negative staining of the specimen.

The digested bacterial cellulose microcrystals were also studied by x-ray diffraction analysis by using a Siemens generator equipped with a flat film Wahrus vacuum camera.

RESULTS AND DISCUSSION

A typical preparation of Valonia microcrystals is shown in Figure 1. The crystals consist in segments of the initial cell wall microfibrils. They have the same width (ca.15-20 nm) and perfection than the original microfibrils, but are of various lengths, ranging from 500 nm to several microns. In Figure 1, it can also be seen that the tips of the microcrystals have irregular shapes, ranging from very sharp oblique cuts to blunt extremities, sometimes carrying microfibril debris. In addition, several microcrystals (see arrows in Figure 1) display defects which correspond to areas attacked by acid, but not fully disrupted by the mechanical agitation.

Figure 1. Transmission electron micrograph of Valonia microcrystals after negative staining with uranyl acetate

When the Valonia microcrystals were digested by CBHI (1), they became degraded by erosion and sub-fibrillation. This is illustrated in Figure 2 where one can see that the crystals have become narrower while their initial length appear maintained. In several instances, a longitudinal sub-fibrillation is clearly evident.

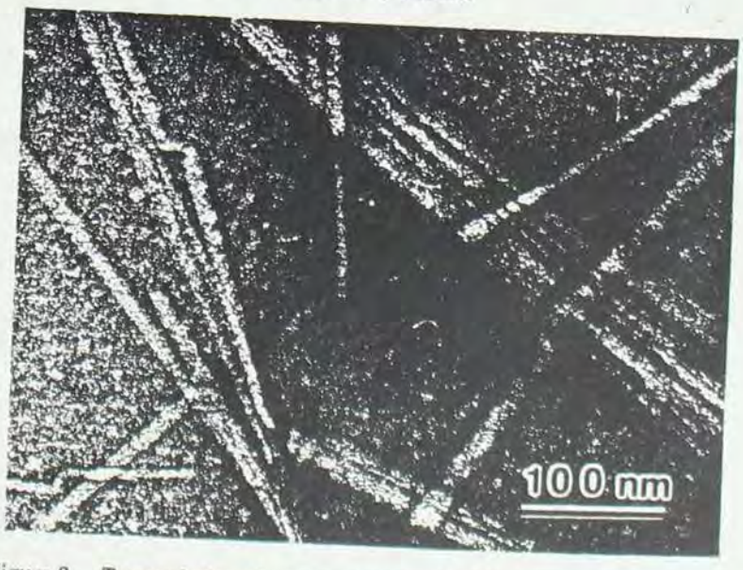

Figure 2 Transmission electron micrograph of Valonia microcrystals after 36 hours of interaction with CBHI.Specimen negatively stained with uranyl acetate.

A suspension of bacterial cellulose microcrystals attacked by CBHI was analysed by x-ray. The results are displayed in Figure 3 and compared with those of the initial sample . In the hydrolyzed sample, one notices a marked decrease of the intensities of the equatorial diffraction lines ($1\bar{1}0$), (110) and (020) whereas the meridional (004) together with the (102) lines have maintained their initial intensities. These x-ray experiments corroborate previous electron diffraction data obtained on hydrolyzed Valonia microcrystals (1).

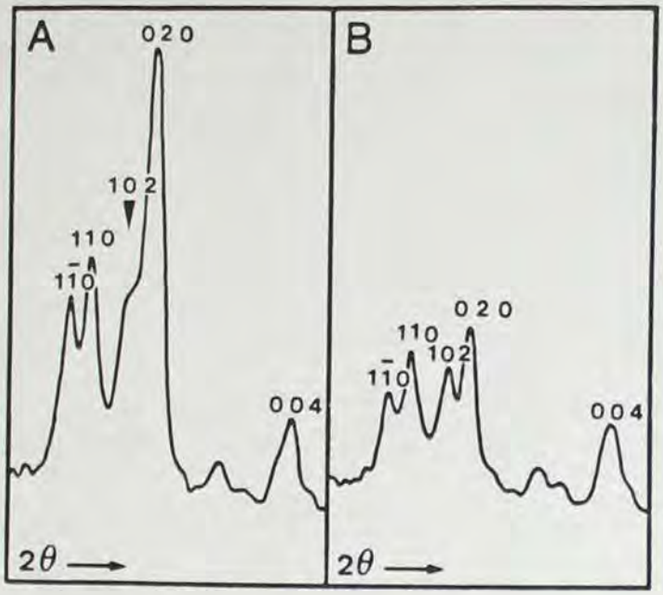

Figure 3 Radial densitometer tracings of x-ray powder diagram obtained with, A) initial bacterial cellulose microcrystals. B) same sample but after 16 hours of digestion with CBHI.

The action of CBHII on Valonia microcrystals (2) differs markedly from that of CBHI and corresponds to what one could expect for a classical exo-enzyme. In that case, each of the crystals became eroded at only one of their two tips, whereas the other tips remain unaffected. This is illustrated in Figure 4. Typically, the eroded tip displays an elongated pointed shape, with the point roughly centered along the long axis of the crystal.

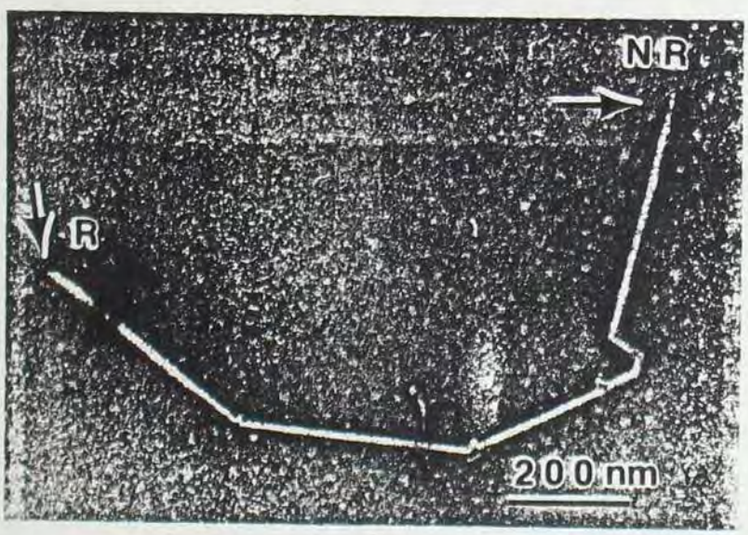

Figure 4 Transmission electron micrograph of one Valonia microcrystal after 16 hours of interaction with CBHII. The specimen was negatively stained with uranyl acetate. NR and R correspond to non-reducing and reducing tips of the crystal.

When the microcrystals are digested with a mixture of CBHII and EGII, the erosion occurs not only at one of the tips of the microcrystals, but also at the kinks and defects which become also sites of unidirectional attack. Such a phenomenon is illustrated in Figure 5. It corresponds to a sample treated as in Figure 4, the only difference being that the enzymatic solution contained a 60:40 mixture of CBHII and EGII. In that case, the digested specimen appears as a string of pointed tip fragments, each point being oriented toward the pointed tip of the partially digested crystal.

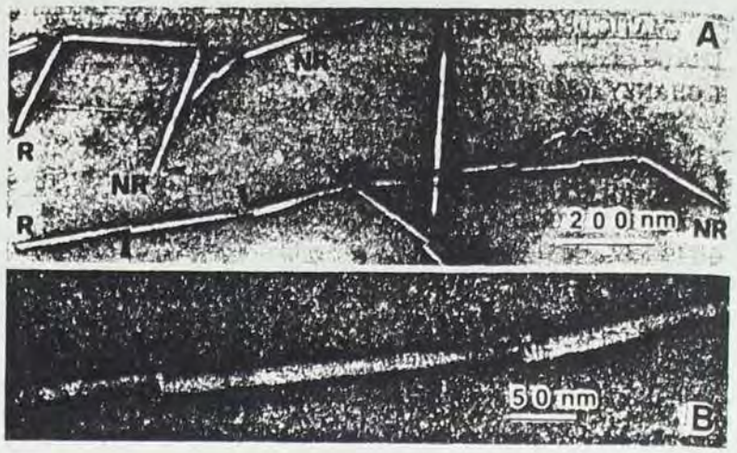

Figure 5 Transmission electron micrograph of Valonia microcrystals digested for 16 hours with a 60:40 mixture of CBHII and EGII. A) low magnification. B) enlarged area of A. The specimen was negatively stained with uranyl acetate.

CONCLUSIONS

The results presented here bring some clarification on the following points:

- CBHI is able by itself to degrade fully highly crystalline cellulose substrates. Its initial mode of attack appears to be of an "endo" rather than an "exo" type.
- CBHII follows the classical "exo" attack mode as it erodes the cellulose microcrystals at only one of their ends. This in particular confirms the parallelism of the cellulose chains in the Valonia cellulose microcrystals.
- when CBHII and EGII are mixed, the erosion occurs not only at one of the crystals tips but also at the defects found along the crystals. Such observations illustrate well the synergism between EGI and CBHII.
- Since CBHI and CBHII have different modes of attack, their synergism can also be explained.

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STRUCTURAL CHANGES IN LIGNIN DURING STEAM HYDROLYSIS OF Aspen wood

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Keywords : lignins, steam hydrolysis, ^{13}C NMR, DEPT.

In order to find in biomass an inexpensive and large supply of chemicals and organic materials, procedures involving steam hydrolysis of wood have been lately, reconsidered extensively (1). These techniques make readily available directly from wood chips, its three major components : cellulose, hemicellulose and lignins.

In this study, we have been concerned by the structural analysis of lignins fractions, extracted from Aspen wood, using one of these procedures : the Iotech process (2). An attempt to correlate the data obtained, with the experimental conditions of the steam hydrolysis has been made.

SAMPLES

We have been supplied with lignocellulosic materials, by the Pilat plants, build in Centre Technique du Papier of Grenoble (France). These samples come from two set of experiments :

1ST SET OF EXPERIENCES

P = 40 BARS CONSTANT

T = VARIABLE (LENGTH OF HYDROLYSIS)

1	10"
2	15"
3	20"
4	40"
5	60"
6	90"
7	165"

2ND SET OF EXPERIENCES

P(BARS) AND T(SEC) VARIABLE

1	45	205"
2	35	240"
3	45	45"
4	25	45"
5	35	10"
6	25	205"
7	20	125"
8	50	125"
9	35	125"

To extract the lignin part, we used a basic fractionation scheme (1b), where the dry lignocellulosic materials extruded from the blower tank, is dried, washed with water, to get rid of the hemicelluloses, and low D.P. phenols, then extracted either, with dioxan-water 9/1, or with acetone. Precipitation in ether, has been considered as a way to purify the lignins from extractives, and from low molecular weight phenols, still in the materials.

STRUCTURAL ANALYSIS

^{13}C NMR in liquid phase : the spectra are recorded at 62.9 MHz or 50.3 MHz from samples in DMSO-D6 - T° 323 K.

Quantitative analysis : the yield of extracted lignin translates the efficiency of the process, and allows correlations between the data and the experimental conditions. The perturbing effects on signal intensities are suppressed by using an inverse gate decoupled sequence (3).

Hydroxyl groups (acetylated samples) : the data are given in figure 1 for the first set of experiments ; for the second set of experiments, the correlation between the yield of extracted lignin, and the number of free phenolic groups is given in figure 2a).

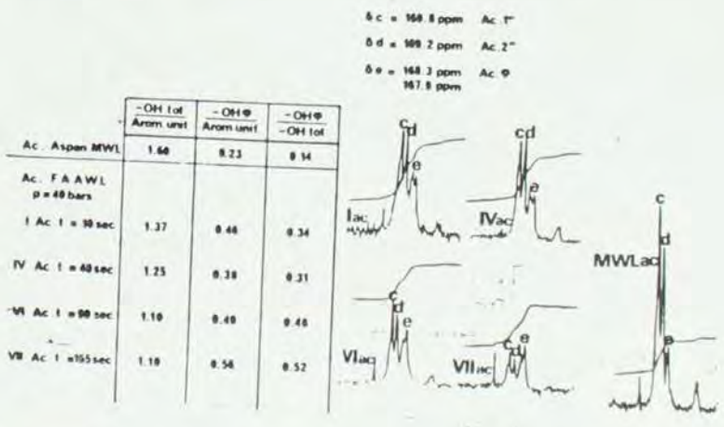
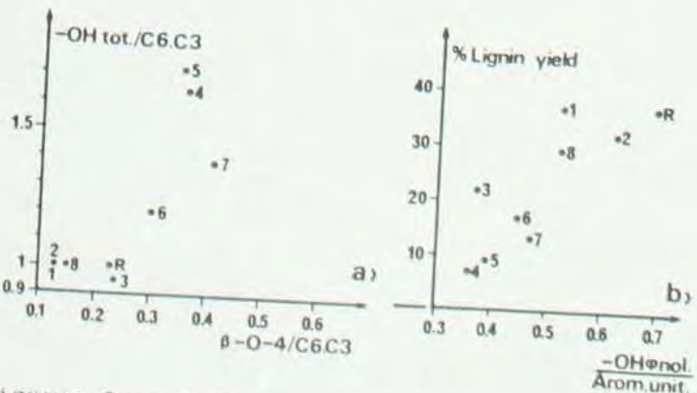


Figure 1. Quantitative determination of the -OH groups from the acetoxyl ^{13}C NMR signals.

β-O-4 syringyl structures : there is a cleavage of the alkyl-aryl ether bonds, which can be traced by the signal intensity of the aromatic carbons C-3/C-5, and correlated to the yield of extracted lignin (figure 2b). The two correlations in figure 2 are coherent.



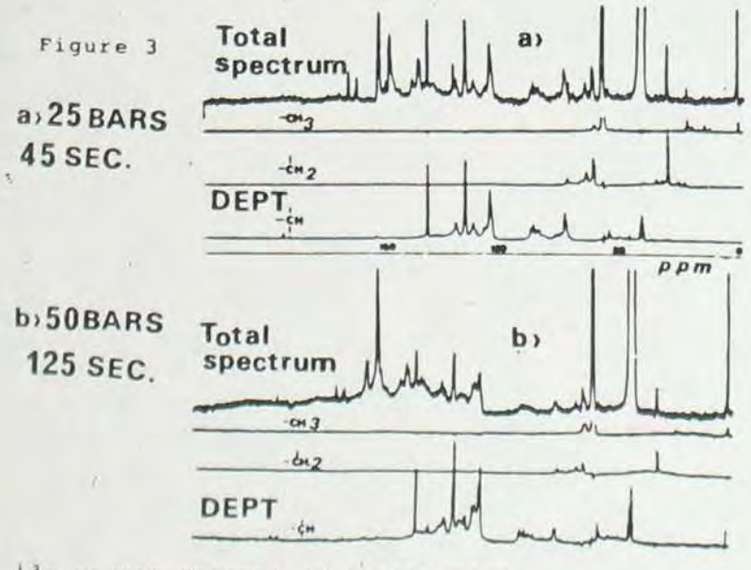
Figures 2a and 2b

Propane side chains : NMR reveals that there is an impressive decrease in the signals intensities of the C-α, C-β and C-γ carbons of the propane side chain which belongs to the basic structure of the C-9 units. The ratio of this C-3 chain per aromatic unit, which is about 1 in Aspen MWL, drops to 0.5 and 0.2 respectively in sample 3 (45 bars - 45 sec.) and sample 1 (45 bars - 205 sec.).

^{13}C NMR DEPT experiments : this special pulse technique greatly facilitates and improves the ^{13}C NMR structural analysis of lignins (4). It allows the separate observation of the CH3, CH2 and CH signals, which in addition benefit of a large intensity enhancement (figure 3). From these spectra we have :

- Discriminated between quaternary and tertiary aromatic carbons, and concluded from this ratio, the degree of condensation of the aromatic ring, which increases with the severity of the hydrolysis.
- Detected on the DEPT -CH2-subspectrum a broad signal, between 20 and 50 ppm which can be assigned to saturated benzylic carbons, that might explain the structural changes in the propane side chain, and the higher degree of condensation on the aromatic ring.

Figure 3



^{13}C CP/MAS SPECTRA IN SOLID PHASE

The spectra recorded at $\nu^{13}C$ = 50.3 MHz confirm the cleavage of the β-O-4 linkages, and structural changes can be traced on these spectra.

MONOMERS AND DIMERS FRACTIONS

This study has been carried along with Dr. K. LUNDQUIST (University of Göteborg - Sweden) on the fractions isolated by GPC (5) from the acetone extract : we observed a low yield in monomers, and syringaresinols as the main constituent of the dimers fractions. Conceivable reactions routes for the cleavage of the β-O-4 linkages have been proposed.

p-HYDROXY BENZOATES STRUCTURES

These structures have been found through the whole range of lignins fractions : attached to the polymer material, as well as free moieties in the monomers fractions.

CONCLUSION

The lignins fractions, extracted from Aspen wood by a steam hydrolysis based on the Iotech process, have undergone, degradations and chemical changes more or less important according to the experimental conditions, which can be summarized as follow :

- cleavage of the alkyl-aryl ether linkages ;
- partial loss of the C-9 structure ;
- increase in the degree of condensation of the aromatic ring ;
- continuous presence of p-hydroxy benzoates structures, free or attached to lignin.

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TRANSITION METAL ION CATALYSIS OF THE HYDROGEN PEROXIDE OXIDATION OF A LIGNIN MODEL COMPOUND

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ABSTRACT

The kinetics of reactions occurring during delignification of softwood kraft pulp with H_2O_2 (or oxygen) under alkaline conditions were studied in a model system. Very low levels of Fe and Mn salts were found to catalyze H_2O_2 decomposition to a greater extent than oxidation of a residual lignin-related compound. In contrast, catalytic levels of either ferricyanide or Cu salts produced an overall increase in the degradation of the lignin model at lower levels of H_2O_2 decomposition.

INTRODUCTION

The feasibility of using hydrogen peroxide as a delignifying agent in the first stage of a bleach sequence for alkaline chemical pulps has recently received considerable attention (1,2). This process, like oxygen bleaching, offers pollution abatement as a major advantage, but has the additional advantage of not requiring pressurized equipment.

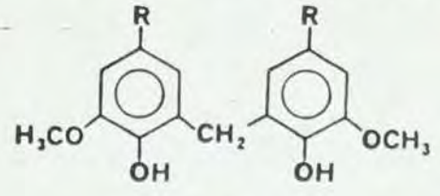
Studies (2,3) have shown that the removal of heavy metals from pulp (by pretreatment with acid and/or chelating agents) significantly enhances the extent of peroxide delignification. The negative effect of these metals is believed due to metal ion catalyzed decomposition of hydrogen peroxide.

On the other hand, Agnemo and Gellerstedt (4) have demonstrated that peroxide decomposition is necessary for phenolic structures of the type present in lignin to be attacked by hydrogen peroxide. Peroxide decomposition involves the intermediate formation of radical species such as $O_2^{\cdot}$ and $HO^{\cdot}$ (5-7). It is likely that oxygen and these oxy-radicals are the species which attack phenolic lignin units during peroxide delignification (4).

Transition metal ions can be involved in this reaction in a second way. The rate determining step in the oxidation of phenols with oxygen and peroxide in alkali is believed to be phenoxy radical formation (8,9). Many transition metal ion species are quite effective single-electron oxidants. Landucci (8,10) has demonstrated that the salts of heavy metals commonly found in pulp (Cu, Mn, Fe) catalyze phenoxy radical formation under alkaline conditions and in the presence of oxygen.

It is evident that transition metal ions should play a central role in the reactions of lignin with hydrogen peroxide (and oxygen) in alkali. The present study was directed toward understanding the relationship between transition metal ion catalysis of hydrogen peroxide decomposition and oxidation of a lignin-related compound.

The compound shown below - 1,1-methylenebis-(2-hydroxy-3-methoxy-5(2-carboxyethyl)benzene) or MBB - was selected as a model representing condensed phenolic units in residual lignin. The effects of catalytic quantities of Cu, Mn and Fe salts (and complexed Fe) on the kinetics of both hydrogen peroxide decomposition and MBB oxidation were studied. Experimental details are given elsewhere (11,12).



MBB R = $-CH_2-CH_2-COOH$

RESULTS

H_2O_2 Decomposition Kinetics

The kinetics of hydrogen peroxide decomposition in the reaction system without MBB present were studied first. The rate expression for this reaction is given by:

$$-d(H_2O_2)/dt = k_1 (H_2O_2)^{n_1} \quad (1)$$

Note that all rate constants evaluated in this study are for constant (HO^-) and temperature (45°C). Although the pH of the reaction solutions (with or without MBB present) were observed to increase slightly as the peroxide decomposed to oxygen, their pH remained in the interval 11.0-11.4 and the (HO^-) was considered constant.

Data collected from decomposition runs over the initial (H_2O_2) range of 15-840 mM (without any additives) were analyzed by the initial rate and differential methods. Rates were determined graphically from the (H_2O_2)-time plots. Results of this analysis indicate that the reaction order (n_1) changes

from 2.5 to 2.0 as the (H_2O_2) is decreased below about 60 mM (rate constants are listed in Table I). The level of decomposition observed in this experiment is attributed to a "background" level of catalysts present in the reaction system in trace levels.

Table I. H_2O_2 Decomposition Kinetics in the Absence of MBB. Metals added as the salts: $MnSO_4$, $CuSO_4$, $FeSO_4$. Conditions: pH 11.0-11.4, 45°C, (H_2O_2) range 90-150 mM.

Metal Ion Additive	Additive Level, μM	Reaction Order, n_1	Rate[a] Constant, k_1
None	-	2.0[b]	1.36 ± 0.51
None	-	2.5	1.69 ± 0.34
Fe	18.2	1.0	3.50 ± 0.09
Fe	285	1.0	5.80 ± 0.33
Cu	1.8	1.0	8.45 ± 0.07
Cu	9.1	1.0	8.72 ± 0.26
Cu	18.2	1.0	8.83 ± 0.49
Cu	285	1.0	26.4 ± 3.1
Mn	9.1	1.0	4.85 ± 0.06
Mn	18.2	1.0	7.33 ± 0.14
Mn	285	1.0	202 ± 58

[a] Units (order): $min^{-1} \cdot 10^{-3}$ (1.0), $mM^{-1} \cdot 10^{-5}$ (2.0), $mM^{-1.5} \cdot min^{-1} \cdot 10^{-6}$ (2.5). ± 95% confidence limits.

[b] (H_2O_2) less than ca. 60 mM.

The effects of added transition metal ions on the decomposition kinetics were also investigated. In agreement with previous studies (4,5) first order kinetics were observed in these experiments (Table I). The data showed an excellent fit (correlation coefficient, r>0.99) to the integrated form of equation (1) with n_1=1.0.

Hydrogen peroxide decomposition during each MBB oxydation run (Table II) was monitored (independently of its consumption by MBB) by measuring the volume of oxygen evolved. The rate law for decomposition under these conditions was assumed to be:

$$d(Ox)/dt = k_2 (H_2O_2)^{n_2} \quad (2)$$

The term (Ox) represents the concentration of decomposed H_2O_2 as measured by oxygen evolution ($2H_2O_2 \rightarrow O_2 + 2H_2O$). The effects that the additives had on the decomposition and total consumption of H_2O_2 in the MBB oxidation runs are shown in Figures 1 and 2, respectively.

Table II. Peroxide Decomposition Kinetics in the Presence of MBB. Metals added as their salts: $FeSO_4$, $K_3Fe(CN)_6$ (FC), $MnSO_4$, $CuSO_4$. Reaction conditions: (MBB)o = 20 mM, (H_2O_2)o = 100 mM, pH 11.0-11.4, 45°C.

Reaction	Additive Conc., μM	Reaction Order, n_2	Rate[a] Constant, k_2
Control	-	2.0	5.42 ± 0.20
Fe	300	1.5	11.6 ± 1.1
FC	300	1.5	7.28 ± 0.57
Mn	21	1.0	19.5 ± 0.6
Cu	12	1.0	10.8 ± 0.3

[a] Units (order): $mM^{-1} \cdot min^{-1} \cdot 10^{-5}$ (2.0), $mM^{-0.5} \cdot min^{-1} \cdot 10^{-4}$ (1.5), $min^{-1} \cdot 10^{-3}$ (1.0). ± 95% confidence limits.

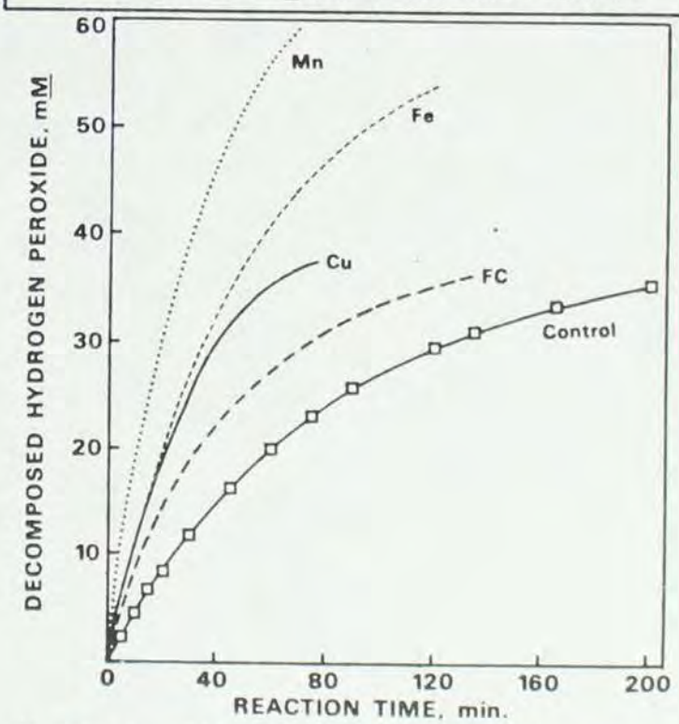


Figure 1. Effects of added metal ions on H_2O_2 decomposition during the MBB reactions (conditions given in Table II).

The data in Figure 1 were analyzed by the differential method, with the rates, d(Ox)/dt, determined graphically. This analysis showed that the reaction order (n_2) for the Control, Cu and Mn reactions were essentially the same as the orders (n_1) found in the absence of MBB (2, 1 and 1, respectively). The presence of MBB in the Fe reaction caused the reaction order to increase from 1.0 (n_1) to 1.5 (n_2). A 1.5 order (n_2) was also found in the reaction catalyzed by ferricyanide ions (FC).

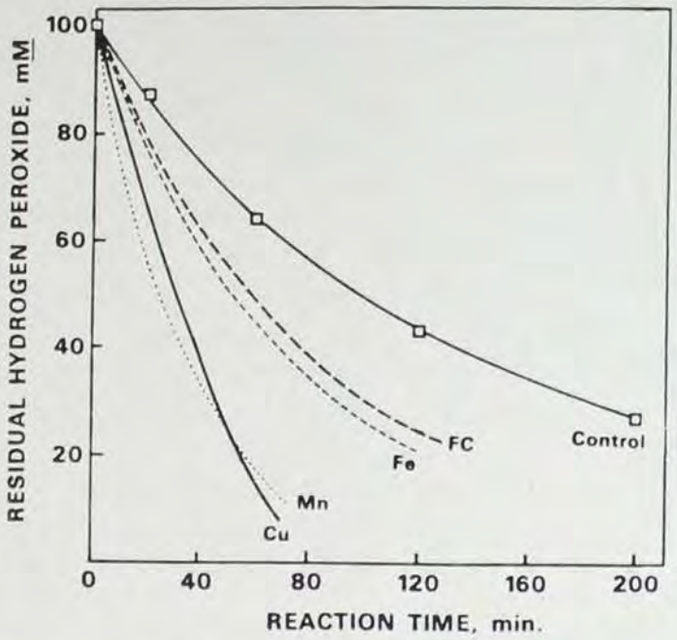


Figure 2: Effects of added metal ions on the residual level of H_2O_2 during the MBB oxidation reactions (Table II).

The rate constant, k_2, for each oxidation run was evaluated using the integral method (Table II). Integration of equation (2) gives:

$$(Ox) = k_2 \int_o^t (H_2O_2)^{n_2} \, dt \qquad (3)$$

The integral was approximated by applying Simpson's Rule to the (H_2O_2)-time data of Figure 2. Plots of equation (3) for the oxidation runs (Control, FC, Fe, Cu and Mn with n_2 = 2.0, 1.5, 1.5, 1.0 and 1.0, respectively) showed excellent linearity, $r>0.99$.

MBB Oxidation Kinetics

The MBB concentration-time curves in Figure 3 represent the net effect of the metal ion additives on the two overall reactions: hydrogen peroxide decomposition and MBB oxidation. In order to compare the catalytic effects of the metals on the MBB oxidation rate, the same general kinetic model was applied to the data from each reaction.

The model, defined by equations (4) and (5), represents a useful but simplified description of the complex reaction systems under study. A first order dependence on (MBB) was assumed on the basis of a similar kinetic study by Agnemo and Gellerstedt (4). As a first assumption, the order with respect to (H_2O_2), n_3, was set equal to one. The first term of equation (5) represents peroxide decomposition; the values k_2 and n_2 from Table II were used. The second term represents H_2O_2 consumption by MBB (and its products).

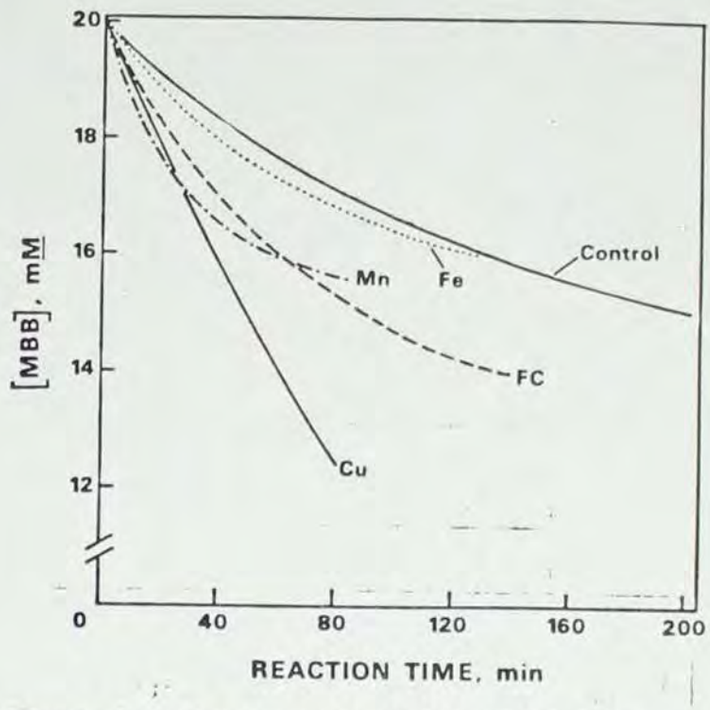


Figure 3. Kinetic plot of MBB degradation by H_2O_2 with and without metal ions added (Table II). The curves result from the computer model described in the text.

$$-d(MBB)/dt = k_3 (MBB)(H_2O_2)^{n_3} \qquad (4)$$

$$-d(H_2O_2)/dt = k_2(H_2O_2)^{n_2} + k_4(MBB)(H_2O_2)^{n_3} \qquad (5)$$

A computer program for parameter estimation from multiresponse data (13) was employed to obtain optimal values for the rate constants, k_3 and k_4 (12). The experimental data from the Control, Fe, FC and Mn reactions showed a good fit to the resulting calculated (H_2O_2)-time and (MBB)-time curves using the above model.

Table III summarizes the rate constants found by this analysis for the five MBB oxidation reactions. For the Cu reaction the model accurately described the experimental data only when a zero order dependence on (H_2O_2) was assumed (n_3 = 0). Application of the differential and integral methods confirmed that the MBB oxidation rate was independent of (H_2O_2) for this reaction.

DISCUSSION

H_2O_2 Decomposition

The results presented above illustrate some of the complexities associated with the chemistry of hydrogen peroxide decomposition. The bulk of the literature concerning peroxide decomposition indicates that this reaction proceeds via a radical chain mechanism catalyzed by transition metal ion species (5,14). Figure 4 depicts a set of reactions which we believe are important in describing hydrogen peroxide decomposition in alkali (12).

Table III. Rate Constants Evaluated by the Kinetic Model Analysis.

Reaction	Constants ($mM^{-1} \cdot min^{-1}$) $k_3 \times 10^5$	$k_4 \times 10^4$	St.[a] k_4/k_3	Relative[b] k_3
Control	2.69	2.06	7.7	1.00
Fe	3.60	2.30	6.4	1.34
FC	5.39	3.78	7.0	2.00
Mn	8.60	7.23	8.4	3.20
	Constants (min^{-1}) $k_3 \times 10^3$	$k_4 \times 10^2$		
Cu	5.90	4.95	8.4	-

[a] Stoichiometry.

[b] Ratio of k_3 for the given reaction to k_3 for the Control reaction.

The observed changes in the reaction order, n_1, with changes in the H_2O_2 or metal ion concentration is consistent with a complex reaction proceeding by two or more parallel paths (15). Other researchers have reported changes in this reaction order with changes in pH or metal ion concentration (5). In the presence of Fe salts the addition of MBB also caused a change in the order (n_1 = 1.0, n_2 = 1.5).

$$H_2O_2 + M \longrightarrow HO\cdot + HO^- + M^+ \quad (1)$$

$$H_2O_2 + HO^- \rightleftharpoons HO_2^- + H_2O \quad (2)$$

$$HO_2^- + M^+ \longrightarrow HO_2\cdot + M \quad (3)$$

$$HO_2\cdot + HO^- \rightleftharpoons O_2^{\cdot-} + H_2O \quad (4)$$

$$O_2^{\cdot-} + M^+ \rightleftharpoons O_2 + M \quad (5)$$

$$O_2^{\cdot-} + HO\cdot \longrightarrow O_2 + HO^- \quad (6)$$

$$2\,O_2^{\cdot-} + H_2O \longrightarrow O_2 + HO_2^- + HO^- \quad (7)$$

$$HO\cdot + HO_2^- \longrightarrow H_2O + O_2^{\cdot-} \quad (8)$$

$$HO\cdot + M \longrightarrow HO^- + M^+ \quad (9)$$

$$HO\cdot + HO\cdot \longrightarrow H_2O_2 \quad (10)$$

Figure 4. Proposed metal-catalyzed radical chain mechanism for decomposition of H_2O_2 in aqueous alkali.

Hydrogen peroxide decomposition was accelerated by MBB in the Control, Mn and Cu reactions (cf. Tables I and II). A similar acceleration was also observed in a study in which glucose was added to alkaline H_2O_2 (16). This is probably due to the organic substrate acting as a chain transfer agent in the radical decomposition reaction. For example, the single electron oxidation of MBB by M^+ provides an additional route for M to be formed which, as shown in Figure 4, is involved in the chain mechanism for peroxide decomposition (step 1).

MBB Oxidation

At the levels added the metal ions can be listed in order of decreasing catalytic activity with respect to MBB oxidation as follows:

Cu > Mn > FC > Fe (>Control)

Landucci (8) found the same ranking for these additives with respect to their ability to catalyze phenoxy radical formation. This provides strong evidence for the contention that the important, rate-limiting step in the degradation of phenolic lignin units in alkaline hydrogen peroxide is phenoxy radical generation.

On the basis of the results of this study and others (4,8,9) the reaction scheme depicted in Figure 5 may be considered to represent the mechanism of destruction of phenolic lignin units by alkaline hydrogen peroxide. The single-electron oxidation of the phenolate anion (step 2, Figure 5)

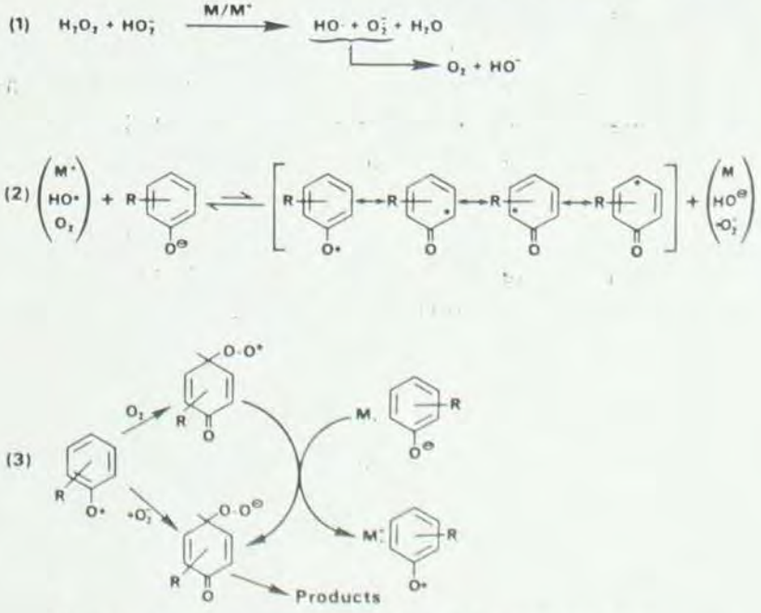


Figure 5. Proposed oxidation scheme for substituted phenols under alkaline oxygen and/or H_2O_2 conditions.

results in the formation of a resonance-stabilized phenoxy radical. Reaction with superoxide and/or oxygen (step 3, Figure 5) gives a cyclohexadienone hydroperoxide which is degraded to lower molecular weight products by ionic mechanisms involving attack by hydroxyl and hydroxperoxy anions (12,17). The mechanism of Figure 5 is equally applicable to oxygen bleaching since all of the same species are present there.

The observed independence of oxidation rate on (H_2O_2) for the Cu reaction can be explained in terms of this mechanism. It is postulated that the Cu catalyst effectively competes with the phenoxy radical for superoxide ions. Thus reaction of phenoxy radicals (which are generated at high rates by the Cu catalyst) with oxygen in step 3 (Figure 5) becomes the favored pathway to the formation of cyclohexadienone hydroperoxide intermediates. Since the decomposing hydrogen peroxide maintains a saturated solution of oxygen (i.e., constant concentration), the reaction rate depends only on the MBB concentration.

A large number of metal ions and their complexes are known to catalyze superoxide dismutation:

$$H_2O + 2O_2^{\cdot-} \rightarrow HO_2^- + O_2 + HO^-$$

For example, hydrated Cu(II) ions have been shown to catalyze this reaction at diffusion controlled rates ($k \sim 10^{10}$ $\underline{M}^{-1}$ s^{-1} (18)). However not all metal species are this active. Superoxide dismutation in the presence of ferricyanide/ferrocyanide ions occurs at much slower rates ($k \sim 10^3$ $\underline{M}^{-1}$ s^{-1} (19)). This likely explains why the dependence of MBB oxidation rate on (H_2O_2) was the same in both the Control and FC reactions.

CONCLUSIONS AND PRACTICAL SIGNIFICANCE

The results of this study are consistent with our present understanding of the complex mechanisms of H_2O_2 decomposition (Figure 4) and phenol degradation by H_2O_2 (or oxygen) under alkaline conditions (Figure 5). The kinetics of these two reactions were shown to be strongly influenced by different transition metal ions added at catalytic levels.

The relationship between the catalysis of H_2O_2 decomposition and phenol oxidation by the metal ion species is illustrated in Figure 6. In this figure, the level of peroxide decomposed is plotted as a function of the amount of MBB reacted. The slope of the lines in the plot represents the ratio of the rates of H_2O_2 decomposition to MBB oxidation. The Cu reaction gave a non-linear response due to the independence of MBB oxidation rate on (H_2O_2).

Figure 6 graphically demonstrates that the added transition metal ions catalyzed H_2O_2 decomposition and the oxidation of the lignin model to different extents. In the context of peroxide delignification of pulp, these results suggest that the presence of some metals (e.g., Fe and Mn) waste H_2O_2 through increased decomposition to oxygen. However, results of the Cu and FC reactions indicate that not all metal species may be considered detrimental. For instance, it might be possible to increase the extent and rate of delignification for a given H_2O_2 charge by controlling the levels and types of metal ions species in the pulp. As a further extension, it may be feasible to increase selectivity by means of catalysts which preferentially direct peroxide attack to the lignin fraction, thus minimizing damage to the carbohydrates.

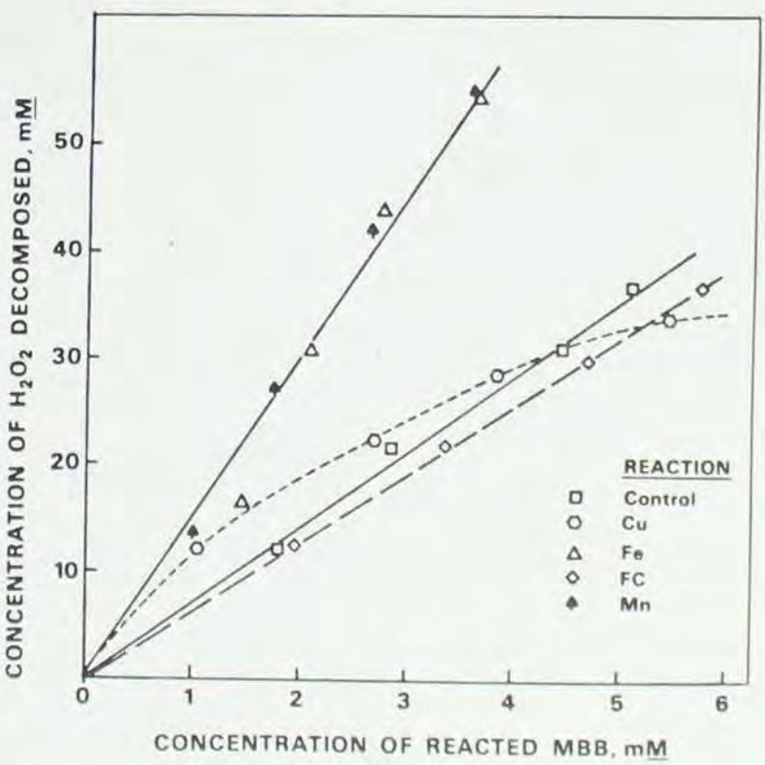


Figure 6. Influence of metal ions on the relationship between H_2O_2 decomposition and MBB oxidation (Conditions in Table II).

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REACTION OF ASPEN AND SOUTHERN PINE WOOD FLAKES WITH GASEOUS KETENE

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ABSTRACT

Acetylation of wood flakes prior to flakeboard manufacture has been shown to greatly improve the dimensional stability of the finished boards. Previous work has centered on the use of acetic anhydride under various conditions as the acetylating agent. The need to remove the acetic acid co-product of acetylation by acetic anhydride prompted us to examine the reaction of ketene with wood flakes since ketene is known to acetylate hydroxyl groups without forming by-products. The use of ketene to acetylate wood was examined briefly by Tarkow in 1948 and by Karlson et al. in 1972.

Ketene reacted both with southern pine and with aspen flakes at atmospheric pressure in the absence of solvent or catalysts at 50-60°C to give maximum weight gains of about 17% and 20%, respectively. Aspen reacted more rapidly than did southern pine, but both reactions were quite slow - at least 10 hr reaction time was needed to reach maximum weight gains. Some darkening of the flakes was noticed; reactions run at higher temperatures gave much more discoloration.

Infrared spectroscopy, solid-state ^{13}carbon NMR spectroscopy, and acetyl analysis established that ketene did effect acetylation of both species, but weight gains above 12% did not correlate with acetyl content. Thus aspen which was reacted to a 20% weight gain showed only 12.4% acetyl content on analysis. The non-acetyl weight gain did not take the form of extractable material, and we suspect that part of the ketene is being converted to chemically bound homopolymers in the flakes.

Flakeboards made from the ketene-modified flakes showed a greatly reduced rate and extent of swelling because of sorption of liquid water or water vapor when the results were compared to those of the control boards. The improvement in dimensional stability was greater for aspen than for southern pine. Thus boards made from aspen flakes modified at the 12% weight-gain level gave only 10% swelling in thickness after 4 hr exposure to liquid water, whereas a corresponding experiment with southern pine gave 29% swelling. Control boards made from unmodified flakes of aspen and southern pine exhibited 61% and 40% swelling, respectively, under these conditions.

Ketene modification was, in general, about as effective as acetylation with anhydride in improving the dimensional stability of aspen flakeboards, but ketene modification was much less efficient for southern pine.

COMPARISON BETWEEN LIGNINS PRODUCED BY STEAM EXPLOSION AND ORGANOSOLV PRETREATMENTS

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ABSTRACT

A comparison between lignins isolated in wood pretreatments of steam explosion and organic-aqueous solvent delignification (organosolv) with lignin isolated by mild wood ball milling is presented for aspen (Populus tremuloides). Wet analysis, quantitative carbon-13 nuclear magnetic resonance (NMR), molecular weight distribution by size exclusion chromatography, and ultraviolet absorption spectroscopic data are presented. The comparative ability of steam exploded and organosolv lignins with that of conventional kraft materials to replace phenol in phenol-formaldehyde thermosetting resins is examined.

KEYWORDS: Lignin, Steam Explosion, Organosolv, Pretreatments, Thermosetting Resins, Aspen

INTRODUCTION

A number of methods have been suggested to pretreat wood (primarily hardwoods) so the biopolymers can be easily fractionated and the cellulosic fraction can become accessible to enzymes for hydrolysis to glucose and fermentation to ethanol. Examples of these methods are steam explosion, autohydrolysis, wet oxidation, and rapid steam hydrolysis/continuous extraction (RASH), reviewed recently by Schultz et al. (1), as well as hydrothermolysis (2), and organosolv (3). The first five processes listed employ steam and heat; the sixth type of process employs an aqueous/organic solvent and heat. A comparative economic evaluation of steam explosion, organosolv with methanol- or ethanol-water, and wet oxidation indicated that the pretreatment costs were comparable. High value applications of the lignins could largely decrease or offset wood pretreatment and lignin isolation costs (4). All three of these pretreatments produce cellulosic substrates that can be hydrolyzed by enzymes. Potential markets for lignin utilization have been reviewed (5). This paper compares various lignins produced in biomass-to-ethanol conversion processes based on steam explosion and organosolv pretreatments.

EXPERIMENTAL SECTION AND RESULTS

Lignin sample preparation

Steam explosion. The aspen exploded wood was supplied by Iotech Corp. (55 s at 240°C). The procedure of isolation of the lignin through ethanol extraction has been described (6). Alternatively, after removal of the hemicellulosic fraction by water extraction, the lignin materials were isolated by extraction with 0.2 M KOH or methanol soxhlet extraction. These samples are abbreviated as EESEAL, AESEAL, and MSESEAL respectively for ethanol, alkaline, and methanol preparations of steam-exploded aspen lignins.

Organosolv lignins. Aspen wood chips were pulped using methanol/water (70:30 % v/v) in a liquor-to-wood ratio of 4:1 in the presence of $NaHSO_4$ (0.04 M and 0.1 M), H_2SO_4 (0.05 M), or H_3PO_4 (0.05 M). The time at temperature of 165°C was 2.5 hours and rate of heating to temperature from ambient was 2.7°C/min. After time at temperature, the digestor was cooled overnight and the liquor collected. This procedure allowed some lignin to reprecipitate onto the cellulose fibers. The organic solvent was removed by evaporation under reduced pressure. Redissolution of the hemicellulosic fraction and low-molecular-weight, water-soluble lignins left a lignin fraction, which was filtered off. About 15% of the dry weight of wood was isolated in this way. The aspen wood used contained 17.1% lignin (Klason and soluble) based on extractives-free wood. The yield of the dry fibrous materials relative to the amount of dry wood charge varied between 49% (H_2SO_4) and 59% (0.04 M $NaHSO_4$). The permanganate number of these pulps ranged from 19 (0.1 M $NaHSO_4$) to 35 (H_2SO_4).

Ball-Milled Aspen Lignin. The procedure of Lundquist et al. (7) was used. The yield of purified milled wood lignin obtained was 13.4 g from 136 g of ethanol/benzene extracted aspen wood.

Kraft lignins. A liquor-to-wood ratio of 4.5:1 was used with 14% active alkali and 20% sulfidity. Pulping was carried out at 165°C for one hour. Lignin isolation was carried out after concentration of the liquor to about 40% solids and precipitation with carbon dioxide (50 psi, 80°C, 3-4 h). Lignin was purified by dissolution in base and reprecipitation by addition of acid.

Other kraft lignins. Indulin AT, Reax 27, and Reax 31 were supplied by Westvaco Chemicals Division.

Analytical methods

The analytical methods used to characterize the lignins investigated in this work have been described by some of us (6). Quantitative carbon-13 nuclear magnetic resonance, employing the pulse sequence described by Robert and Gagnaire (8), was employed. In addition, independent methods were employed to confirm the NMR data. Acetylated lignin samples were used both in the NMR and in the high performance size exclusion chromatography.

Quantitative acetylation of lignins. Lignin (0.2-1.0 g) is dissolved in 40 ml of a mixture of pyridine and acetic anhydride (1:1) under nitrogen atmosphere, heated to 55°C, and stirred for 48-60 h. After the reaction is completed, toluene (500 ml) is used to azeotropically remove both the pyridine and the acetic anhydride in a rotary evaporator (40°C). Small amounts of acetone are added to solubilize the acetylated lignins while toluene is being removed. Then, ethanol:acetone (1:1, 250 ml) is used to azeotropically remove toluene left in the sample. The lignin sample is vacuum dried to constant weight. This procedure was checked with monomer and dimer lignin model compounds. For instance, for acetovanillone this procedure gave 100.5% of the expected acetylated material, whereas conventional methods (precipitation and extraction) gave only 84% of the expected amount. A blank of the acetylation reaction (for 1 g of lignin) gave about 10 mg of a material, indicating the possible presence of 1% by weight of impurities, which are not detected by carbon-13 NMR, and which are low-molecular-weight materials by size exclusion chromatography (295 and 209 amu).

High performance size exclusion chromatography. The acetylated lignins were subjected to size exclusion chromatography using four μ-spherogel columns (10,000; 500; and two 100 Å) from Altex. The solvent was tetrahydrofuran (Burdick and Jackson) at 1.0 ml/min. A Hewlett Packard 1090 (or 1084) high performance liquid chromatograph was employed with a HP 1040 diode array UV absorption spectrometer detector. Calibrations were performed with polystyrene standards (Beckman/Altex), Igepal polymers (Aldrich), and lignin model compounds.

Adhesive testing. The ability of the various lignins to replace phenol in phenol-formaldehyde thermosetting resins was tested. The type of resin used in the adhesive testing was Cascophen 313H, a high-temperature setting phenol-formaldehyde adhesive, manufactured by Borden Chemical Co. Levels of 30%-50% by weight of replacement of phenol with lignin were tested using the British Standard 1204: Part 1:1964, and testing between 20-30 specimens per evaluation.

DISCUSSION

Our sample of milled aspen lignin analyzed as $C_9H_{8.5}O_{3.4}(OCH_3)_{1.46}$, which compares very well with literature $C_9H_{8.3}O_{3.0}(OCH_3)_{1.45}$ (9) prepared by milling for 128 h vs. 720 h in our case. The NMR proportions of phenolic, primary, and secondary hydroxy to aromatic carbons are 0.18, 0.63, and 0.62 respectively, which compare well with Robert et al. (10) of 0.22, 0.77, and 0.61. The integration of carbons 3 and 5 (152.3 ppm) assigned to syringyl groups containing β-O-4 ether units is 0.47 compared to 0.6 (10).

Steam exploded and organosolv lignins are formed in acid hydrolytic processes. As a result, the α-O-4 and to some extent the β-O-4 alkyl aryl ether bonds that are predominant in the lignin polymer as well as the lignin-carbohydrate bonds are hydrolyzed, thus leading to an increase of free phenolic units. AESEAL and MSESEAL have 0.25 and 0.22 β-O-4 ether content respectively in syringyl units and 0.6 in phenolic hydroxy/aromatic units. The organosolv lignins investigated here are obtained under progressively more drastic acid conditions (0.04 M $NaHSO_4$, H_3PO_4, 0.1 M $NaHSO_4$, H_2SO_4). On going from 0.04 M to 0.1 M $NaHSO_4$ the β-O-4 ether content in syringyl units decreases from 0.32 to 0.21 while the free phenolic content increases from 0.46 to 0.65/aromatic unit. These NMR results agree within the experimental error with phenolic OH determinations by conductimetric method. Detailed analytical data will be published elsewhere (11)

The molecular weight distributions of the various acetylated lignin preparations are a distinct function of the delignification procedure as well as the extraction procedure. Acetylated AESEAL has the highest apparent weight- ($\bar{M}_w$= 2100), number-, and z-average molecular weights of the steam exploded lignin materials investigated. Acetylated EESEAL ($\bar{M}_w$=1050) molecular weight distribution is intermediate between alkaline and methanol ($\bar{M}_w$=920). The solvent extracted materials have smaller polydispersity than AESEAL (1.6 and 2.7 respectively). The nature of the isolated organosolv lignins is a marked function of the nature and concentration of the acid catalyst employed. There is a decrease in apparent number-, weight-, and z-average molecular weight as the pH of the pulping liquor decreases. Polydispersities also decrease as the pH decreases (Figure 1).

The absorption spectra in the 210-400 nm range of the various acetylated lignins at >600 apparent molecular weight show one absorption peak at about 275 nm, a shoulder with an absorption peak at about 240 nm, and a much more intense peak toward the UV, as expected for the three $\pi \rightarrow \pi^*$ transitions. The absorption spectra of the lower molecular weight lignins (paucidisperse components present in all samples except ball-milled) display more pronounced peaks toward the visible. For instance, in the H_2SO_4 sample distinct peaks are at about 220, 240, 275, and 320 nm. The peaks at >300 nm can be correlated with structures containing carbonyl or unsaturated carbon-carbon bonds conjugated to the aromatic ring. Both vinyl side chains and carbonyl groups have been detected at levels of 0.1-0.2/C_9 each in the steam explosion and organosolv samples. The spectral data indicate a heavy concentration of conjugated carbonyl or unsaturated structures in the low-molecular-weight materials. Thus the need for analytical methods that do not fractionate the lignin materials.

The ability of the various lignins described here to replace phenol in phenol-formaldehyde thermosetting resins was tested (Table 1). The set time was such that all lignin samples would have time to cure at temperature. There were no significant differences between the lignins tested and the controls at 30% replacement by both shear strength measurements and wood failure. At 50% replacement, differences emerge, and Reax 27, pine kraft, sweet gum kraft, Reax 31, Indulin AT, and organosolv aspen (0.04 M $NaHSO_4$) were found to be adequate replacement materials in order of decreasing suitability.

Acknowledgements: Profitable discussions with Profs. K. Sarkanen and W. G. Glasser are gratefully acknowledged. We thank Dr. Danielle Robert for obtaining some of the NMR spectra discussed in this paper. Borden Adhesives provided materials for the testing performed and repeated some of the tests. We thank Mr. J. Schmitz (Borden) for his assistance in the adhesive testing. This work was sponsored by the Biomass Energy Technology Division/DOE under FTP No. 516.

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Table I. Lignin adhesive testing results in terms of: normalized average stress strength, $\bar{S}$ in psi and corresponding standard deviation, σ_s, and normalized wood failure, $\bar{F}$, in %.

Level of Phenol Replacement with Lignin	30%			50%			30% Cold Soak		
Type of Lignin	$\bar{S}$	σ_s	$\bar{F}$	$\bar{S}$	σ_s	$\bar{F}$	$\bar{S}$	σ_s	$\bar{F}$
Steam-Exploded Aspen									
MSESEAL	702	52	37	578	58	26	490	91	31
EESEAL	668	55	48	439	95	17	507	67	40
AESEAL	626	68	59	565	108	30	524	71	60
Kraft									
Aspen	657	58	70	521	92	16	530	93	44
Pine	721	50	110	653	65	40	485	103	48
Sweet Gum	681	77	60	624	34	35	555	74	58
Commercial									
Indulin AT	696	61	64	601	57	40	550	95	43
REAX 27	673	75	44	667	87	38	552	103	39
REAX 31	707	70	47	607	90	38	612	67	32
Organosolv Aspen									
0.04 M $NaHSO_4$	658	63	57	600	40	39	460	87	48
0.1 M $NaHSO_4$	664	98	50	581	64	16	522	49	57
0.05 M H_2SO_4	672	77	47	499	100	17	561	73	72
0.05 M H_3PO_4	641	71	54	597	81	29	549	72	67
Control	675	70	67	675	70	67	500	80	38

*$\bar{S} = (\bar{S}_{day}/\bar{S}_{control,\ day}) \times \bar{S}_{control,\ year}$, where $\bar{S}_{control,\ years}$ is the testing average of all controls over the entire duration of the test. Wood failure is a very subjective number. Arbitrary numbers were selected and all average wood failures were normalized to the selected values. Numbers of samples: 20-30 test specimens per test.

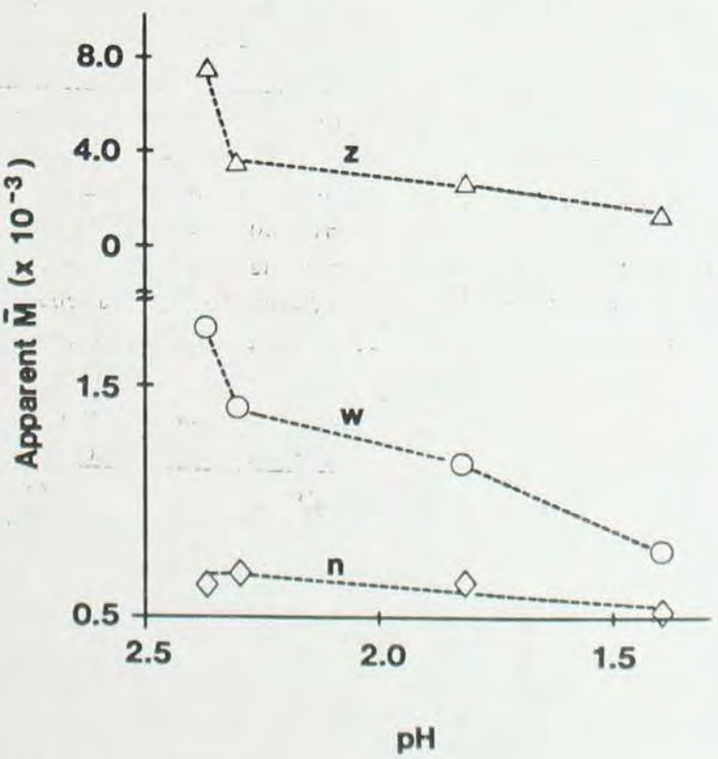

Figure 1. Apparent number-, weight-, and z-average molecular weights of acetylated organosolv aspen lignins as a function of the pH of the liquor at 40°C.

REACTIONS OF GLYCOSIDLS WITH BORATE IONS AT ELEVATED TEMPERATURE

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ABSTRACT

Simple glycosides were heated with sodium hydroxide and borate solutions. The borate ions acted not only as generators of hydroxide ions, but also reacted direct with some glycosides, degrading them rapidly into acidic products. Even a weakly alkaline reagent such as borax degraded e.g. methyl α-L-arabinopyranoside much faster than did sodium hydroxide of the same concentration. Glycosides able to form complexes with borate ions were degraded faster than others by borate solutions at elevated temperature.

INTRODUCTION

When using sodium borate solutions as pulping agents (1), it is important to know how their alkalinity varies with temperature. When some 1,2-trans-glycosides were used as indicators of the hydroxyl ion content of borate solutions at elevated temperature (100 - 170°C), these solutions were found to degrade the glycosides much faster than could be expected from their content of hydroxide ions. However, the alkaline hydrolysis of 1,2-trans-glycosides is thought to proceed with the assistance of an ionized hydroxyl group at C_2 (2). As a consequence, the rate of hydrolysis at a given temperature and ionic strength would be expected to depend only on the hydroxide ion content of the solution, regardless of the presence of other nucleophiles. This discrepancy between theory and experiment motivated a closer look at the interaction between borate ions and glycosides at elevated temperature.

RESULTS

Alkaline hydrolysis of the glycosides was studied by heating samples with solutions of various composition in sealed autoclaves at 170°C, followed by deionization, evaporation, acetylation and gas chromatography. Isomeric glycosides were used as internal standards.

Preliminary experiments showed (figure) that sodium borate solutions with sodium:boron molar ratios between 0.5 and 2.0 degraded methyl α-L-arabinopyranoside at 170 °C at a much higher rate than did sodium hydroxide solutions of comparable concentration, even though e.g. borax ($Na_2B_4O_7$) solution is only very weakly alkaline (pH 9 at room temperature).

Insert the figure here.

In a series of experiments with a constant sodium ion concentration of 2.4 mol/l, methyl α-L-arabinopyranoside was treated at 170°C with solutions of NaOH, $NaBO_2$ and mixtures thereof. The action of each reagent alone followed the rate equation derived by Lai (3):

$$k_{obs} = \frac{C_a}{b_1 C_a + b_2}$$

where k_{obs} is the observed pseudo-first order rate constant, C_a the concentration of the alkali used and b_1 and b_2 constants. Experiments were also carried out in which the concentration of one reagent (NaOH or $NaBO_2$) was kept constant and that of the other one varied. In aqueous solution $NaBO_2$ is protolysed in different ways as follows:

$$m \cdot BO_2^- + (n+1)H_2O \rightleftarrows B_mO_{2m}H \cdot (H_2O)_n^{(m-1)-} + OH^-$$

$$(= m \cdot B(OH)_4^-)$$

Referring to the borate species on the left as the base and to the borate species on the right as the acid, it appeared that both the acid and the base, as well as the hydroxide ion, degraded the arabinoside, the action of the acid being especially strong.

To shed further light on this phenomenon, the four methyl glycosides of each L-arabinose, D-xylose, D-galactose and D-glucose were subjected to hydrolysis with NaOH and with $NaBO_2$ at 170°C.

It appeared, that those 1,2-trans-glycosides that form strong borate complexes in paper electrophoresis also degrade rapidly in borate solutions, e.g. α-L-arabinopyranoside and β-D-galactopyranoside. Also, the very low stabilities of β-D-xylo- and -glucofuranosides towards hydroxide observed earlier (4) were matched by

similar low stabilities towards borate ions. On the other hand, 1,2-cis-glycosides were generally less affected by borate.

The mechanism of the borate-induced hydrolysis of glycosides is unknown. One possible explanation might be that formation of a borate complex e.g. from the hydroxyl groups at C_3 and C_4 in methyl α-L-arabino-pyranoside, changes the equilibrium between the two chair conformations $^1C_4$ and $^4C_1$ in favour of the one ($^1C_4$) that can undergo hydrolysis via assistance of an alkoxide ion at C_2.

CONCLUSIONS

The sensitivity of certain glycosidic links towards alkaline borate solutions might help explain the behaviour of wood polysaccharides in kraft or hydroxide pulping involving borate liquors of the composition NaOH + $NaBO_2$ (i.e. Na_2HBO_3) in place of NaOH as the main alkali source with the aim of autocausticizing the pulping alkali.

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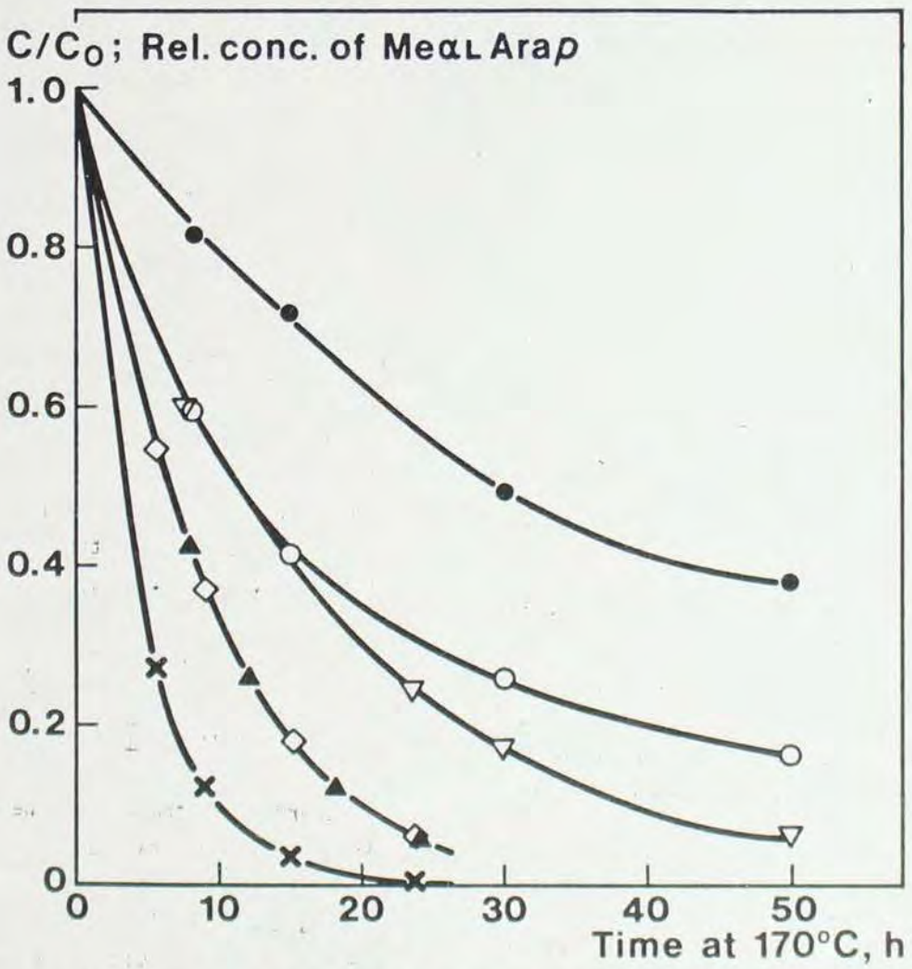

Hydrolysis rate of methyl α-L-arabinopyranoside at 170°C with various alkaline solutions

- ● 1M NaOH + 1M NaCl
- ○ 0.25 M $Na_2B_4O_7$
- ▽ 1M NaOH + 1M $NaBO_2$ (=1M Na_2HBO_3)
- ▲ 1M $NaBO_2$
- ◇ 1M $NaBO_2$ + 1M NaCl
- × 1M $Na_2B_4O_7$

INFLUENCE OF DIVALENT METAL SALTS ON ANTHRAQUINONE PULPING

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Abstract

Small levels of calcium hydroxide resulted in a gain in pulp yield when applied with anthraquinone in an alkaline pulping system. The effect was observed with other divalent metal cations but was most pronounced with calcium hydroxide. The benefit obtained is attributed to the ability of calcium and other divalent metal salts to catalyze a more selective formation of alkali-stable acid end-groups which provides for a greater stabilization of carbohydrates from alkaline degradation.

Key Words: Anthraquinone, Carbohydrates, Metal Cations, Alkaline Pulping

Introduction

During the 1970's, St. Regis Corp. developed the Hydropyrolysis recovery process as an alternative to the conventional Tomlinson recovery system. The Hydropyrolysis process[1] consisted of the heating of kraft black liquor under pressures in the presence of water and in the absence of oxygen to a temperature sufficient to convert the organic material to a carbonaceous insoluble material. Approximately 90% of the organic material present in the black liquor could be converted to the insoluble and carbonaceous form while 10%, consisting mainly of low molecular-weight organic acids, remained with the filtrate. The filtrate was subsequently causticized and used in the alkaline-pulping process.

The kraft pulping liquors generated via Hydropyrolysis were found to provide significantly higher pulp yields per given lignin content when used in the cooking of a Southern pine wood furnish than did the pulping liquors generated from conventional chemical recovery. We later established that the yield increase resulted from an increased stabilization of carbohydrates towards alkaline degradation, catalyzed by the combined and interactive effect of polysulfide and calcium ions. Polysulfide was present in significant but relatively low concentrations as compared to typical polysulfide cooking liquors and was formed as a result of a partial air-oxidation of sodium sulfide, catalyzed by the residual organic matter present, under the conditions of calcium hydroxide-causticization. It was demonstrated that soluble forms of calcium, probably introduced into the final cooking liquor as soluble organo-metallic salts, played a synergistic type role in the polysulfide-catalyzed stabilization of carbohydrates from alkaline degradation.

Aqueous calcium polysulfide solutions have been shown to have a greater stabilizing effect on hydrocellulose than corresponding sodium polysulfide solutions.[2] It has also been previously shown that calcium hydroxide can enhance the effectiveness of polysulfide in one-and two-stage polysulfide pulping processes.[3] This ability of calcium to enhance the stabilization of carbohydrates towards hot alkali treatment is believed to be due primarily to its acceleration of a stereoselective rearrangement, of the benzilic-acid type, of α-ketoaldehydes into alkali-stable aldonic acids. Glucosone, a probable intermediate in the polysulfide catalyzed oxidation of glucose, gives preferentially gluconic and mannonic acids when treated with calcium hydroxide, while treatment with sodium hydroxide gives preferentially arabinonic and erythronic acids which are less stable in hot alkali mediums.[4,5,6]

This marked catalytic effect of calcium hydroxide observed with polysulfide treatments would therefore seem to be related to observations previously made by others; the effectiveness of calcium-, barium-, and strontium hydroxides in accelerating the conversion of phenylgloxal to mandelic acid which involves an intramolecular Cannizzaro-type rearrangement,[7] the improved catalysis of the benzilic acid rearrangement by alkaline earth metals relative to that obtained with alkali metals[8,9], the requirement for zinc in the glyoxylase enzyme system which catalyzes a reaction very similar to an intramolecular Cannizzaro rearrangement[10] and, the preferential formation of mannonic acid when either calcium- or barium chloride is present in the reaction of glucose with 2-anthraquinonesulfonic acid.[11]

In each of the above cases, the effect of a divalent metal cation on the fragmentation and/or rearrangement pattern of carbohydrates has been

documented. In view that such rearrangements can impart a stabilizing influence on the carbohydrates toward alkaline degradation, it was of interest therefore to expand our evaluation of calcium-polysulfide pulping to include not only the study of other divalent metal salts, but to also include other pulping additives which promote a stabilization of carbohydrates through an initial oxidation step similar to that catalyzed by polysulfide. Of particular interest was the study of the effects of calcium and other divalent metal salts with anthraquinone additive pulping.

The objectives of our studies were to increase our understanding of the effect of metal salts on carbohydrate chemistry as it relates to alkaline pulping and, to search for methods by which the cost effectiveness of pulping additives such as AQ could be improved.

Results

The carbohydrate stabilization effect resulting from the introduction of small levels of anthraquinone (and polysulfide) to an alkaline pulping system is ascribed to an oxidation of the aldehyde end-group of the starting aldose with formation of a carboxylic acid end-group. With AQ, the amount of aldonic acids corresponding to end-group oxidation increases while a lower yield of alkaline stopping acids is obtained.[12] As with polysulfide pulping, the formation of aldonic acids catalyzed by AQ presumably proceeds through an α-ketoaldehyde intermediate. The dicarbonyl sugar intermediate then can proceed through either a hydrolytic-cleavage reaction to give arabinonic and erythronic acids or through a rearrangement which gives preferentially mannonic and gluconic acid end-groups.[4]

In view of the ability of calcium and other divalent metal cations to accelerate the type of rearrangement characteristic of not only the stopping reactions but also the formation of stable aldonic acid-forms, the addition of a divalent metal salt to kraft/anthraquinone pulping was anticipated to have a beneficial effect on pulp yields by accelerating those reactions which compete with the so-called peeling process.

Using a Southern pine wood furnish, consisting primarily of loblolly and slash, kraft pulping was carried out with the addition of anthraquinone (0.1% AQ on oven-dried wood basis) and calcium hydroxide (0.5% Ca^{++} on O.D. wood). Under otherwise typical kraft conditions, a yield-enhancing effect resulted from the combined addition of the quinone and the divalent metal salt relative to kraft cooks where either AQ or calcium hydroxide alone were applied.

Pulp yield increases of 2-3 percentage points were obtained relative to kraft pulping over the unbleached kappa range studied when both Ca^{++} and AQ were employed while yield increases of 1-2 percentage points were obtained when only AQ was applied.

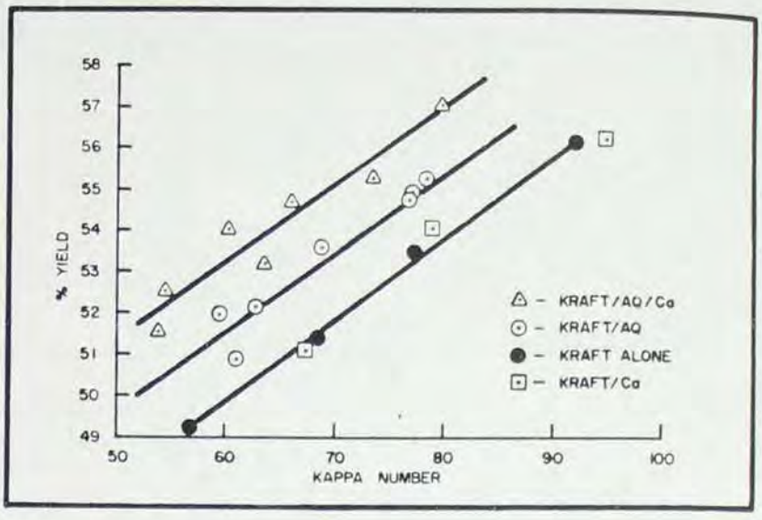

Figure 1 - The Effect of Calcium Hydroxide Addition on the Pulp Yields Obtained in Kraft/AQ Cooks

Comparison of the kappa and yield results obtained as a function of cooking time indicated that addition of calcium hydroxide had only a marginal effect, if any, on delignification rates at the 0.5% application level.

It was anticipated that the addition of calcium in the form of calcium hydroxide would have added to the total effective alkali concentration of the cooking liquor by contributing free hydroxide ions and thus, would have provided a slightly faster rate of pulping. This probably did occur to some degree but its extent is difficult to determine since the contribution to alkalinity would be dependent upon the solubility of calcium hydroxide which is constantly varying during the cooking cycle because of varying temperature, alkali concentration and varying concentration of complexation ions such as carbonate. If any improvement in rate was obtained, then our observation that no increase in the rate of kappa reduction occurred at the 0.5% Ca application would therefore indicate that a second effect slowed the rate such that it canceled any benefits obtained from the contribution of free hydroxide ions.

At higher levels of calcium hydroxide addition, the effect of the increased alkalinity was detected, as reflected by reductions in the kappa number. In the 0-1.5% range of applications studied, however, no adverse effect was obtained on delignification rates although it can be expected that application rates greater than those studied will in fact retard the rates.

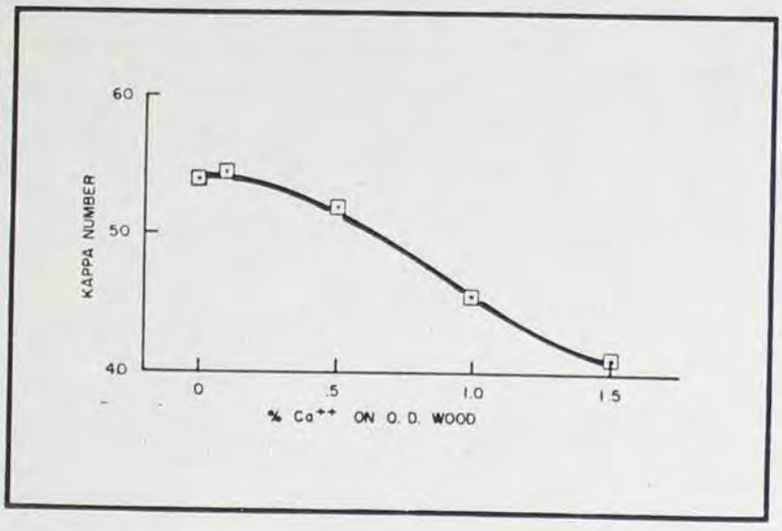

Figure 2 - The Effect of Calcium Addition at Various Levels on the Kappa Number Obtained in Kraft/AQ Cooking

It has previously been shown that with a two-stage polysulfide process, variation in calcium concentration can influence the pulping rate.[3] Lower levels of calcium hydroxide result in a small acceleration of delignification while higher levels retard the rates. The latter is probably a result of a decreased solubility of lignin caused by calcium complexation of lignin.

To determine whether the yield enhancing effect observed with calcium is unique to calcium or is characteristic of other metal cations, a limited screening evaluation was conducted. As evident from a comparison of the yield-kappa relationships, calcium was not unique in its ability to enhance the pulp yields from a kraft/AQ pulping process. Other divalent metals such as zinc, barium, strontium and magnesium all had a positive influence but to varying degrees. The monovalent lithium cation and the tri-valent boron and aluminum cations showed no activity.

Of the metals studied, calcium was most effective in enhancing the pulp yield when comparison is made on an equimolar basis. The pulp yields reported were corrected for the ash content which was found to be slightly higher than for the control case. The increase in ash content can be attributed to both the replacement of the divalent metal cation for the sodium ion and to the low solubility of some of the metal salts.

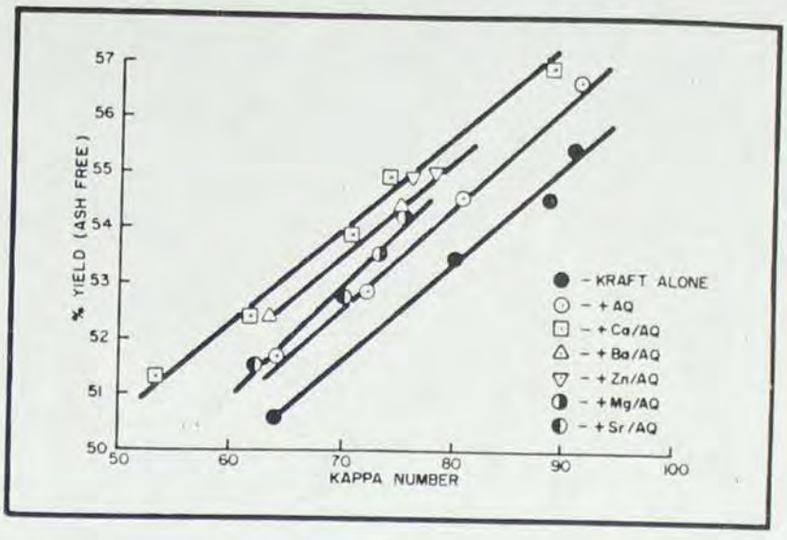

Figure 3 - The Influence of Various Divalent Metal Salts on the Ash-free Pulp Yields Obtained in Kraft/AQ Cooking

In the absence of anthraquinone, the divalent metal cations had no significant enhancing effect on kraft pulp yields when determined on an ash-free basis. This finding indicates that the gain in the ash-free yield is not the result of a deposition of metal-carbohydrate or metal-lignin fragments onto the pulp. In addition, this result indicates that the observed gain in pulp yields cannot be solely attributed to an acceleration of the "stopping" reaction which involves the formation of a metasaccharinic acid via the benzilic acid-type rearrangement of a diketone since this reaction would be occurring in both kraft and kraft/AQ pulping.

The greater effectiveness of calcium ions over other divalent metal cations appears to be related to the ability of calcium to form stronger complexes with carbohydrates. Analyses of the pulps generated from the digester cooks show that calcium was retained on the pulp fiber to a greater extent than the other metal cations after thorough washing. The order of apparent binding ability is in agreement with the order of benefit obtained. It is noted, however, that the order of metal retention on the pulp fiber observed in our studies does not necessarily correspond to the relative affinity of the various cations for cellulose since our analysis did not take into account the difference in the solubility of the various salts. Differences in solubility would thus result in a difference in the concentration of available cation for complexation. This could explain therefore our

observation that calcium was retained on the pulp to a greater extent than zinc despite previously reported results which show that the zinc has a greater affinity for cellulose than calcium.[13] A comparison based on equimolar concentrations of soluble cations may therefore reveal a greater enhancement in pulp yield resulting from zinc cations relative to calcium ions.

While it is well-known that carbohydrates possess the property to form soluble complexes with alkali and alkaline metals, uncertainty remains concerning the nature, stability and structure of such complexes. Interaction of the alkaline-earth metal hydroxides with carbohydrates results in an increased solubility of the hydroxide through formation of either an alcoholate, carbohydrate-metal hydroxide or carbohydrate-metal oxide adduct. The greater enhancement associated with the calcium ion over the other cations may be related to the critical ion-size requirements for complex formation with the α-dicarbonyl compound.

Irrespective of the nature of the complex, a strong complex can result and such a complex can increase the rate of the benzilic, or Cannizzaro-type rearrangement by either hindering the isomerization of the initial aldose and/or stabilizing the transition state of the hydride shift that is required in such a rearrangement. Based on the relative effect of the metal salts studied, the stability of the metal complex thus appears to be more important than the basicity of the metal hydroxide.

Conclusions

The results of these studies have shown that the yield enhancing effect of pulping additives such as anthraquinone and polysulfide in alkaline pulping can be further enhanced through the combined use of the additive with a divalent metal hydroxide. No significant effect on pulping rates occurred and the divalent metal hydroxides had no influence on yields from kraft and soda pulping when employed by themselves in the absence of either anthraquinone or related quinone.

The benefit obtained is attributed to the complexation characteristics of the metal ions, which are not fully understood, but such metal ions are known to have an effect on the fragmentation pattern and the intramolecular rearrangements of carbohydrates.

While these results provide for an increased understanding of means by which such pulping additives can be made more effective, the feasibility of the specific application of the divalent metal cations for use in pulping is uncertain. Of the metals evaluated, calcium was most effective and perhaps most practical for application. In view of our belief that the addition of divalent metal cations in this manner provides a simple means to reduce the effective cost of yield enhancing pulping additives, investigation of the system effects of such additions is underway in our Pensacola facility. Patent protection is pending.

Experimental

Pulping experiments were carried out on a Southern pine wood furnish consisting of both slash and loblolly pine. The chips were screened then thoroughly blended and stored at 4°C until used in cooking. Cooking was conducted using a 2.5 ft^3 steam-jacketed rotating digester (0.67 rpm). The digester contents were vented initially then heated indirectly with steam to temperature in 60 minutes. After cooking, the pulp was pressure blown into a blow chest then washed successively with three water washings. After each wash, pulps were dewatered by suction draining until a stable consistency was reached.

For cooks with black liquor fillback, a kraft black liquor of ∿25% solids content was used. Total fillback corresponded to 7% v/v of total liquor volume. All cooks were carried out using a 5:1 liquor to wood ratio.

Pulp yields were determined on unscreened samples. Unscreened samples were fiberized using a Sprout Waldron disk refiner set at 0.02" plate clearance. The pulp samples were tested for kappa number and ash content (Tappi T-211m-58). Metal content of pulp and liquor samples were determined by atomic absorption after wet ashing with perchloric and nitric acids.

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ACOS - ACCELERATED HYDROLYSIS OF WOOD BY ACID CATALYSED ORGANOSOLV MEANS

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ABSTRACT

Ethanol is rated as an important alternative liquid fuel since it can be readily manufactured by fermentation of sugars from renewable vegetable materials. Economical production of sugars from perennial woody materials is complicated by the chemical and physical heterogeneity of these materials. Solubilization of the decomposition products requires multicomponent solutions to accommodate both hydrophilic (sugars) and hydrophobic (lignin and extractives) products. The ACOS process (Acid Catalysed Organosolv Saccharification) uses an aqueous acetone solution and a minor amount of a mineral acid as the hydrolysis solvent and accomplishes up to 700 times faster hydrolysis rates than possible with dilute acid solutions at up to one hundred times higher acid concentration. A transient acetonation (isopropylidine formation) is thought to be responsible for the high hydrolysis rates and near theoretical survival of the sugars. Application of the ACOS technology to such diverse substrates as coniferous or hardwood sawdust, agricultural residues from sugarcane and fibers from grain production and processing indicate that the process treats all types of lignocellulosics equally. Hydrolysis of the bagasse and corn stower have the same effect on alcohol yield as tripling and doubling the land base, respectively, thereby creating more favourable economic conditions in these sectors. The ACOS process further allows introduction of some novel processing technologies in cogeneration of products such as vegetable oils, rubber etc.

INTRODUCTION

Long-term future liquid fuel supplies continue to pose some serious questions. Interim supplies from petrochemicals, though apparently stable at the present time, are expected to decline as we approach the year 2020, and might be interrupted at any time. Another energy crisis is forecast for the late 80's.

Recent reports (4) indicate dim hopes for new major oil discoveries whereby the flurry of drilling activity experienced in 1979-1983 has fallen sharply. The number of marginal finds and "dry holes" continue to drain oil company profits and largely discourage further research into locating new oil deposits. As a result alternate liquid fuels should loom high on the agenda for future development.

Developments in the cellulose-to-ethanol field have suffered long from marginal economics of presently available conversion technologies and the severe competition of prevailing low gasoline prices. Alcohol was introduced into the liquid fuel market only after government subsidies were assured. Customer acceptance of gasohol was largely affected by population concerns over environmental issues rather thar better automobil performance whereby in 1984 gasohol (10% ethanol 90% gasoline blends) was sold in some 20 states at selected gas stations in the USA and Mohawk Oil in Canada has embarked on gasohol marketing in Ontario. Gasohol sales reached 13.5 billion liters by 1983, up 90% from 1982 in the USA (7).

A particularly strong impetus for alcohol use in gasoline blends comes from the 1984 U.S. EPA ruling (2) whereby a 91% cut in lead content in gasoline will be required by January 1, 1986. Of the 375 billion liters of gasoline consumed in the U.S., some 143.5 billion liters of gasoline are affected. Lead replacement in leaded gasoline will require immediately some 18.6 billion liters of alcohol (assuming that 1 liter of alcohol is equal to 1.3 g of lead in terms of octane boosting power) (2). If all the lead is replaced with alcohols (methanol and ethanol) alone an estimated 218 billion liters (172 million tonnes) could be required to provide gasoline blends with the required octane rating. Ultimately, the level of alcohol usage by the refiners for octane boosting purposes will be set by the competitive pricing and availability of alcohols and other octane boosting agents (aromatics, such as benzene, toluene and xylene, and methyl-tert-butyl ether (MTBE) (1). Thus the competitive position of alcohols as mere alternate fuels has now been radically changed to that of a higher value octane booster additive allowing speculations (3) that the alcohol price will rise slightly to a level which is competitive with that of the proposed alternate octane boosters. This puts new life into the cellulose-to-ethanol prospects albeit under a completely new set of conditions.

Present federal and state tax breaks in the USA have helped in establishing ethanol as a cost competitive component of gasoline. Lead removal from gasoline to protect the environment is a further significant impetus for increased use of ethanol as a lead substitute (octane enhancer) and alternate liquid fuel to reduce gasoline consumption. Gasohol with 10% ethanol is only the beginning in modified liquid fuels. Only minor engine adjustments will be required to raise the proportion of ethanol to 20 to 25%. It then appears that limits to ethanol usage are set mainly by availability of ethanol at a competitive price.

Sources of Ethanol

The subject of alternate ethanol sources and their respective economics has been reviewed widely (12, 13, 15). Due to increasing petrochemical and gas feedstock costs, most ethylene conversion facilities have largely been shut down whereby again most of the commercial ethanol is produced by fermentative processes.

For obvious reasons grain fermentation to ethanol has made fast advances to fill the ethanol supply needs which are created by shutdown of ethylene plants. Grain fermentation has the advantage of simplicity of technology and that it has well established markets for its by-products (germ oil and stillers' grain). However, due to the high grain costs the profit margins are thin on grain alcohol and the industry is not viable without the by-product credits (16). Presently only 2.3 billion liters of ethanol is produced from corn in the USA. The actual ethanol required to fill all the octane gap in the USA is about 18.6 billion liters (5 billion US gallons) per year. It would take more than 20% of the U.S. corn production to meet the total requirement whereas less than half would be required if an equivalent proportion of the corn biomass (stower cobs and straws) would also be processed.

Cellulose-to-ethanol technologies have seen little innovation in recent years in spite of the fact that lignocellulosics offer by far the highest potential as feedstock for alternate fuel (ethanol) and chemicals manufacture. Work seems to continue mainly in two directions viz. a) acid hydrolysis and b) enzymatic hydrolysis.

The Scholler-Madison process has now been closely analysed (23) and a modified version of it, developed in New Zealand, is now proposed as a pilot plant for the British Columbia Interior (Quesnel) (8). Reports on the low-temperature concentrated hydrofluoric acid hydrolysis process, earlier researched by Canertech Inc. in Winnipeg, indicate some progress and good sugar yields and a pilot plant is proposed for Saskatchewan (15). Other pilot plant studies based on acid hydrolysis by TVA (14) and NYSERDA-GEO Products are also underway and a 20 million liter ethanol facility is planned by the Virginia Ethanol Partnership for McKenny, Virginia based on southern hardwoods as feedstock (6).

Advances with enzymatic hydrolysis processes continue to be hampered by the need to delignify lignified tissues before enzymatic attack on the cellulose can take place. Hopes on wide-scale selective enzymatic delignification of lignocellulosic materials have substantially been tempered by recent reports indicating that the new lignin-specific strain (Phanerochaete chrysosporium) does not only lack the required delignification power to treat softwoods but requires at least three weeks under sterile incubation conditions to remove 17 to 28% of the lignin from birch wood. The necessity to further remove lignin and mechanical disintegration of the chips before enzyme hydrolysis is expected to make this pretreatment economically prohibitive for hydrolysis by enzymes. It seems much more work will be required in this direction.

The concept of the "forest refinery" has now been widely evaluated (17, 18) and economic constraints were calculated by SERI (10) for organosolv delignification as a pretreatment for enzymatic hydrolysis of lignocellulosics. These evaluations were largely based on the data released by Katzen et al. (19) and Diebold et al. (11) relating to their organosolv (alcohol) pulping process. By analysis, the process was found to be highly energy demanding as a pretreatment due to the added energy required for recovery of the solvent from the pulp. According to Chum et al. (10) the minimum economically viable plant size at which pulp feedstock could be produced for enzyme hydrolysis at a cost competitive with other pretreatments, was 2000 tpd. This capacity is not exactly of the order of magnitude accepted as the average chemical pulp mill and is far in excess of the preferred small-scale mills at 150-200 tpd. Major problems with 2000 tpd mills would arise from securing adequate raw material supplies for continuous operation and the large transportation costs (collection costs) for raw material hauling. Further limitations of the Diebold et al. (11) process are its inability of delignifying conifers and high density hardwoods. Total

saccharification of lignocellulosics by the Diebold et al. (11) alcohol pulping process is possible only on substantial modification (acidification) of the solvent a process which is covered by U.S. Patent No. 2 959 500 that issued to Schlapfer and Silbermann in 1960 (22).

Total Organosolv Saccharification of Lignocellulosics by the ACOS Process

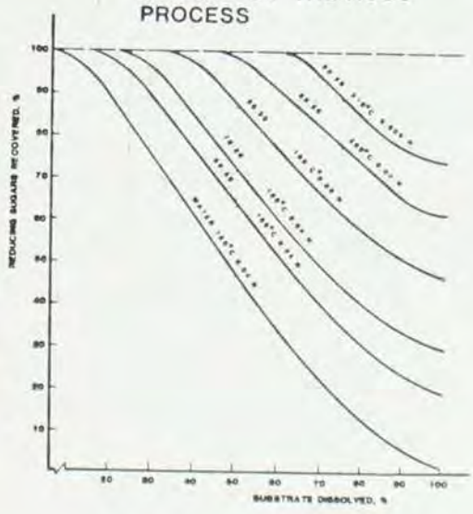
Theoretically organosolv saccharification can be looked at as the ideal process that is capable to decompose wood into its chemical components viz. largely monomeric sugars and lignin. By selection of a suitable water miscible simple solvent, simultaneous depolymerization of both the carbohydrate fractions and lignin could conceivably remove the usual obstacles experienced in aqueous hydrolysis by the Schoeller/Madison processes where secondary condensation of the lignin creates substantial accessibility problems and therefore the sugar recovery is less than 60%, typically around 45 to 50% of the theoretical.

The saccharification power of organic solvents depends largely on the acidity of the solvent itself, its competition for acidic protons for catalysis of secondary reactions that can lead to unwanted condensation products of the solvent. To some extent, the solubility of the depolymerized lignin in the organic phase is also of importance. Thus in previous work with the Schlapfer and Silbermann (22) process it was found that while the system (acidified aqueous lower aliphatic alcohols which did not react with the acid catalyst used) had high initial hydrolysis rates, total dissolution required several liquor changes to dissolve the crystalline cellulose. At the same time, extended saccharification in acidified aqueous alcohol solutions resulted in substantial conversion of the hydrolysed sugars to furfurals when the alcohol concentration was below 60% and yielded large quantities of diethyl ether and ethyl sulfate among other reaction products.

Unexpectedly, all these problems could be eliminated by Chang and Paszner (9) when ketones were substituted for the alcohol as the organic solvent. Particularly fast hydrolysis rates were obtained with acidified aqueous acetone solutions whereby at 200°C in 60% acetone solution Douglas-fir wood could be dissolved in 16-18 min depending on the acid concentration. The sugar recovery ranged from 68 to 74% with traces of furfurals present on total saccharification without a liquor change. The process was covered by U.S. Patent No. 4 409 032 that issued to Paszner and Chang in 1983 (21). On recovery (flash evaporation) of the solvent the lignin fraction precipitated out and was shown to have a molecular weight of between 300 to 4300 ($\bar{M}_w$).

Further studies into the effect of solvent composition on the rate of cellulose (cotton linters) hydrolysis have shown that at acetone concentrations higher than 80 per cent some unique carbohydrate derivatization chemistry (known to occur only on monomeric sugars under anhydrous conditions) became operative under the conditions normally used in this process. The benefits that accrued from increasing the solvent concentration became substantial. They included phenomenal hydrolysis rates which were higher than those obtainable with concentrated mineral acids and 700 times greater than that obtainable with dilute acid at hundred times the acid concentration. For the first time, we could recover theoretical amounts fo reducing sugars from our hydrolysates without traces of furfurals. Temperature became the only kinetic parameter by which the rate of dissolution and sugar survival could be regulated. Some kinetic plots for cotton linters are presented in Figure 1, where the effect of solvent composition, acid

FIGURE 1. RATES OF SUGAR SURVIVAL ON HYDROLYSIS OF COTTON LINTERS BY THE ACOS PROCESS



concentration and temperature are examined in terms of amount of substrate dissolved and per cent sugars recovered. These results became the basis of another U.S. Patent No. 4 470 851 which issued in 1984 (20).

Reactor throughput is substantially affected by the rate of dissolution and liquor residence time during the hydrolysis process. The allowable liquor residence time, on the other hand, reflects the stability of the dissolved products but has a considerable effect on the production economics since it controls the solvent-to-wood ratio required for total dissolution of the sub-

strate. The composite data in Table 1 indicate the effect of acid concentration, and reaction temperature on the hydrolysis rate and sugar

TABLE 1. EFFECT OF ACID CONCENTRATION AND REACTION TEMPERATURE ON THE HYDROLYSIS RATE AND SUGAR SURVIVAL ON TREATMENT OF COTTON LINTERS.

REACTION TEMP. °C	DISSOLVED CELLULOSE %	REACTION TIME min	REACTION RATE 10^3 min^{-1}	REDUCING SUGARS %
0.04 N (0.190 %) H_2SO_4				
180	50 75	13 26	52.7	96 73
200	50 75	2.3 4.6	301	98 78
210	50 75	0.93 1.86	745	92 80
0.01 N (0.045 %) H_2SO_4				
180	50 75	48.1 96.3	14.4	87.7 64.8
200	50 75	7.4 14.8	94.2	91.5 73.5
210	50 75	2.0 5.7	241.4	93.0 75.7
0.005 N (0.0235 %) H_2SO_4				
200	50 75	17.7 35.5	39.2	93.0 74.4
210	50 75	6.9 13.8	100.4	94.0 78.4
220	50 75	2.7 5.4	257.8	96.3 81.0
230	50 75	0.25 0.36	659.9	99.0 89.5

NOTE: SOLVENT= 80:20 ACETONE:WATER, L/W= 10:1.

survival of cotton linters. It can be seen that at low acid concentration (0.0235%) between 50 to 75% of the substrate can be dissolved without virtually any loss of sugars.

The high hydrolysis rates and sugar survival in the ACOS process are due to the unique sugar-solvent complexes which form at high solvent concentration. These complexes, known as ketals or isopropylidines, appear to prevail even at high temperature. Their formation may involve conformational changes at end units of the cellulose thereby weakening the glycosidic bonds against hydrolysis. The presence of these complexes in solution have now been proven by gas chromatography. Since isopropylidines of different sugars have different physical properties (volatility, solubility and stability in acid medium) properly stabilized hydrolyzate solutions can be worked up in a manner which allows facile separation of the pentose and hexose sugars as a primary option or alternately isolation of each of the five individual sugar species in wood is achievable by use of this chemistry. In bulk processing of the hydrolysate, hydrolysis of the sugar-acetone complexes is obtained by brief boiling in a weakly acid medium for 20 min. Some possible isopropylidine structures of cellulose are presented in Figure 2.

A particular advantage of the ACOS process is the fact that on removal of the solvent from the hydrolysate the dissolved sugars are automatically concentrated some five times if the solvent was 80:20 and ten times if the solvent was 90:10 with respect to the ratio of

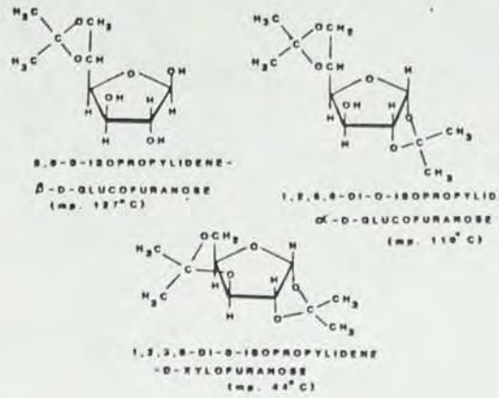


FIGURE 2. SOME ACETONE (KETAL) DERIVATIVES OF WOOD SUGARS

acetone:water. Thus ultimate sugar concentrations in the aqueous hydrolysate exceed 25% when total liquor to wood ratio is under 15:1 making these hydrolysates eminently suited for use in continuous fermentation/distillation processes such as the BROSTIL and others.

The lignin is normally recovered as a light brown powder, free of carbohydrate contaminants, low in ash and having a weight-average molecular weight ($\bar{M}_w$) of about 1800 to 2300. This lignin is soluble in alkali as well as the usual lignin solvents (acetone, DMSO, THF, chloroform, alcohol, etc.).

Applications of the ACOS Process

From the foregoing it should be clear that the ACOS process must be viewed as a stand-alone chemical technology with unparalleled capabilities for simultaneous hydrolysis and decomposition of lignocellulosic materials to component monomeric sugars, lignins, and other extraneous products. Under suitable arrangements, recovery of the component chemicals is quantitative and the hydrolysis is complete. Separation of the pentose and hexose sugar fractions, if desired, can be done either on basis of the physical properties of their acetone derivatives or by internal reactor arrangement. Short solvent retention times within the reactor and the protective effect of transient acetone complexes effectively prevent degradation (dehydration) of the sugars and secondary condensation of the sugar dehydration products (furfurals) to infusible by-products.

The ACOS process was found to be effective equally on all types of lignocellulosic materials thereby being ideally suited for mixed residue hydrolysis/processing. In this context wood residue hydrolysis could establish itself

as a major forest products industry equal or substantially greater than the pulp and paper sector. Canada alone disposes of some 200 million tonnes of wood waste per year in its forestry and forest products operations. The potential alcohol yield, at 400 liters per tonne, would be 80 billion liters. This amount of alcohol is about four times that required for the gasohol market in the USA in 1986. There is ample uncommitted capacity for growth and export of ethanol which could be opened up by this process. It is also important to note that since there are no wood quality criteria to fulfill in ethanol production, the ethanol industry would not be competing for wood raw material with the existing lumber and pulp and paper industries. Therefore it would actually contribute significantly to better utilization of the renewable forest base in Canada and elsewhere.

Some calculations with respect to alcohol yields from sugarcane processing reveal the startling fact that the ethanol yield can be doubled from 5,600 liters per hectare to 10,880 liters per hectare if advantage is taken of the glucose locked up in the extraction residue, bagasse. Normally, the leaves and cane tops are burned off/severed in the fields. Including these residues together with the free sugars and bagasse in the cane biomass destined for hydrolysis would effectively triple the potential ethanol yield per unit harvesting area to 16,130 liters per hectare as evidenced in Table 2. The

TABLE 2 . POTENTIAL ETHYL ALCOHOL YIELDS FROM SUGARCANE CONVERSION BY THE ACOS PROCESS

SUBSTRATE	GREEN YIELD T/HA	OVEN-DRY YIELD T/HA	ETHANOL YIELD L/T_{WET}	ETHANOL YIELD L/HA
1. CANE JUICE ONLY	(80)	--	70	5 600
2. TOTAL CANE ONLY	80	21.2	136	10 880
3. BAGASSE ONLY	20	11.2	265	5 300
4. BAGASSE INTEGRAL	40.4	20.2	243	9 817
5. SUGARCANE BIOMASS*	96	30.4	168	16 128

* BIOMASS INCLUDES: CANE, TOPS AND LEAVES.

process does not only contribute to improved economics of alcohol production from sugarcane but also has the same effect as tripling the land base for energy related production of sugarcane.

A similar situation can be demonstrated for ethanol production from corn. As indicated in Table 3 the ethanol yield per unit area of corn operation can be doubled from 4,500 liters per hectare to 9,150 liters per hectare on hydrolysis of the corn fiber, cobs and stower besides substantial quantities of xylose and lignin which could be marketed separately.

TABLE 3 . POTENTIAL ETHANOL YIELD FROM CORN PLANT BIOMASS

SUGAR SOURCE	YIELD T_{WET}/HA	YIELD T_{DRY}/HA	SUGARS, KG/T C_5	C_6	ETHANOL YIELD, L/T C_6	C_5	C_5+C_6	ETHANOL L/HA	ETHANOL C_5+C_6 L/HA	LIGNIN T/HA
CORN KERNEL	16	14	-	740[1]	444	-	444	4 596	4 596	-
CORN COB	3	2	420	370	252	213	465	505	930	0.28
CORN STOVER	26	9	175	435	297	90	378	2 668	3 483	1.44
CORN BIOMASS	45	25	110	590[2]	309	57	366	7 723	9 150	4.00

1. STARCH ONLY; 2. INCLUDING STRACH.

ANALYSES:

CORN PLANT:
GRAIN ..... 53 %
COB ..... 10 %
STOVER ..... 37 %

GRAIN:
STARCH ..... 72.0 %
PROTEIN ..... 9.6 %
FAT ..... 4.7 %
FIBRE ..... 2.4 %
SUGAR ..... 1.9 %
ASH ..... 1.4 %

COB:
C_6 SUGARS .... 37.8 %
C_5 SUGARS .... 42.0 %
LIGNIN .... 14.0 %
PROTEIN .... 4.0 %
ASH .... 2.0 %

STOVER:
CELLULOSE ... 43.5 %
HEMICELLULOSE 37.5 %
LIGNIN ... 16.0 %
PROTEIN ... 13.0 %
ASH ... 3.0 %
SOLUBLES ... 7.0 %

Preliminary calculations of ethanol costs by the ACOS process indicate that alcohol costs would range around 33¢ per liter from wood/sawdust without by-product credits from plants of 300 tonnes per day feedstock capacity. With by-product credits with allowances for lignin, mixed fertilizer and methanol, the production cost would be 21¢ per liter for the same size plant. At the current price of $450 US per tonne of ethanol (or $0.480 CDN per liter) the breakeven plant capacity is about 100 tonnes per day for a non-credit-rated and 50 tonnes per day for a credit-rated operation. With high capacity plants (600 to 1,000 tonnes per day) the credit-rated production cost of alcohol is lower (13 to 16¢ per liter) than the current price of methanol ($0.20 per liter).

CONCLUSIONS

Alternate fuel technologies have come of age with the USA requiring 18 billion liters (4.7 billion US gallons) of ethanol to satisfy the needs of its growing gasohol industry in 1986. Total lead replacement in gasoline could require ten to twenty times this amount within the next decade.

Cellulose-to-ethanol technology developments were sluggish during the past decade for want of an economically viable and efficient wood hydrolysis process. Problems related to low sugar yields, low energy conversion ratios and high capital costs. None of the available processes were universally applicable to all cellulosic feedstocks.

The ACOS process is a universal wood hydrolysis process that shows excellent hydrolysis rates and provides quantitative product yields on total hydrolysis of any lignocellulosic feedstock. The process clearly separates a natural lignin and fermentable monomeric sugars. The solvent is recycled.

Economic analysis of the process shows that ethanol can be produced by the ACOS process at relatively moderate plant capacities. The process offers substantial profit margins on establishment of large capacity plants. Up-scaled pilot plant testing is now underway in Brazil and under construction elsewhere.

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MICROCOMPUTER-BASED IMAGE PROCESSING AS APPLIED TO EVALUATION OF SURFACE PHENOMENA OF PAPER SHEETS AND PULP SUSPENSIONS

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Abstract: A microcomputer-based image processing system coupled with a video system provides a means for visualization and quantitative evaluation of the static and dynamic surface phenomena on paper sheets and in flowing pulp suspensions.

Résumé: Un système de traitement d'image basé sur un micro-ordinateur associé au système vidéo permet de visualization et évaluation quantitative des phenomènes statiques et dynamiques des surfaces sur les papiers et dans les suspensions fibreuses en mouvement.

Keywords: Image processing, Microcomputer, Surface phenomena, Paper sheets, Pulp suspensions.

INTRODUCTION

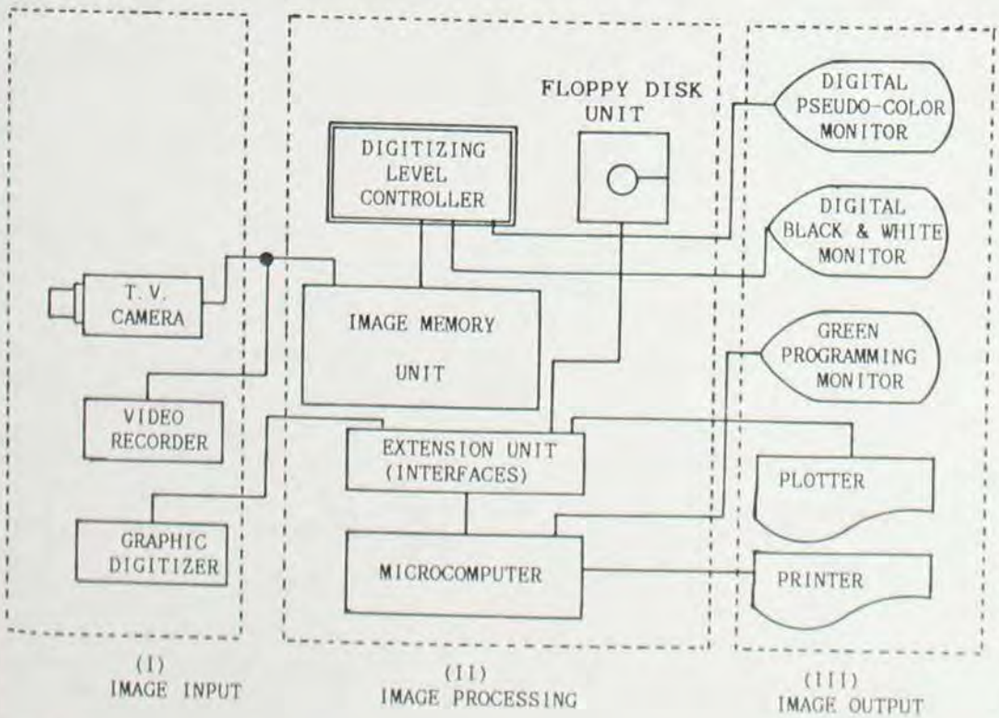
The recent availability of lower-cost image memory((D-RAM) coupled with a microcomputer system has made the digital image processing possible on a laboratory scale. This paper describes the design and operational experiences of this system.

METHODS

Hardware

The hardware system(**Fig. 1**) is based on NEC's 8-bit microcomputer PC-8001(CPU:Z80) with user's memory capacity (RAM) is ca. 19KB when DISK BASIC is running. The image memory unit permits conversion of an analog image to its digital image and its storage(32KB RAM). The digital image consists of 256 x 256 pixels with 4-bit digitizing levels, i.e., 16-level greyscales.

Figure 1.: The Hardware System.



The "Digitizing Level Controller(DLC)"(**Fig. 2**) developed by the author permits extraction of characteristics from an object image on real-time basis without using software. That is, (1)control of image contrast and black level(i.e., the lowest birghtness level); (2)selection of pseudo-color digitizing levels (2, 4, 8), (3)selection of greyscale digitizing levels(2, 4, 8, 16), and (4)reversal of digitizing levels of both greyscales and pseudo-colors.

Image processing performances of this system were compared between 8-bit(PC8001) and 16-bit (NEC's PC9801E:CPU 8086) microcomputers.

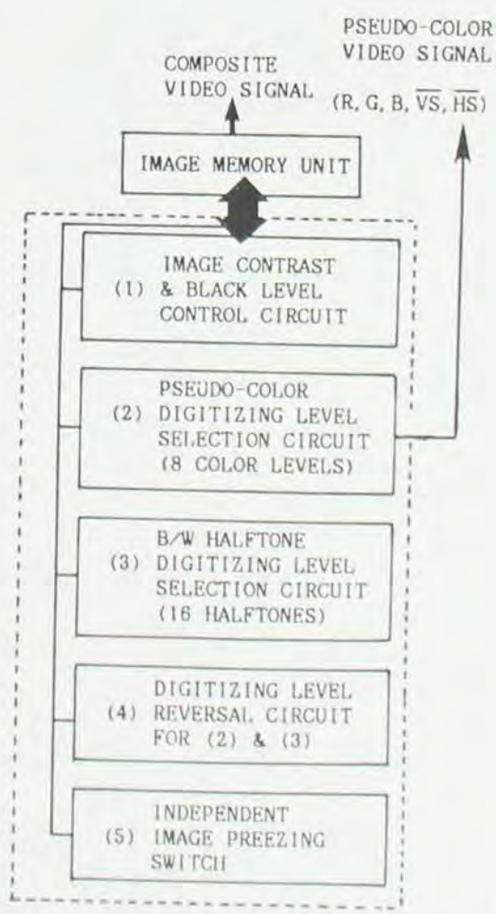
Software

A series of softwares were developed using BASIC, although the machine language were used partly in repetitive parts of the programmes. This interactive(i.e., conversational) system facilitates the development and modification of softwares.

Sequence of digital image processing

An analog picture of an object is taken by a video camera and recorded on a video-tape. The picture is freezed in 1/60 second followed by

Figure 2.: Digitizing Level Controller(DLC).



digitizing. Then the characteristics of picture are extracted using DLC followed by storage in a floppy disk. A histogram is first obtained for each digital image in order to see the distribution of greyscale of the image. A threshould level for binarization and method for noise removal are selected using the histogram and the hexadecimal display of the digial image.

Noise removal

Operational experiences of the system showed that the removal of noises from various sources are prerequisite for obtaining clear-cut digital images. The extent of noise removal required depends upon how an object image is contrasted from its background.

For poorly contrasted images, two countermeasures were taken to have clear-cut digital images of objects: (i)adjustment of the level and contrast of video signals, and (ii)conversion of the histogram of original image to its narrower greyscale regions. Other smoothing methods for digital images are being tested.

EXAMPLES OF APPLICATIONS

Practical applications of the system are presented.

(i) Ink penetration into paper sheets:

The first example is the evaluation of ink penetration into paper, in which the contrast of an object image from its background(i.e., white paper) is, in general, clear and no noise removal was required. A binarization of the image at certain greyscale level was sufficient to obtain a clear-cut image of the object.

In this experiment, analog images on the process of ink penetration into paper both in two-dimensional direction(surface) and in z(thickness) -direction were recorded on a video-tape followed by digitizing using the system described above. The area of ink penetration was obtained by counting the number of digitized points(i.e., pixels-picture elements) in the penetration area.

The penetration nature differed according to (1)the homogeneity of paper(filter paper or hand-made paper or machine-made paper), (2)the acidity in papermaking (i.e., acidic or alkaline), (3)the nature of ink(i.e., aqueous ink or oily ink), and (4)the nature of additives(i.e, sizing agents and fillers, etc)

The hexadecimal display of the penetration area is shown in Fig.3.

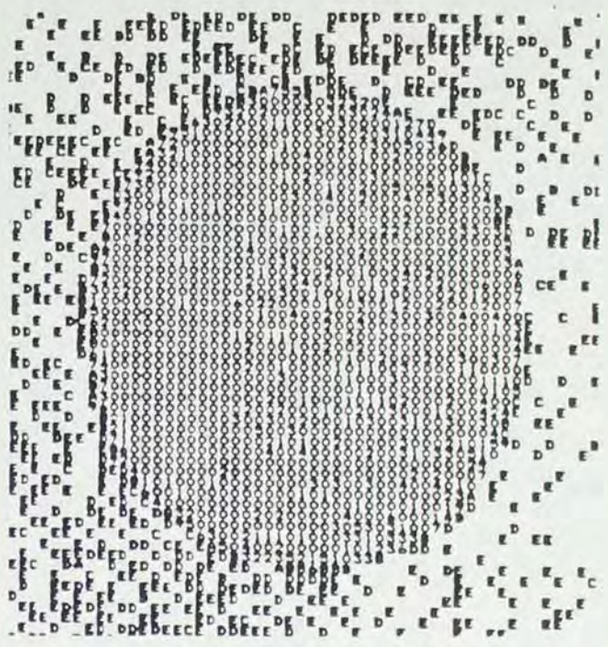


Fig.3: The hexadecimal display of ink penetration before noise removal. Two minutes after contact of aqueous ink on a filter paper.
0=the lowest greylevel(black).
F(16)=the highest greylevel(white).
Noises on the background(B,C,D,E) are due to inhomogeneity of illumination on paper.

(ii) Floc formation and sedimentation of pulp suspensions:

The second example concerns the evaluation of consistency, sedimentation, and floc formation in flowing pulp suspensions, in which the contrast of an object image(pulp) from its background(water and white paper) is not clear and noise removal was requird. Observations of these phenomena are based on the scattering of light by fine pulp fibers(i.e., "Tyndall effect"). In this case, the histogram conversion was performed to enhance the contrast of images.

CONCLUSIONS

The technique described so far provides a means of non-contact analysis and permits visualization and quantitative evaluation of slight differences in changes in static and dynamic surface phenomena on paper sheets and in pulp suspensions. Within the scope of the present work, the digitizing level(4-bits) and the resolution of the images (256x256) are sufficient. Although the system with higher digitizing levels and higher resolutions provides more detailed information on the object image, the processing time and the cost of the system may increase considerably.

LIGNINASE FROM PHANEROCHAETE CHRYSOSPORIUM: CATALYTIC PROPERTIES OF A NOVEL ENZYME

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ABSTRACT

Ligninase isolated from Phanerochaete chrysosporium catalyzes cleavage of β-1 and β-O-4 lignin models between C_α and C_β of their propyl side chains, and it also catalyzes a number of other oxidations in various lignin-related compounds. Some of the reactions, including C_α-C_β cleavage, consume both H_2O_2 and O_2, whereas others consume only H_2O_2. Based on studies of the mechanism of oxidation of several substrates, a unified scheme for ligninase action on lignin-related compounds is proposed.

KEYWORDS: Lignin biodegradation, peroxidase, hemeprotein, cation radicals

INTRODUCTION

The recent discovery of the first lignin-degrading enzyme (1,2) has opened the field of lignin biodegradation to biochemical inquiries. Efforts are being made to clone the gene(s) that encode ligninase, and to understand the enzyme's mechanism. This report summarizes our research on the mechanism of ligninase; these investigations have entailed characterizing the nature of the reactions catalyzed as well as studying reaction kinetics. Our results indicate that the wide range of substrates attacked by ligninase, its apparent oxygenase activity (3), and the diversity of reactions catalyzed (1-3) can be explained by free radical formation in the substrates.

MATERIALS AND METHODS

Enzymes. Ligninase was isolated from Phanerochaete chrysosporium Burd., strain BKM-F-1767 ATCC 24725) (3) and purified by ion-exchange chromatography using a Mono-Q HPLC column from Pharmacia (4). Ligninase used in these studies is the same as that initially isolated and described by Tien and Kirk (1,3) and has subsequently been designated ligninase H8 (4). Bovine erythrocyte superoxide dismutase (Worthington), used for some electron spin resonance (ESR) experiments, was further purified by ion-exchange HPLC on the Pharmacia Mono-Q-column (4). Superoxide dismutase activity was assayed according to McCord and Fridovich (5).

Chemicals. 1,4-Dimethoxybenzene was obtained from Aldrich Chemical Co. The tetramethoxybenzenes were synthesized and purified as described by Kersten et al. (6). Model I was prepared earlier (3,7), and model II was synthesized according to Hammel et al. (8). 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) (Sigma) was vacuum-distilled before use. All other chemicals were reagent grade and used without further purification.

ESR Experiments. ESR measurements were performed on Varian E-9 or E-109 spectrometers. The operating conditions have been described (6,8). The contents of the reaction mixtures are described in the figure legends.

Product Identification. The products benzoquinone and methanol (as a derivative) from oxidation of 1,4-dimethoxybenzene by ligninase were identified by gas chromatography/mass spectroscopy (6). Contents of the reaction mixtures and techniques for product identification have been described (6). Incubation conditions and methods for quantitation and identification of veratraldehyde and benzaldehyde from model II oxidation were according to Hammel et al. (8).

Other Assays. Ligninase (H8) was quantitated by its absorption at 409 nm [ε = 168 $mM^{-1} \cdot cm^{-1}$ (9)]. Oxygen uptake was measured with a YSI Model 53 O_2 electrode.

RESULTS AND DISCUSSION

Recent studies have shown that ligninase is a hemeprotein peroxidase (10). It is characterized as a peroxidase based on its spectral properties (3,10) and on its requirement for H_2O_2 for catalysis (3). Steady-state kinetic studies have shown that the enzyme operates by a ping-pong mechanism (9). It first reacts with H_2O_2 to form a two-electron oxidized intermediate. This intermediate then oxidizes the lignin substrates and returns to the resting (ferric) state. According to the nomenclature of Chance (11), the two-electron, H_2O_2-oxidized

intermediate of peroxidases is called Compound I. The 2-electron oxidation of substrate can occur sequentially, forming a one-electron oxidized intermediate (Compound II). Based on the need to conserve charge, researchers have proposed that formation of Compound II by peroxidase is evidence for free radical formation in the substrate (11), which is known to be the case with numerous peroxidase substrates. Our work with stopped-flow rapid scan techniques has shown that ligninase also undergoes formation of Compounds I and II during catalysis (9). The formation of Compound II is important for understanding the mechanism of the ligninase.

Figure 1 shows the ligninase-catalyzed cleavage of the C_α-C_β bond in β-1 model I. Products are syringaldehyde methyl ether and 3,4-dimethoxyphenylglycol; the latter contains a new hydroxyl group. In certain respects, the oxygenase activity of this reaction resembles the peroxide-dependent hydroxylation reactions catalyzed by cytochrome P450 (12). In fact, Shimada et al. (13) have demonstrated the oxidation of a similar β-1 model using a cytochrome P450 model, tetraphenylporphrinato-iron complex plus tert-butylhydroperoxide. But in contrast to the cytochrome P450 system, the ligninase system incorporates oxygen from dioxygen rather than H_2O_2 into the hydroxylated diol product shown in Figure 1 (3). Spectroscopic results also demonstrate clear differences between

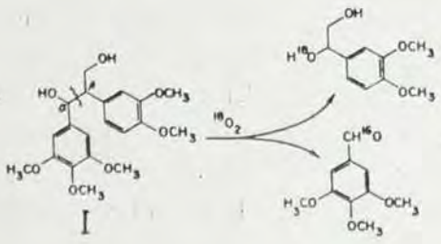


Figure 1. Reaction scheme illustrating the products and isotope labelling pattern from ligninase-catalyzed cleavage of model I. Syringaldehyde methyl ether is formed from the lower ring and a diol is formed from the upper ring. The oxygen atom inserted into the β carbon (benzylic carbon of the diol product) is derived from dioxygen. The diol can be further cleaved by ligninase (see (4) for further details).

cytochrome P450 and ligninase; the peak in the reduced CO difference spectrum of ligninase is not at 450 nm (14).

The catalytic properties of ligninase are similar to those of lipoxygenases and cycloxygenases (15). These iron-containing enzymes utilize dioxygen in their oxygenation reactions and require peroxides for maximal activity. Because free radicals have been shown to be involved in catalysis with soybean lipoxygenase, we tested this possibility with the ligninase. A free radical mechanism was also seemed to be attractive since ligninase catalyzes a number of seemingly disparate, nonstereoselective reactions (1-3). Several substrates were tested for free radical formation by ESR spectroscopy. Because each phenylpropanoid unit in lignin contains one or two aryl methoxyl groups, we initially tested simple methoxy-substituted benzenes.

As shown in Figure 2A, an ESR signal was detected in incubations containing ligninase and H_2O_2 with 1,4-dimethoxybenzene. The signal was relatively stable at room temperature and was detected in the absence of a spin-trapping agent. The free radical was subsequently identified as the cation radical of 1,4-dimethoxybenzene based on the gauss (g-) value and the hyperfine splitting constants (hfsc) of its ESR signal. This cation radical had not previously been detected in biological systems.

Incubation with other methoxybenzene congeners yielded equally intense ESR signals (6). Figures 2B and 2C show the ESR signals from the cation radicals of 1,2,3,4- and 1,2,4,5-tetramethoxybenzenes, respectively. The magnetic parameters of these two radicals agree well with the literature data reported for the corresponding cation radicals generated chemically (16). No ESR signal was observed with 1,2-dimethoxybenzene, although UV-spectrophotometric results clearly show that it is a substrate. Radicals from penta-, 1,2,3,5,-tetra- and tri-methoxybenzenes were also not detected. Activity was not restricted to the methoxybenzenes; ESR signals were also observed in incubations containing 1,4-diethoxybenzene.

We attribute the stability of the methoxybenzene cation radical to the low pH of the ligninase reactions [pH 2.5 is optimum (3)],

which stabilizes such radicals, and to the number and positions of the methoxyl groups. The oxygens have two types of effects on the radicals: resonance and inductive. The resonance effects from the lone-pair electrons tend to stabilize the radical. In contrast, the inductive effects (from the electronegativity of the oxygens) tend to destabilize the positive charge of the cation radical. Thus an ESR signal is observed with 1,4-dimethoxybenzene (favorable charge distribution), but not with 1,2-dimethoxybenzene.

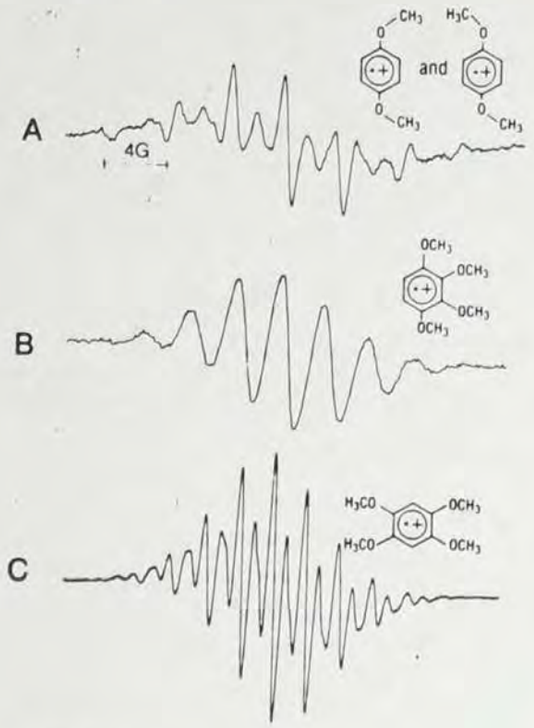


Figure 2. ESR spectra of cation radicals of methoxybenzene congeners. The 2-ml reaction mixtures contained 0.5 μM ligninase, 0.32 mM H_2O_2, 0.1 M sodium tartrate pH 2.5, and 5 mM of either 1,4-dimethoxybenzene (A), 1,2,3,4-tetramethoxybenzene (B) or 1,2,4,5-tetramethoxybenzene (C). Reproduced from (8).

The major products from ligninase-catalyzed oxidation of 1,4-dimethoxybenzene are benzoquinone and methanol (6). This demethylating activity is unlike that of the O-demethylase activity catalyzed by mono-oxygenases, in which formaldehyde is produced (17). The products benzoquinone and methanol are quite consistent with the known chemistry of cation radical decomposition in aqueous systems. Figure 3 shows a hypothetical scheme for benzoquinone and methanol elimination which is consistent with our results. Methanol was also formed from the ligninase-catalyzed oxidation of 1,2-dimethoxybenzene, suggesting a similar mechanism of oxidation even though no stable free radicals were detected.

Although methoxyl loss in lignin does occur during fungal attack (18), suggesting that these activities may be operative in vivo, demethoxylation by ligninase is a minor reaction in lignin models. The predominant biodegradative reaction of lignin and in lignin model compounds is C_α-C_β cleavage of the propyl side chains (3,18, Kirk et al., unpublished). To test whether free radicals are involved in this important reaction, we examined several dimeric models of lignin.

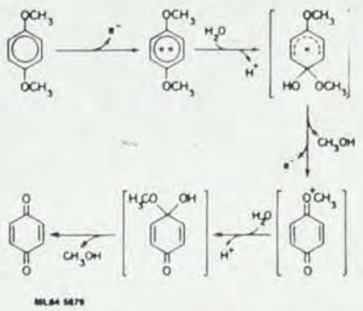


Figure 3. Hypothetical scheme showing two sequential one-electron oxidations of 1,4-dimethoxybenzene and additions of water with elimination of methanol.

The incubation of model II with ligninase and H_2O_2 yields veratraldehyde and benzaldehyde quantitatively in a 1:1 stoichometry. During catalysis, an ESR signal is observed, but only in the presence of a spin trap such as DMPO. Radicals with half-lives too short for direct detection can be stabilized by reacting with DMPO to form a more stable spin adduct. The g-values and the coupling constants from the protons of DMPO are affected by the nature of the parent free radical (19). Thus these parameters yield information on the structure of the trapped free radical.

The g-value and the hfsc of the signal from the incubation of model II with the ligninase under anaerobic conditions are indicative of a carbon-centered radical (Fig. 4A). When oxygen is allowed into the incubation, the signal intensity of the carbon-centered radical is diminished and a new signal appears (Fig. 4B). The g-value and hfsc of the new signal resemble those of a peroxy radical (8). Since it is the

beta carbon of β-1 models that is hydroxylated by dioxygen during catalysis (3), we suspected that the radical exists on this carbon. To test this hypothesis, model II was synthesized with ^{13}C on the beta carbon. As predicted from the nuclear spin of ^{13}C (I=1/2), the ESR spectrum was further split into doublets (Fig. 4C). The ESR spectrum, however, also indicated the presence of another radical which is carbon-centered. That signal, arising from the ^{12}C-centered radical, closely resembles the signal of the α-hydroxybenzyl radical adduct and so probably represents the α-hydroxy dimethoxybenzyl radical. In any case, these results indicate that the cleavage reaction proceeds, at least in part, via the formation of a C_β carbon-centered radical.

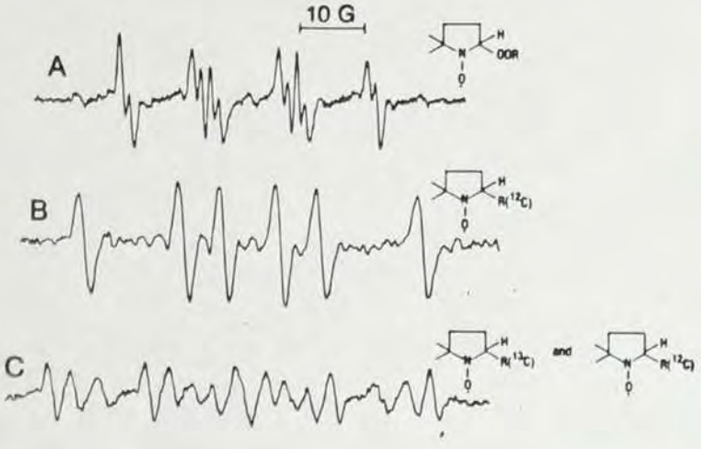


Figure 4. ESR spectra of the spin adducts of reaction products from model II. The 1-ml reaction mixtures contained 2 μm ligninase, 0.16 mM H_2O_2, 0.16 mM model II, 40 mM DMPO in 25 mM sodium tartrate pH 2.5, under anaerobic (A) or aerobic (B&C) conditions.

Carbon-centered radicals can add dioxygen at rates limited only by diffusion (20). Consequently, we suspected the oxygen-centered radical to be the corresponding alkyl peroxy radical. Because this radical adduct would have the same hfsc as that of the superoxide adduct, however, we tested the effect of superoxide dismutase on the signal intensity. These reactions were performed at pH 5, at which both superoxide dismutase and ligninase are active. Superoxide dismutase (20 units·ml^{-1}) decreased the signal intensity but did not totally eliminate it. This result suggests that the oxygen-centered radical adduct of DMPO is a mixture of both superoxide and alkyl hydroxyperoxy radicals. This is not a surprising result in light of the known chemistry of alkyl hydroxyperoxy radicals which disproportionate to yield aldehydes and superoxide (21):

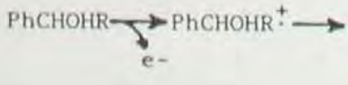
It is often difficult to ascertain whether the radicals observed by ESR spectroscopy are an integral part of a reaction mechanism or whether they are products of insignificant side reactions. This is because the technique is so highly sensitive. On the other hand, because of the reactivity of most radicals and the high rate constants for competing reactions, it is possible that many times only a small fraction of the radicals are trapped. To determine whether the radicals are integral intermediates, we conducted product inhibition studies. If the radicals trapped by DMPO are intermediates formed in catalysis, then DMPO should also decrease the amount of products formed. This proved to be the case. Increasing DMPO concentrations caused a corresponding decrease in benzaldehyde formation; the effect of veratraldehyde formation was negligible (8). These results clearly indicate that the radicals detected by ESR spectroscopy are an integral part of catalysis and not formed via an insignificant side reaction.

Free radical involvement in cleavage of model II is also consistent with the stoichiometry of the reaction. As mentioned above, model II is cleaved by ligninase between C_α and C_β to yield veratraldehyde and benzaldehyde (6). Because these products are not substrates for further oxidation by ligninase (in contrast to those from model I), model II was also ideal for stoichiometry studies. The stoichiometry under anaerobic conditions showed that one veratraldehyde and one benzaldehyde are formed per H_2O_2 and dimer consumed (6). Under aerobic conditions, the products and the product ratio were the same, but sub-stoichiometic amounts of H_2O_2 were consumed per dimer cleaved. The reaction also required H_2O_2, and resulted in oxygen being consumed. This result, in which H_2O_2 is an

activator, resembles the propagation stage of a free radical reaction.

Figure 5 shows a scheme for cleavage of model II which is consistent with the results presented here. The initial reaction is oxidation of ligninase by H_2O_2 to form the two-electron oxidized Compound I intermediate of ligninase. Compound I oxidizes model II by one electron to yield the one-electron oxidized ligninase intermediate Compound II and a substrate radical. On the basis of the work with methoxybenzenes, we speculate that the substrate radical is the cation radical. It breaks down to yield veratraldehyde and the α-hydroxybenzyl radical, or alternatively, benzaldehyde and the α-hydroxy dimethoxybenzyl radical. Under anaerobic conditions, the radicals are further oxidized to yield the corresponding aldehydes. The oxidant may be the Compound II intermediate of ligninase. Under aerobic conditions, the carbon-centered radicals add dioxygen to yield the corresponding α-hydroxyl benzyl peroxy radicals which disproportionate to yield the aldehyde and the superoxide radical. The latter dismutates to produce H_2O_2. We postulate that this H_2O_2-producing activity accounts for the less than stoichiometric amounts of added H_2O_2 consumed under aerobic conditions.

Chemically, the free-radical mechanism accounts for several of the prominent reactions of lignin biodegradation: C_α-C_β cleavage, loss of methoxyls, oxidation of benzylic hydroxyls to ketones, and ring opening are mechanistically consistent with a free radical mechanism. We do not propose, however, that all of these reactions of lignin degradation are catalyzed by ligninase; indeed, several other enzymes are also secreted by ligninolytic cultures of P. chrysosporium (4), and one of those enzymes also has aryl demeth(ox)ylating activity in certain compounds (22). The mechanism proposed in this paper for oxidative C_α-C_β cleavage is in accord with the work of Snook and Hamilton (23) on free radical oxidation of phenylalkanols. Those workers demonstrated that the cleavage of 1- or 2-phenylalkanols, of which model II is a particular example, by Fenton's reagent or by peroxydisulfate, proceeds via cation radical intermediates to yield benzaldehyde and the alkyl radicals as products:



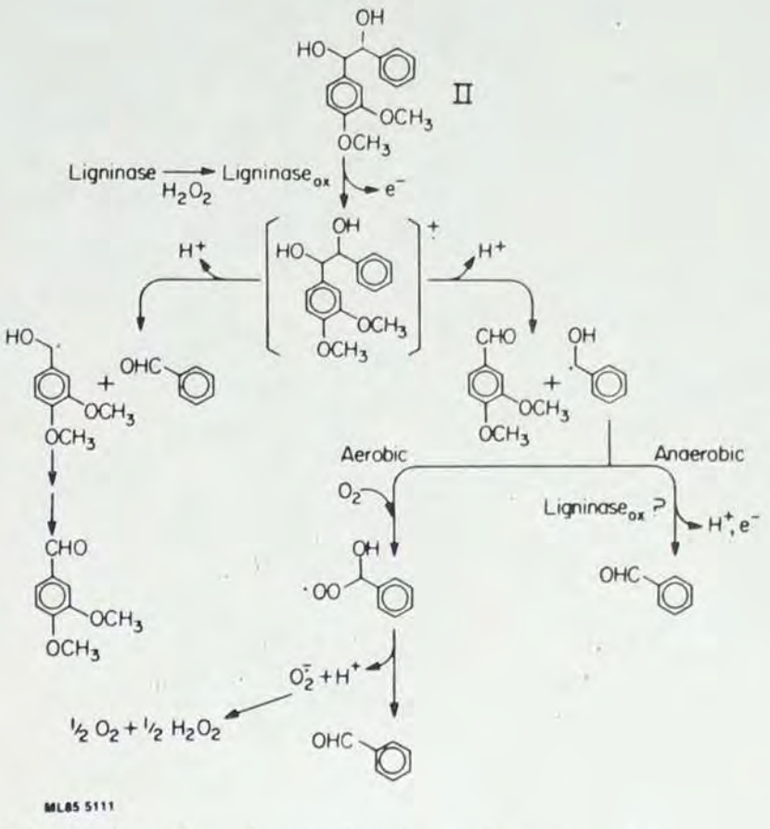


Figure 5. Hypothetical scheme for anaerobic and aerobic cleavage of model II by ligninase. Reactions of the α-hydroxy(dimethoxybenzyl) radical, indicated at the left with two arrows, are proposed to be analogous to those shown at the right for the α-hydroxybenzyl radical.

On the basis of our initial results with methoxybenzenes (6), and on the results of Snook and Hamilton (23) with chemical systems and phenylalkanols, we proposed that the various reactions catalyzed by ligninase involve a mechanism based on aryl cation radical formation (6). The fate of these radicals, we suspect, is determined by their structures (i.e. by the substituents on the ring). We suspect, too, that some radicals are so unstable that they do not diffuse away from the active site of ligninase and therefore undergo two rapid sequential one-electron oxidations. Other substrates, like the ones studied here, are stable enough that the radicals can be detected directly by ESR spectroscopy. A radical mechanism is also consistent with the nonstereoselectivity of the enzyme (4). A radical mechanism for ligninase-catalyzed lignin degradation has also recently been hypothesized by Shoemaker et al. (24). These workers based their conclusion on the known metabolic fate of lignin model compounds and its similarity to the chemistry of cation

radicals. The hypothesis (6, 24) that cation radical formation is the basic reaction catalyzed by ligninase is supported by our experimental results, summarized here. It is thus becoming apparent that radical chemistry plays an integral part in lignin biodegradation, as it does in lignin biosynthesis.

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AN ASSESSMENT OF PRIORITIES IN BIOMASS RESEARCH

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ABSTRACT

Wood and agricultural wastes form a less likely raw material base for biomass fuel industry than agriculturally propogated hybrid poplars. Enzymatic methods of cellulose hydrolysis and lignin conversions have not fulfilled expectations and consequently, higher research priorities should be assigned to the development of chemical processing technologies. The enigmatic question of lignin utilization in the context of biomass processing deserves expanded research effort.

The petroleum crisis in the early seventies gave impetus to research directed toward the development of a special technology for the conversion of biomass materials to liquid fuels and chemicals. Newly evolved methods of microbial gene transfer and enzymatic conversions were envisaged to play a key role in the new biomass technology. In the light of the considerable body of knowledge acquired during the recent years, it is of interest to critically consider whether the directions that appeared most promising ten years ago should continue to retain their dominance in biomass research or should be complemented or replaced by alternative approaches. In the presentation, the author will discuss the following propositions for changes in biomass research priorities.

1. It seems unlikely that available biomass waste will form the raw-material base for future production of fuels and chemicals, because it is a better feedstock for less discriminating combustion technologies. Consequently, search for high-yield agricultural fuel and chemical crops should be intensified, using photosynthetic productivity and suitability for conversion as selection criteria.
2. The prediction that cellulose will largely replace starch, sucrose and glucomannans as industrial sources for glucose remains uncertain. Consequently, increased priority should be given for research directed toward optimization of conventional agricultural and processing practices of starch producing crops.
3. Rapidly growing hardwoods, such as hybrid poplars and eucalypts are, for many reasons, more advantageous raw materials for the production of cellulose-based biomass fuels than either softwood species or agricultural residues, such as corn stover. The improvements made in the growth characteristics of hybrid poplars, which undoubtedly will continue, suggests that these varieties will develop to standard agricultural crops with alternative outlets as raw materials for the production of pulp and paper, of solid fuels or of alcohol fuels. It seems, therefore, that hybrid poplars deserve specific emphasis in biomass conversion research.
4. Recent times have seen impressive progress in developing understanding of the complex mechanisms of enzymatic hydrolysis of cellulose to glucose. At the same time, the observed complexities of the hydrolysis phenomenon form a hindrance to the evolution of a viable and controllable industrial process. It has become clear that enzymic methods, in general, have serious limitations when applied to solid instead of soluble substrates.

   It is clear that the original expectations attached to enzymatic cellulose hydrolysis have not materialized and an industrial application of this process, if it turns out to be successful, lies far in the future. The logical conclusion from this circumstance is that priorities in cellulose hydrolysis research ought to be shifted from enzymatic hydrolysis to the optimization of acid-catalyzed hydrolysis technology where the translation of laboratory-scale results to industrial practice is more straightforward.
5. Modern technology has its true and unquestioned potential in the fermentation processes of soluble carbohydrates. One of the most exciting prospects in this area is the fermentation of pentose sugars to ethanol. The addition of this process to conventional hexose fermentation would substantially increase the alcohol fuel yields obtainable from lignocellulosic materials.
6. Enzymatic hydrolysis research has brought to attention the importance of chemical and mechanical pretreatments prior to hydrolysis. It appears that pretreatments, preferably combined with delignification for

the facilitation of recycling of unhydrolyzed cellulose, deserve to be tested also in the context of acid-catalyzed hydrolysis.

7. The question about the type of lignin products that may be obtained from lignocellulosic biomass processing remains enigmatic but ought not to be ignored. Additives to phenolic adhesives represent a very limited outlet for biomass lignins. Biodegradation studies, while fundamentally rewarding, have so far revealed little application potential for biomass processing. Alkaline oxidation remains the most effective pathway to low-molecular weight lignin products. On the other hand, conversion of lignin, in some manner, to liquid fuel products would ideally complement alcohol fuel production.

8. In the biomass field, the importance of non-utilitarian free scientific inquiry has never been sufficiently recognized. This lack of activity needs to be rectified in order to complement the data base which process technology badly needs for its sound evolution.

THE TOPOCHEMISTRY OF ACID-SULPHITE PULPING
A THEORETICAL ANALYSIS – PART II

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We have recently demonstrated [1] how the mathematical theory of degelation, using limited assumptions, can provide a good fit to the experimental data [2] on the topochemistry of the acid-sulphite delignification of thin wood sections. Whiting and Goring [3] have since developed a technique which gives almost complete separation of middle lamella and secondary wall tissues, and have pulped each tissue separately. The results differ somewhat from the previous data, particularly at high levels of delignification. The difference is shown in Figure 1, which is a graph of the extent of delignification in the middle lamella, $(w_s)_{ml}$, and secondary wall, $(w_s)_s$, plotted against the extent of delignification in the whole wood, $(w_s)_t$.

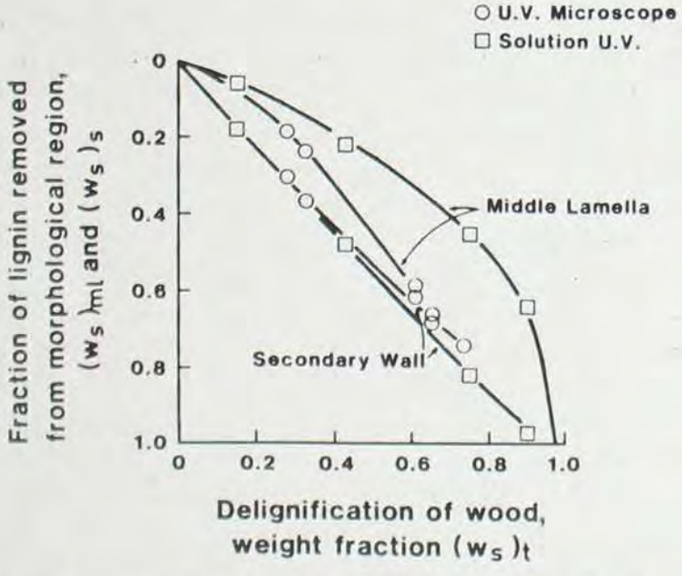

Figure 1. Comparison of the topochemical effect measured on isolated tissue fractions [3] and in situ by U.V. microscopy [2].

Since preliminary calculations suggested that analysis of the new data might permit a simplification of the previous assumptions concerning the structure and reactivity of lignin, a detailed investigation was undertaken.

The theory of Bolker and Brenner [4] proposes that lignin behaves during acid-sulphite delignification as if it were composed of stable chains joined by cleavable benzyl-ether crosslinks. Three parameters define the mathematical expression of the theory: i) the degree of polymerisation of the preformed chains (y), ii) the initial degree of crosslinking (ρ'), and iii) the rate of crosslink cleavage.

It was found previously [1] that a good fit could be obtained to the experimental data by assuming that y was the same in each morphological region, while ρ' and the rate were different. More precisely, it was assumed that the crosslink cleavage was a first order reaction, with its rate determined by crosslink density, but with different rate constants (k_s, k_{ml}) for the reaction in each morphological region. This was expressed mathematically for time, t, by Equation 1 which was rearranged to give Equation 2. The values obtained for ρ_s'/ρ_{ml}' and k_s/k_{ml} were 0.5 and 0.64 respectively.

$$t = \frac{\ln (\rho_s'/\rho_s)}{k_s} = \frac{\ln (\rho_{ml}'/\rho_{ml})}{k_{ml}} \qquad (1)$$

$$\ln (\rho_s'/\rho_s)/\ln (\rho_{ml}'/\rho_{ml}) = k_s/k_{ml} \qquad (2)$$

It has now been found that the best fit to the new data is given by the same scheme but with changed values of ρ_s'/ρ_{ml}' and k_s/k_{ml}. New values of 0.64 for ρ_s'/ρ_{ml}' and 0.873 for k_s/k_{ml} gave the lowest percentage standard deviation. The excellent match between the experimental data and the theoretical scheme is shown in Figure 2.

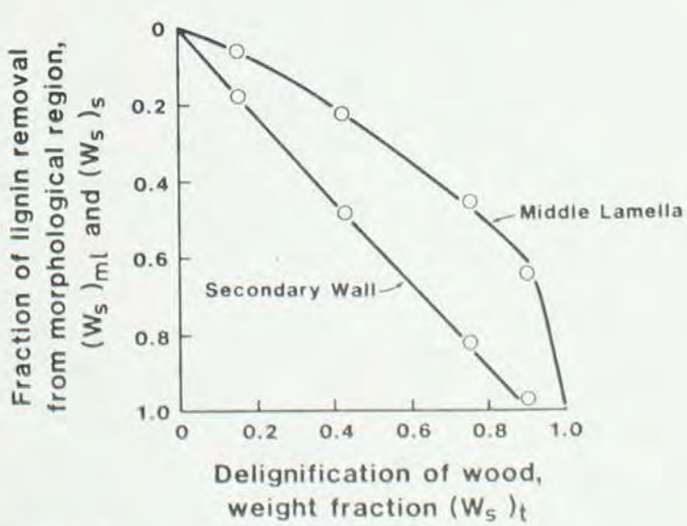

Figure 2. The experimental points fit the theoretical curves when $\rho_s'/\rho_{ml}' = 0.64$ and $k_s/k_{ml} = 0.873$ (data from Reference 3).

These calculations brought the best value for the ratio of k_s to k_{ml} rather close to a value of 1. If the ratio is given the value of 1, then a considerably more exacting theoretical scheme is introduced in which the rate constants for the crosslink cleavage ractions (k_s, k_{ml}) are assumed to be the same in each morphological region. The result from the analysis of this new scheme is illustrated in Figure 3. Although the standard deviation is higher than in the best fit, the match between experiment and theory is good considering the very restrictive assumptions being made. This result contrasts with the analysis of the older data which were very poorly described when k_s was made equal to k_{ml}. The new scheme predicts that the ratio of benzyl-ether crosslinks in the secondary wall and middle lamella, ρ'_s/ρ'_{ml}, is about 0.75.

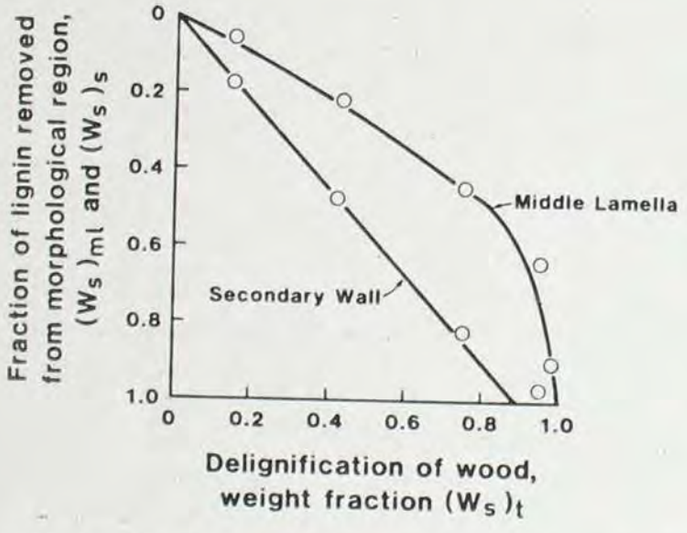

Figure 3. The fit to experimental points given when $k_s/k_{ml} = 1$ and $\rho'_s/\rho'_{ml} = 0.764$ (data from Reference 3).

If Whiting and Goring [3] are correct in saying that their new results are indeed more accurate, rather than simply different, then the new analysis suggests that the topochemical effect exhibited in acid-sulphite pulping is solely dependent on the degrees of crosslinking in the two regions and that the presence or absence of any other wood component does not affect the course of delignification in either the secondary wall or the middle lamella as long as the wood has been saturated with liquor before cooking. An alternative hypothesis, however, is that the isolation of tissue fractions from the wood matrix removes the physical barriers contributing to the topochemical effect, thus leaving only chemical factors to affect the system. If this hypothesis is valid, then the original data constituted a better description of what was occurring during the pulping of intact wood.

The analysis in this paper strengthens the evidence for the validity of two concepts. First, it reinforces the concept that lignin is a gel and that degradation of a gel explains many phenomena exhibited during pulping. In acid-sulphite pulping, the fixing of only three parameters, ($y = 18$, $\rho'_{ml} = 0.338$, and $\rho'_s = 0.258$), and the application of a very specific form of gel-degradation theory permits the description of: (1) the relationship between weight-average degree of polymerisation and extent of delignification; (2) the relationship between degree of crosslinking and extent of delignification; and finally (3) the topochemical effect.

Second, the analysis supports the concept that the topochemical effect is largely if not wholly dependent on lignin chemistry during acid sulphite pulping. This conclusion can probably be extended to include the topochemical effect observed in kraft pulping. The latter would be even less likely than acid-sulphite pulping to show interference from the wood hemicelluloses – which are cited [6] as affecting the pore size and hence the rate of diffusion of soluble material from the fibre – because hemicelluloses are rapidly removed during kraft pulping [5]. The difference, then, between the magnitudes of the topochemical effects observed in kraft and acid sulphite pulping has to be described in terms of differences in chemistry.

Even the topochemical effect observed during acid-chlorite delignification can largely be described in terms of chemistry. The results presented by Whiting and Goring [3] show there is a sudden increase in the topochemical effect halfway through an acid-chlorite cook. This was explained by invoking a surge in secondary wall delignification due to a sudden removal of hemicellulose from the secondary wall. The results of Table I from Reference 3, however, show that the rate of removal of lignin from the secondary wall remains constant. Delignification of the middle lamella, on the other hand, almost ceases after 50% lignin removal. This is not what one would expect if hemicellulose were causing the topochemical effect because hemicellulose concentration is highest in the secondary wall. The result obtained is rather what would be expected if the middle lamella lignin were less reactive and less tractable than the secondary wall lignin.

The topochemistry of acid chlorite delignification may therefore be better accounted for

by considering the differing phenolic content and crosslinking densities of the middle lamella and secondary wall lignins, differences that have been demonstrated by experimental results [7] and theoretical analysis [1].

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HYDROGEN PEROXIDE DECOMPOSITION BY METAL CATALYSTS: BAD ACTORS IN A BLEACHING STAGE

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ABSTRACT

The decomposition of hydrogen peroxide by first row transition metal catalysts has been examined. The reaction rates are pH dependent, increasing with increased alkalinity. For chromium there exists a pH region (4<pH<6) in which the decomposition rate is greatly enhanced. A series of stabilizing agents was studied and all were found to be effective against decomposition by manganese. However, with iron and copper, catalytic enhancement was observed. Oxygen evolution measurements during peroxide bleaching of metal-impregnated pulps were used to determine peroxide lost to decomposition processes. Results of this aspect of the study give support to the theory that some peroxide is consumed by "nonbleaching" reactions with pulp.

INTRODUCTION

The bleaching of mechanical pulp with hydrogen peroxide has long been regarded as an overall compromise between three reaction types: those which lead to either bleaching or darkening of the pulp and those which lead to decomposition of the peroxide. Yet, there have been few studies which have attempted to distinguish between these reactions.

Methods are continually sought which will favour the bleaching reactions over all others. The use of sodium silicate as a bleach liquor stabilizer, for instance, was found early in the development of peroxide bleaching to result in considerable improvements in the bleaching response of mechanical pulps (1,2). Later, the adoption of organic chelating compounds, as pretreatment agents, brought about further improvements attributed to diminished peroxide decomposition through removal of metal catalysts (3).

This paper describes results from our studies into the catalytic decomposition of hydrogen peroxide, as well as factors which influence this reaction.

RESULTS AND DISCUSSION

A) Studies In the Absence Of Pulp

i) Peroxide Decomposition

The decomposition of hydrogen peroxide by catalysts has been studied extensively by many researchers (4). The importance of understanding this decomposition is highlighted by the deleterious effect that "bad actors", such as Mn, Cu and Fe (present in catalytic quantities in the incoming wood supply and mill white-water systems), have on peroxide pulp bleaching.

The results of our study (Figure 1) show that pH has a pronounced effect on reactivity. The speciation (metal complexes, oxidation states, form of peroxide, etc.) is enormously complex and precludes a detailed mechanistic study. However, all the catalysis observed can be accounted for qualitatively by either the existence of intermediate inorganic peroxides or the occurrence of conditions (ie. pH, oxidation potential, precipitate formation) suitable for oxidation-reduction reactions. The metals which fall into the latter category are Mn(II), Fe(II), Co(II), Ni(II), whereas the marked acceleration in reaction rate seen for Cr(III) in the region 4<pH<6 may be attributed to peroxygen complexes which have been proposed (5) to form under similar conditions.

The results show that in the pH region of interest in peroxide bleaching, 9<pH<11 most transition metals studied are active towards peroxide decomposition and, therefore, must be controlled to achieve maximum bleaching efficiency. As seen by these results, cobalt and manganese are the most effective decomposition agents in this region, although manganese is far more important in pulp bleaching.

ii) Hydrogen Peroxide Stabilization

Diethylenetriaminepentaacetic acid (DTPA),

diethylenetriaminepenta-monophosphonic acid (DTMPA), and sodium silicate were examined for their effectiveness in preventing the decomposition of hydrogen peroxide by Mn(II), Fe(II) and Cu(II). Figure 2 illustrates the results in the presence of 2.5 ppm Mn(II). All the additives examined had a stabilizing action with the following order of effectiveness:

silicate < DTPA ≈ DTMPA

However, at 10 ppm manganese(II) (Figure 3) DTMPA is superior to the others. In the case of iron at 50 ppm all the additives had a catalytic effect on the decomposition (Figure 4), whereas for copper at 10 ppm (Figure 5) addition of silicate and DTMPA proved to be similar in their stabilizing ability.

It is postulated that rather than stabilizing the peroxide, intermediate species are formed between the additives and iron which are better catalysts than the metal salt itself. Similar reactions likely occur between silicate and copper. This same unexpected catalytic action has been seen before in a study on the decomposition of hydrogen peroxide by iron in the presence of DTPA (6).

B) Peroxide Pulp Bleaching Studies

A groundwood pulp sample was demineralized by multiple chelation applications. The pulp was then treated with 100 ppm of either manganese(II), iron(III) or copper(II) sulphate. Table 1 indicates the metal contents of these pulps.

TABLE 1 Analyses of Pulp Samples

Pulp Type	Mn(ppm)	Fe(ppm)	Cu(ppm)	Brightness
Original	62.8	17.8	1.3	64.9
Extracted	0.6	27.6	0.7	65.2
Mn-treated	86.6	39.7	1.2	65.3
Fe-treated	1.1	142.1	1.2	62.4
Cu-treated	1.0	52.9	85.2	64.8

Peroxide bleaching experiments were carried out on each of these samples under identical conditions (2% H_2O_2, 2% NaOH, 4 consistency, 50°C), but varying levels of additive (silicate, Epsom salt, DTPA or DTMPA). Oxygen evolution during the bleaching stage was monitored gasimetrically and the volume converted to give the amount of H_2O_2 decomposed.

Figures 6, 7 and 8 illustrate the relationships which exists between brightness gain and peroxide residual, peroxide consumed by the pulp and peroxide decomposed, respectively. In these three figures the curves tend to converge towards the "metal-free" results. The surprising result is Figure 7 which indicates that less brightness is obtained when more peroxide reacts with the pulp. This, combined with the results in Figure 8 suggests that some reactions of hydrogen peroxide with the pulp consume peroxide, yet, do not provide colour reduction. Figure 9 illustrates this same data but in terms of a bleaching efficiency factor:

$$\frac{\text{Br. Gain}}{\%\ H_2O_2 \text{ consumed.}}$$

As more peroxide decomposes there is a reduction in bleaching efficiency, due in part to the loss of peroxide available for bleaching but also due to other reaction pathways. At least two interpretations are possible: either the decomposition of hydrogen peroxide causes darkening of the pulp which is counteracted by bleaching reactions which consume more peroxide or metal-catalysed reactions with the pulp which consume peroxide and cause formation of chromophores resulting in a reduced final brightness. Further study is necessary in order to distinguish between these possibilities.

SUMMARY:

The results of this study emphasize the importance of proper management of metals in mills currently using hydrogen peroxide. Several other findings can be highlighted:

1. Cobalt and manganese were the most effective of the peroxide decomposition catalysts studied above pH7.

2. Chromium was the only catalyst found to decompose peroxide efficiently under acidic conditions.

3. Chelating agents do not necessarily improve peroxide stability with all metals.

4. Hydrogen peroxide is consumed during pulp bleaching through reactions which do not lead directly to brightening.

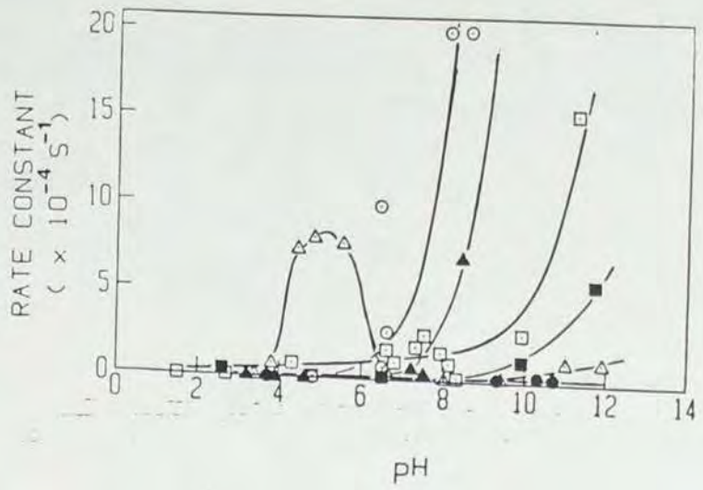

Figure 1. Pseudo First-Order Rate Constants For Peroxide (0.24M) Decomposition As A Function of pH For The Chloride Salts (5.4×10^{-4}M in Metal) Of:

○ - Cobalt(III)
● - Nickel(II)
△ - Chromium(III)
▲ - Manganese(II)
□ - Copper(II)
■ - Iron(III)

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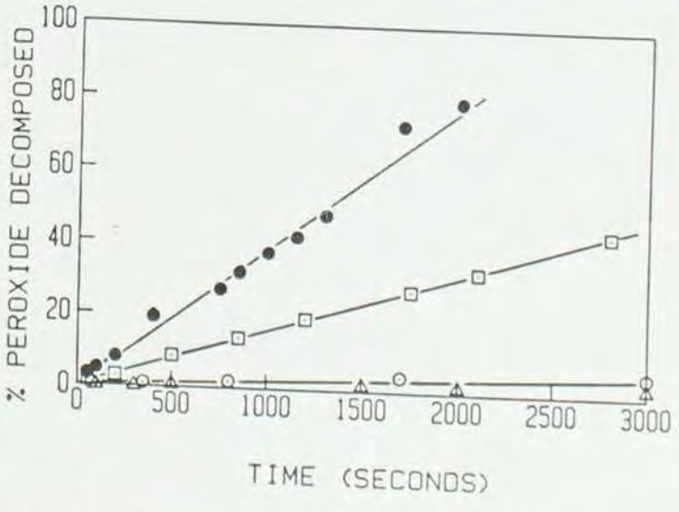

Figure 2. Decomposition Of Hydrogen Peroxide (4.0×10^{-2}M) By 2.5 ppm Manganese(II) With Various Additives:

● - No Additives
○ - DTPA
△ - DTMPA
□ - Silicate

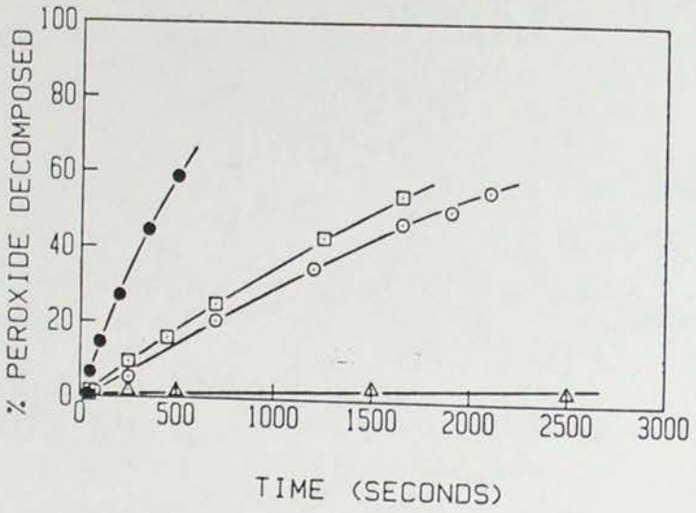

Figure 3. Decomposition Of Hydrogen Peroxide (4.0×10^{-2}M) By 10 ppm Manganese(II) With Various Additives:

- ● - No Additives
- ○ - DTPA
- △ - DTMPA
- □ - Silicate

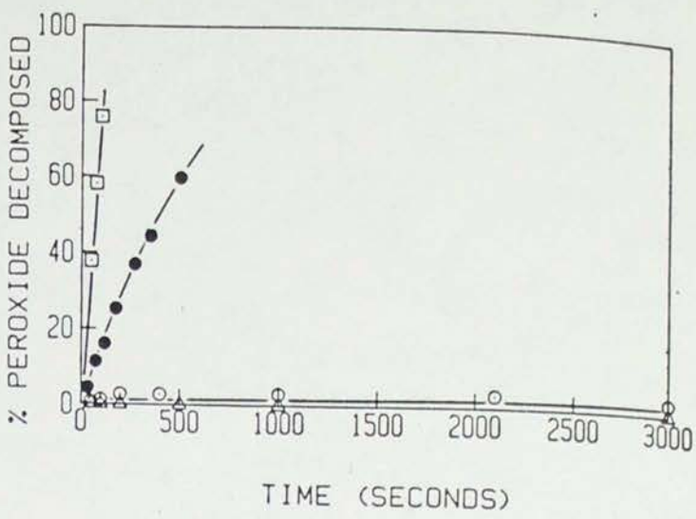

Figure 5. Decomposition Of Hydrogen Peroxide (4.0×10^{-2}M) By 10 ppm Copper(II) With Various Additives:

- ● - No Additives
- ○ - DTPA
- △ - DTMPA
- □ - Silicate

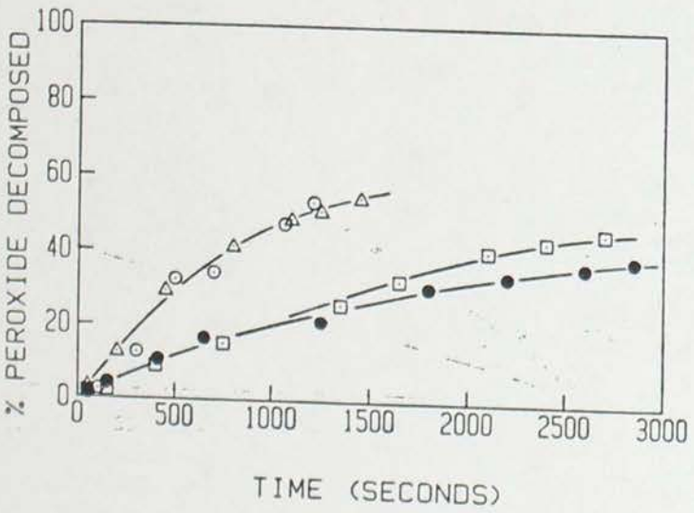

Figure 4. Decomposition Of Hydrogen Peroxide (4.0×10^{-2}M) By 50 ppm Iron(II) With Various Additives:

- ● - No Additives
- ○ - DTPA
- △ - DTMPA
- □ - Silicate

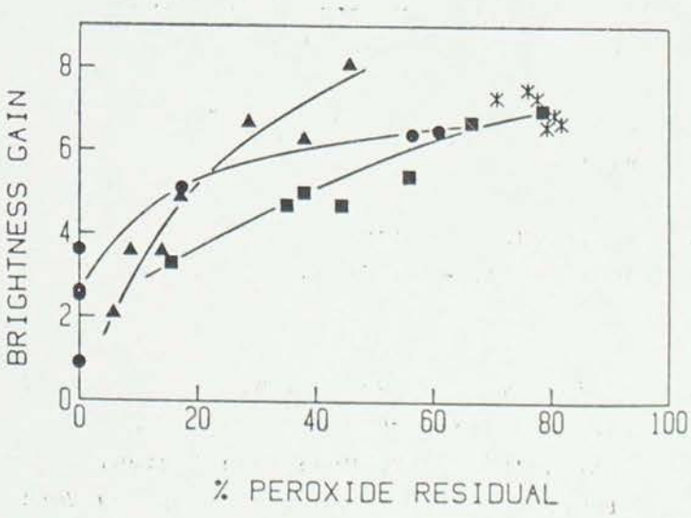

Figure 6. Brightness Gain As A Function Of Peroxide Residual For Bleaching Of Groundwood Impregnated With:

- ● - Manganese
- ▲ - Iron
- ■ - Copper
- * - Metal Free

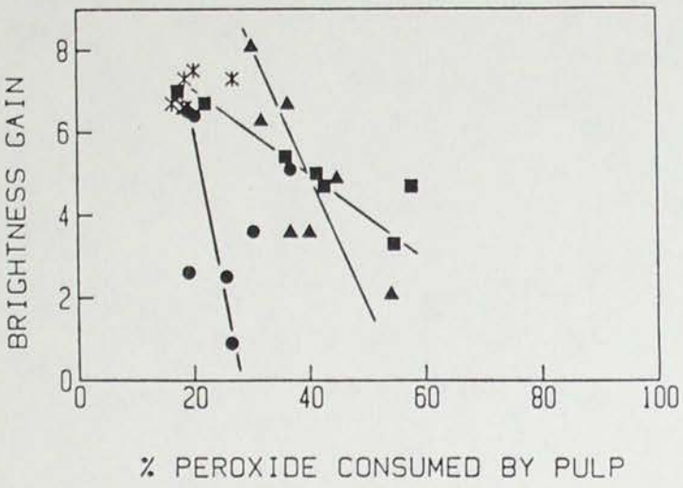

Figure 7. Brightness Gain As A Function Of Peroxide Consumed By Pulp For Bleaching Of Groundwood Impregnated With:

- ● - Manganese
- ▲ - Iron
- ■ - Copper
- * - Metal Free

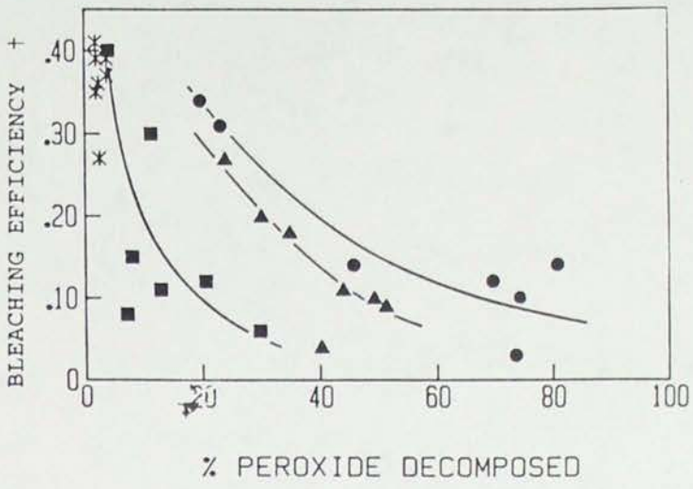

Figure 9. Bleaching Efficiency As A Function Of Peroxide Decomposition For Bleaching Of Groundwood Impregnated With:

- ● - Manganese
- ▲ - Iron
- □ - Copper
- * - Metal Free

† Bleaching Efficiency = $\frac{\text{Brightness Gain}}{\text{\% Peroxide Consumed By Pulp}}$

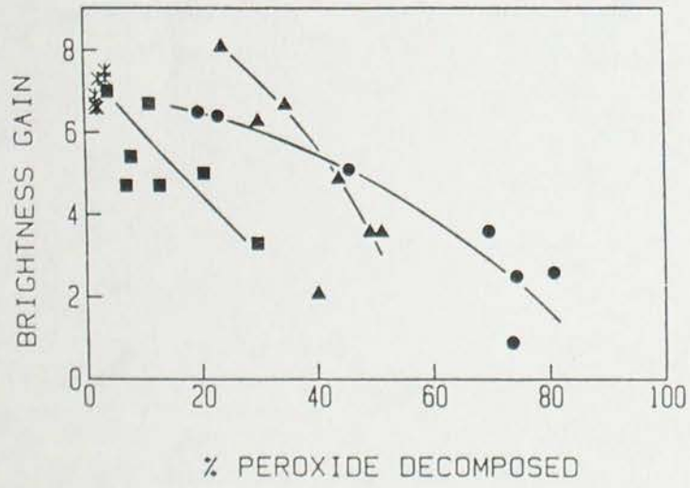

Figure 8. Brightness Gain As A Function Of Peroxide Decomposed For Bleaching Of Groundwood Impregnated With:

- ● - Manganese
- ▲ - Iron
- ■ - Copper
- * - Metal Free

PHOTOACOUSTIC INFRARED SPECTROSCOPIC STUDY OF MECHANICAL PULP BRIGHTENING

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In this study, photoacoustic Fourier transform infrared spectroscopy (FTIR-PAS) was used to try and detect chemical changes occurring during the brightening of refiner mechanical pulp (RMP) from black spruce wood.

The photoacoustic technique is an indirect method of obtaining infrared spectra. The absorption of modulated infrared radiation by the sample gives rise to sound waves which are detected and, then, processed to yield an infrared spectrum. The similarity between photoacoustic and conventional infrared spectra is shown in Figures 1 and 2.

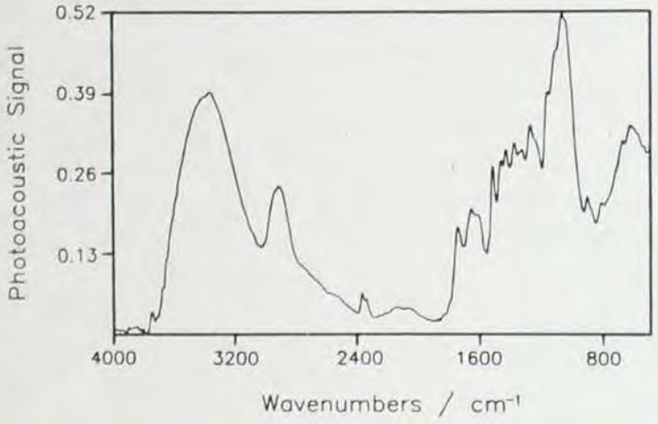

Figure 1. Photoacoustic FT-IR spectrum of black spruce RMP. Signal was corrected as outlined in the text.

As can be seen, the same peaks appear in both spectra, although their relative intensities do vary. This is due to the fact that the photoacoustic signal intensity, which is governed by several variables, is inversely proportional to the frequency (or wavenumber) of the infrared radiation, which explains why the photoacoustic signal is more intense in the low wavenumber region than in the high wavenumber one, when compared to the conventional infrared absorption spectrum.

In the present work all spectra were ratioed to a carbon black reference. As a result, the

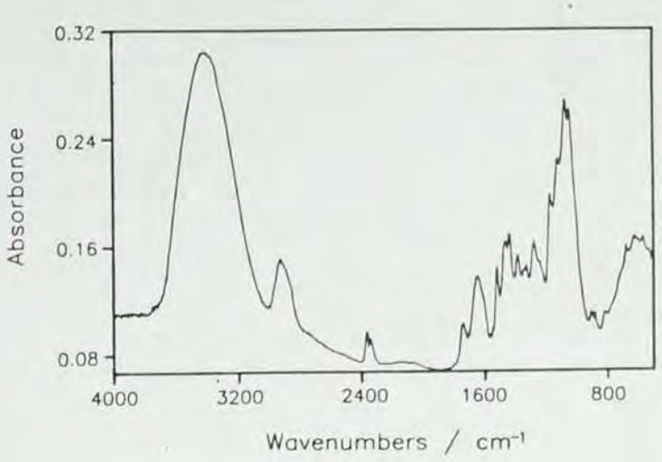

Figure 2. Conventional FT-IR spectrum of black spruce RMP, pressed in a KBr pellet, and not baseline-corrected.

photoacoustic signal seen on the spectra is a unitless quantity, which represents the ratio of the signal generated by the sample to that generated by carbon black. A value of 1 (100% absorbance) is arbitrarily assigned to the carbon black. In general, the baseline value was slightly greater than zero, due to ambient noise and cell window absorption. The signal intensity was corrected by subtracting this value, as measured around 3900 cm^{-1}. This relied on the assumption that the baseline value was constant throughout the spectral range. The validity of this assumption was suggested by the absence of strongly sloping baseline features that are typical of measurements made using KBr pellets. Flat FTIR-PAS baselines were also observed in this laboratory for samples other than pulps.

Photoacoustic spectra of good quality can be measured directly on pulp and paper sheets, with no special sample preparation. However, there is some advantage in grinding the pulp samples to a fine powder by means of a Wiley mill (60-mesh screen), since the smaller particle size causes a significant increase in the signal-to-noise ratio. The absolute intensities were not very reproducible, but if spectra of two samples of the same pulp were compared, all the peaks showed the same relative variation, within experimental error (estimated at about 7% relative uncertainty or better).

Peroxide brightening experiments were performed on unextracted RMP, acetone-extracted RMP, and RMP that had been sequentially acetone and water-extracted, and also on this latter pulp after treatment with sodium hydroxide. All pulps had been treated with EDTA and washed pri-

or to brightening. It was difficult to interpret the changes in the infrared spectra of the non-extracted RMP because a significant amount of extractives was dissolved in the brightening liquor. Each series of brightening experiments was carried out using six liquors with different compositions: 1) normal peroxide liquor (hydrogen peroxide, sodium hydroxide, sodium silicate, magnesium sulfate); 2) peroxide liquor without sodium silicate; 3) sodium hydroxide, sodium silicate, and magnesium sulfate; 4) sodium hydroxide, magnesium sulfate; 5) magnesium sulfate; 6) water only.

In the case of pulps that had not been treated with sodium hydroxide, the most noticeable change in the infrared spectra was a decrease in the intensity of the 1735 cm^{-1} peak coupled with a smaller increase in the intensity of the 1605 cm^{-1} peak upon treatment with any of the liquors, except 5) and 6). This was best rationalized as a hydrolysis of unconjugated esters (peak at 1735 cm^{-1}), possibly present in the hemicellulose, resulting in the formation of carboxylate groups (peak at 1605 cm^{-1}). The change in the peak at 1735 cm^{-1} did not appear related to the brightness gain, since it was essentially the same between liquors 1) through 4), while liquors 1) and 2) gave a brightness gain of approximately 15 points, and liquors 3) and 4) caused a brightness loss of 3 points. The change in the peak at 1605 cm^{-1} due to the formation of carboxylate groups is a problem since it may mask changes in intensity due to an aromatic ring stretching vibration which occurs in the same region. This vibration is sensitive to the presence of α-carbonyl groups, which are chromophores of interest in the study of mechanical pulp.

In the case of pulp that had been previously treated with sodium hydroxide (at the same concentration and temperature, but for a longer reaction time than the usual brightening treatment), the results were much clearer. Although some ester groups were still hydrolyzed, the magnitude of the change in the intensity of the peak at 1735 cm^{-1} was much smaller and, as a result, it was expected that the change in the 1605 cm^{-1} peak due solely to the presence of alkali would be small. Treatment with liquors 3) or 4) caused no significant change in the intensity of the 1605 cm^{-1} peak. However, when peroxide was used (liquors 1) and 2)), the change in the intensity of the 1735 cm^{-1} peak was roughly the same as that observed with liquors 3) and 4), but a decrease in the intensity of the peak at 1605 cm^{-1} was observed. This change, although small, may indicate a decrease in α-carbonyl content. A more noticeable decrease was observed for the 1647 cm^{-1} peak. Conjugated carbonyls, some quinonoid structures, and ethylenic double bonds are known to absorb in the latter region. It is interesting to note that the decrease in the 1647 and 1605 cm^{-1} peak intensities was slightly lower when no silicate was used in the liquor (liquor 2)), corresponding to a slightly lower brightness.

Brightening with sodium borohydride gave the same brightness gain (15 points) as peroxide. However, the decomposition of the borohydride made the medium alkaline, resulting in the hydrolysis of the unconjugated ester bonds. The spectra showed a large decrease in the 1735 cm^{-1} peak intensity with a very slight increase of the 1605 cm^{-1} peak, which would seem to indicate that there is a decrease in α-carbonyl content that completely offsets the effect on the spectra of the increase in carboxylate content. A noticeable decrease was observed in the intensity of the 1647 cm^{-1} peak.

Borane (BH_3) in tetrahydrofuran (THF) was also used for brightening, and gave a slighly better brightness gain (16 points) than peroxide. The effect on the spectra was a noticeable decrease by about the same amount of the peaks at 1735, 1647, and 1605 cm^{-1}. The use of a non-aqueous medium (THF) precluded the formation of carboxylate groups and, thus, made the decrease in the 1605 cm^{-1} peak, attributed to a decrease in α-carbonyl content, more obvious. Since borane attacks ethylenic double bonds, it is possible that some of the decrease observed at 1647 cm^{-1} may be due to the reduction of double bonds on the lignin side-chain which could result in a break in the conjugation and, as a result, a greater brightness gain.

Brightening in slightly acidic medium was carried out with sodium dithionite. No noticeable change in the 1735 cm^{-1} ester peak was detected, as expected. A slight decrease in the intensity of the 1647 cm^{-1} peak was found and a smaller decrease was observed for the 1605 cm^{-1} peak. The fact that these changes were smaller than in pulps brightened with peroxide was consistent with the lower brightness gain achieved with dithionite.

ACKNOWLEDGEMENTS

F.St-G. wishes to thank the Natural Sciences and Engineering Research Council of Canada for a postgraduate scholarship. Thanks are due to Messrs. E. Read and J. Dagg, and Dr. P. Whiting, from the Abitibi-Price Research Center in Mississauga, for their assistance in preparing the refiner mechanical pulp.

BAGASSE DELIGNIFICATION : CHEMICAL COMPONENTS RELATIONS

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ABSTRACT

Morphological and chemical characteristics of bagasse led to search short time and high efficiency delignification processes. Bagasse delignification is a very fast reaction, and it is possible to produce pulps of different qualities -ranging from chemimechanical up to chemical pulps- in shorter times than the usual commercial ones and obtaining higher yield and strength properties just selecting adequate chemical and temperature conditions.

KEYWORDS: Bagasse, Delignification, Chemical Composition

INTRODUCTION

Goring and Kerr (1) established than the delignification rate of wood is higher when hemicelluloses are removed from the cellular wall, increasing in this way the average pore size and making diffusion of lignin degradation products easier. In another paper, Masura (2) indicates the existence of three phases in wood delignification, but only in the second one the greatest lignin removal is produced.

The results of Fernandez (3) -and others- show that bagasse lignin is more reactive and accesible than wood lignin. The object of this paper is to describe the results we have obtained searching shorter and more efficient delignification processes for bagasse.

MATERIALS AND METHODS

Experiments were carried out using a commercial depithed bagasse and another with low hemicelluloses content. For both bagasses the trials were first achieved on stainless steel microdigesters of 800 mL capacity, and the results were checked afterwards on 15 L and 18 L stainless steel digesters.

Table I. Initial chemical composition for both bagasses.

PROPERTIE	UNIT	COMMERCIAL	LOW HEMICELL.
Cellulose	%	47,5	62,5
Hemicelluloses	%	25,7	9,0
Lignin	%	20,8	24,8

RESULTS AND DISCUSSION

Hydroxyl ions concentration (OH^-, mol/L), residual lignin (%) and yield (%) deeply decrease during the earliest moments of alkaline pulping, as is shown for lignin in Fig. 1.

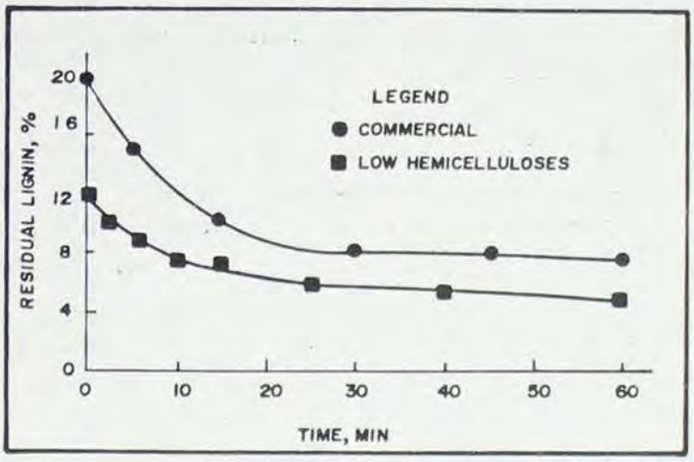

Fig. 1. Residual lignin vs time for both bagasses. Pulping conditions: 16% initial Na_2O, 100°C.

It is evident the existence of an "uneasily removable lignin" for both bagasses. Taking a further look to Fig. 2, it is also clear that this "uneasily removable lignin" decreases when there are favorable conditions for diffusion and/or stronger pulping conditions (higher temperature and/or initial alkali concentration).

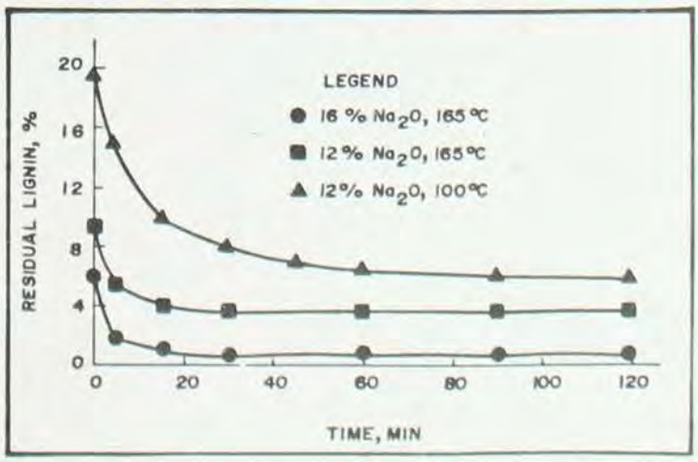

Fig. 2. Residual lignin vs time for commercial bagasse at different pulping conditions.
a.- 16 % initial Na_2O, 165 °C
b.- 12 % initial Na_2O, 165 °C
c.- 12 % initial Na_2O, 100 °C

It was possible to find some mathematical relations between different chemical properties during delignification, as is shown in Fig. 3.

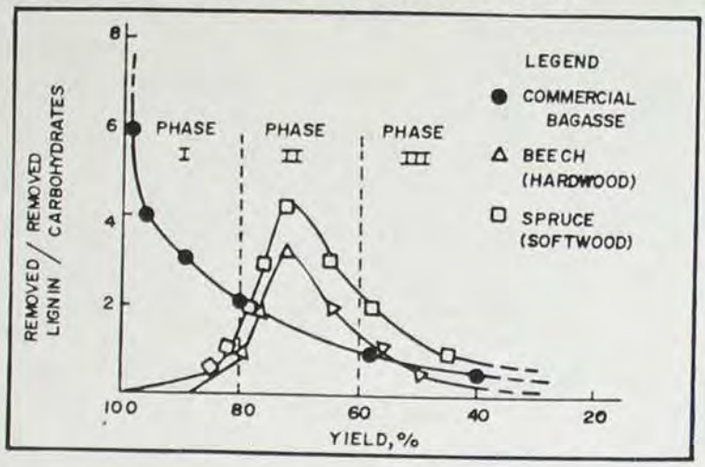

Fig. 3. Delignification phases for wood (2) and bagasse.

Contrarily to wood, bagasse does not have three delignification phases. Bagasse delignification is produced in the earliest moments of pulping and it is not necessary to increase cooking time. The optimal cooking time depends on the desired pulp to be rpoduced, according to what chemicals and temperature conditions must be selected. In this way, it is possible to obtain pulps with good properties and a greater yield than the commercial ones in shorter times, as is shown in Table II.

Table II. Different soda pulping alternatives

	Chemimech.	Semichem.	Chemical
Time,min	0-10	10-15	15
Yield,%	92-96	80-84	60-64
Residual lignin, %	17-20	9-11	3-4
Freeness,CSF	100-200	300-400	300-400
Breaking Length, km	2,5-3,5	4-5	6-7
Tear	35-40	50-55	55-65

CONCLUSIONS

It has been pointed out the existence of an "uneasily removable lignin" in bagasse, which decreases when favorable diffusion and/or stronger pulping conditions are applied.

Removal of hemicelluloses is favorable for delignification and increases bagasse reactivity, probably due to a greater pore size of bagasse cellular wall. This removal, as well as higher temperatures and initial alkali concentration, decrease the amount of "uneasily removable lignin".

According to the relations established between bagasse chemical components, it is now possible to choose more adequate pulping conditions to obtain different pulp qualities for bagasse with higher yields and lower lignin contents in shorter times.

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DELIGNIFICATION DU BAGASSE: RELATIONS ENTRE LES CONSTITUANS CHIMIQUES

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RESUME

Les caractéristiques morphologiques et chimiques du bagasse conduite les recherches vers l'etude des procedés vites et de haut rendement. La délignification c'est une réaction trés vite, et peut etre produire des pates á différents qualitées depuis chimi-mécanique jusqu'a quimiques, dans temps plus has que les utilicées dans l'industrie, avec des meilleurs rendements et propiértés mécaniques par un dosage des produits chimiques et une température de cuisson appropiés.

ORGANOSOLV PULPING WITH ACETIC ACID

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As early as 1916 Pauly has found that lignin can be partly extracted from wood and annual plants by refluxing with aqueous acetic acid in the presence of mineral acids. However, only 72 % of the lignin could be extracted from spruce wood chips after 30 hours cooking (Pauly 1934, Schütz and Knackstedt 1942). We have found that delignification is much more effective and the cooking time can be reduced to 2 - 5 hours when the wood chips or cereal straws are continuously extracted with 95 % acetic acid, containing 0.1 % hydrogen chloride at 110°C. At the end of the extraction, 3 - 5 % hydrogen peroxide (based on wood) are added to the 70 % aqueous acetic acid, instead of hydrogen chloride, and the mixture is stored for eight hours at 80°C. The hydrogen peroxide reacts with the acetic acid in forming peroxyacetic acid, which is a powerful, selective bleaching agent.

In the case of beech wood chips, a kappa number of 7 is obtained after four hours extraction.Additional bleaching leads to a brightness degree of 85 % ISO at a pulp yield of some 40 %. DP values are above 2000 and can be improved significantly by extraction with alkali, indicating that some hemicelluloses are left in the pulp after the extraction and bleaching steps. Breaking lengths are between 8 and 12 km and α-cellulose contents above 90 % being further improved by extraction with alkali.

Kappa numbers below 30 at pulp yields of 47 % are obtained from spruce wood chips after extraction with acetic acid for four hours. Subsequent bleaching with hydrogen peroxide leads to brightness degrees of up to 70 %. Breaking length is around 10 km, burst index 35 m^2 and DP 2.200. Pine wood needs the highest and cereal straw the lowest amounts of acetic acid. Both lead to pulps with acceptable strength properties and brightness degree. The extracts are evaporated in vacuum and the residual sirups are poured into water. Thereafter, the precipitated lignin can easily be filtered off, while the hemicelluloses are obtained in the filtrate. They may be separated from low molecular weight phenols as well as from acetic acid by extraction with methylene chloride. In this way, three fractions are obtained, consisting of lignin, hemicelluloses, and low molecular weight phenols, the latter being only of minor amounts.

According to the mild pulping conditions, the lignin is only weakly condensed, thermoplastic and soluble in many organic solvents. Its molecular weight is between 2000 and 3000 Daltons. It contains up to 10 % acetyl groups, but no chlorine. The acetyl groups are mainly linked to the γ-carbon atoms, while the phenol groups are not esterified and more frequent than in MWL. This makes acetosolv lignin (ACL) a convenient material as an adhesive for particle boards. Liquefaction of ACL by hydrogenolysis and gasification by pyrolysis are under research in our laboratory.

Likewise, the hemicellulose fraction deserves attention as a chemical feedstock. Our present interest focuses on three chemicals, furfural from hardwoods and annual plants and hydroxymethylfurfural from softwood , as well as acetic acid from both. Due to the high concentration of pentosans and hexosans in the hemicellulose fractions, their yield should be higher than from conventional spent liquors that consist mainly of lignin.

If compared with conventional pulping acetosolv pulping offers the following advantages:

- The pulping chemicals, acetic and hydrochloric acids, are recovered by distillation
- Losses of acetic acid may be compensated by acetyl groups in wood
- The evaporation energy of acetic acid is less than one fifth from that of water
- No pressure vessels are needed
- Lignin and hemicelluloses are obtained separately and in a low condensed,sulfur-free form
- No sulfur or chlorine containing effluents are produced
- The amount of wash waters is drastically reduced.

^{13}C NMR SPECTRA OF ACETIC ACID LIGNINS

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Carbon-13 NMR spectroscopy is a meaningful tool for tracing chemical reactions of lignin. In the case of organosolv pulping with aqueous chloroethanol (CE), it can be shown that the solvent forms ether bonds with the α-carbon atoms in lignin. The corresponding signal of the α-carbon atom is shifted downfield from 73.2 ppm to 81.9 ppm and two additional signals appear at 44.5 and 70.3 ppm that can be assigned to the carbon atoms in the chloroethyl groups.

It was found in our laboratory that most of the CE can be replaced by acetic acid. Using 2.5 % CE in 90 % aqueous acetic acid, which is still a powerful pulping mixture, the extracted spruce lignin gives a carbon-13 spectrum lacking the three above mentioned signals indicative for chloroethyl groups. Instead two other signals appear at 171.3 and 64 ppm that can be assigned to acetylated γ-hydroxyl groups.

Similar spectra are recorded from lignins (ACLs) obtained from spruce wood chips by continuous extraction with 95 % aqueous acetic acid containing 0.1 % hydrogen chloride at 110°C.

A closer look reveals characteristic differences between spruce ACL and MWL. Besides the γ-hydroxyl groups, a minor part of the α-hydroxy groups is also acetylated. From the relative intensities of the signals between 145 and 155 ppm, assigned to carbon atoms 3 and 4, it can be seen that ACL contains more free phenolic hydroxyl groups than MWL, indicating a partial splitting of the β-O-4 linkages. This is further confirmed by the relative intensities of the signals at around 136 and 133.5 ppm, indicating carbon atom 1 in etherified and phenolic guaiacyl groups, respectively. The most prominent signals of ACL between 110 and 136 ppm, at 129 and 115.8 ppm, may be partially assigned to carbon atoms 2/6 and 3/5 in p-hydroxyphenyl residues. From the aliphatic part of the ACL spectrum partial acetylation of the γ-hydroxyl groups and splitting of the β-O-4 linkages is further confirmed.

In the spectrum of beech lignin carbon atoms 3 and 5 give a signal at 153.9 ppm in etherified and at 148.7 in phenolic syringyl units. Comparison of the relative intensities of these signals in the spectra from beech MWL and ACL reveals that the latter contains more phenolic hydroxyl groups. From the aliphatic part of the ACL and MWL spectra it is obvious that the β-O-4 ethers in ACL are partially split and the γ-hydroxyl groups are partially acetylated. Similar results are obtained from the spectra of straw lignins.

INTERPRETATION IN CHEMICAL TERMS OF SOME SELECTIVITY PROBLEMS DURING PULPING AND BLEACHING

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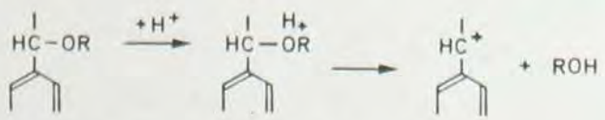
ABSTRACT

The most important lignin degradation reactions taking place during pulping and bleaching follow mechanisms which apply also to the carbohydrate reactions during these processes. Examples for the analogies between the mechanisms of lignin and carbohydrate reactions are given. These provide an explanation for the limited selectivity of current pulping and bleaching processes with respect to lignin degradation and dissolution.

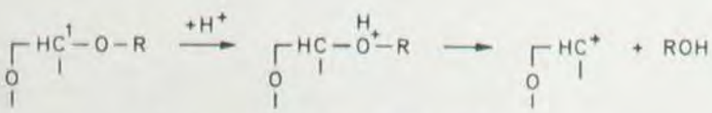
In this paper an attempt is made to identify the main reason for the limited selectivity of pulping and bleaching processes currently applied. The most important reactions of lignin during pulping and bleaching will be compared with those of the carbohydrate constituents, and the parallels existing between the mechanisms of the reactions of these two different substrates will be emphasized.

Examples of fragmentation and condensation reactions of lignins and of corresponding reactions of carbohydrates, taking place during pulping, will be presented. These include

1) Acidic cleavage of aryl ether bonds and glycosidic bonds (Fig. 1)
2) Alkaline cleavage of aryl ether bonds and glycosidic bonds (Fig. 2)
3) Alkali-induced cleavage of α-aryl ether bonds and β-elimination during peeling (Fig. 3)
4) Alkali-promoted cleavage of carbon-carbon bonds in lignins and carbohydrates (Fig. 4)
5) Condensation reactions between lignin fragments (Fig. 5), and between lignin- and carbohydrate fragments (Fig. 6 and 7)

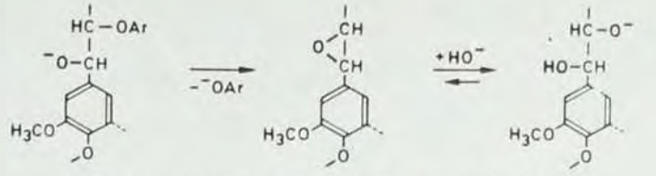


R = adjacent lignin unit

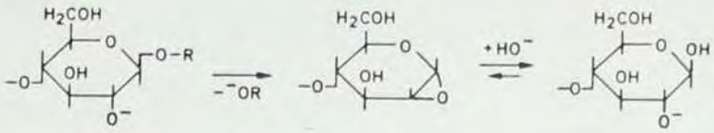


R = adjacent carbohydrate unit

Fig. 1. Acidic hydrolysis of benzylaryl ether bonds in lignin and of glycosidic bonds in carbohydrates

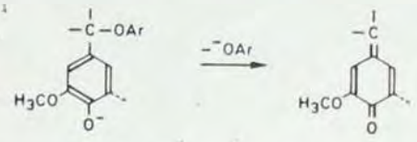


⁻OAr = liberated (phenolic) portion of the lignin molecule

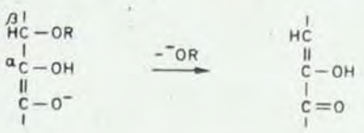


⁻OR = liberated portion of the polysaccharide molecule

Fig. 2. Alkaline cleavage of β-aryl ether bonds in lignin and glycosidic bonds in carbohydrates

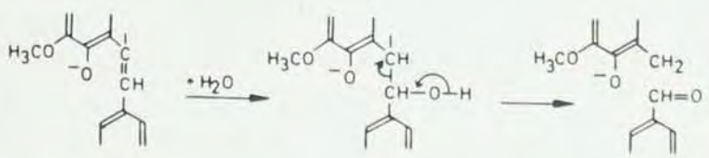


⁻OAr = liberated (phenolic) portion of the lignin molecule



⁻OR = remaining portion of the polysaccharide molecule

Fig. 3. Alkaline cleavage of α-aryl ether bonds in lignin and β-elimination in carbohydrates



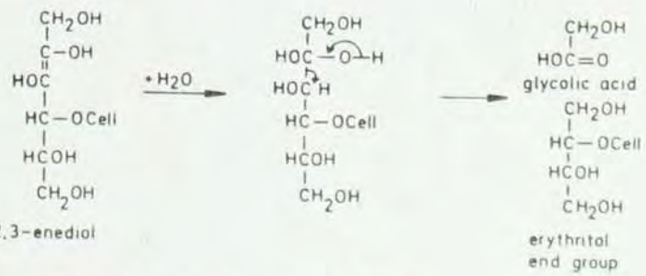


Fig. 4. Cleavage of C-C bonds by alkali

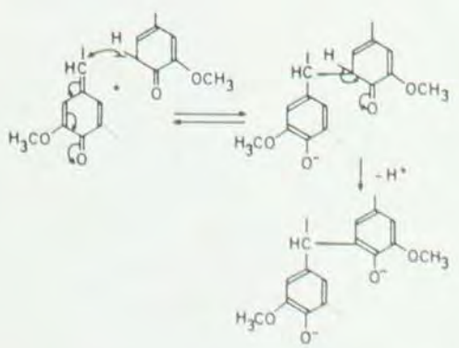


Fig. 5. Lignin condensation. Formation of a diarylmethane structure

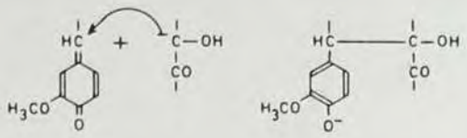


Fig. 6. Formation of a C-C bond between lignin and carbohydrates by conjugate addition

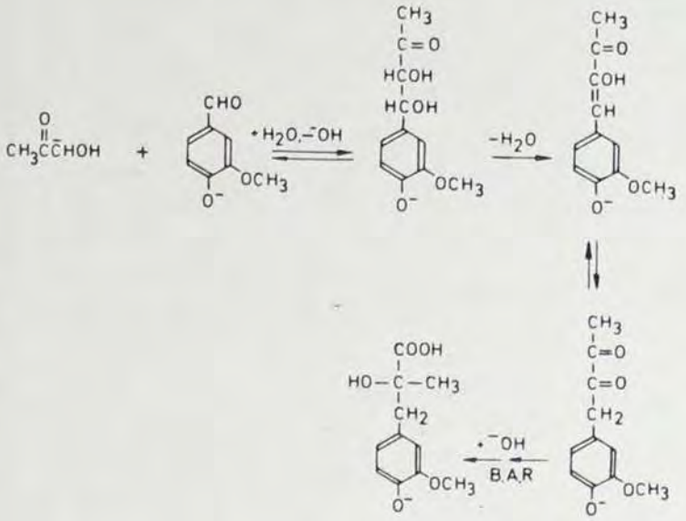


Fig. 7. Formation of a C-C bond between lignin and carbohydrates by aldol condensation

The parallels between the mechanisms of the bleaching reactions of these two substrates are less pronounced, due to the partly aromatic nature of lignin. However, if sufficiently aggressive bleaching species or reactive structures are involved, the following analogies may be discerned.

1) Hydrogen abstraction by radicals, e.g. $HO^{\cdot}$, resulting in the introduction of carbonyl groups (Fig. 8)
2) Electron abstraction from phenolic and enolic structures by oxygen, followed by oxygenation and fragmentation (Fig. 9)
3) Addition of nucleophilic species, e.g. HO^-, HOO^- or ClO^-, to dicarbonyl structures, followed by fragmentation (Fig. 10)

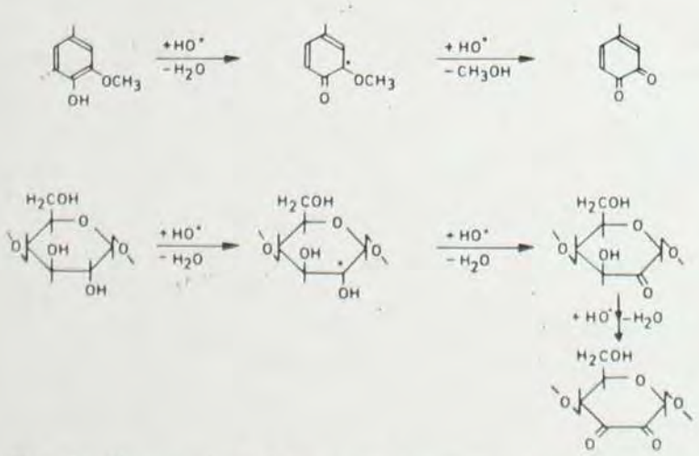


Fig. 8. Abstraction of hydrogen atoms. Introduction of carbonyl groups

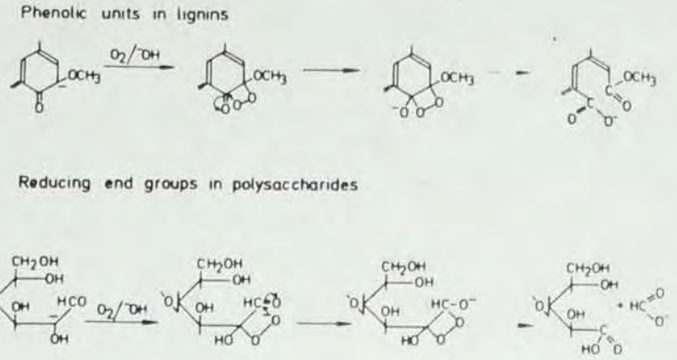


Fig. 9. C-C cleavage by oxygenation followed by rearrangement via dioxetanes

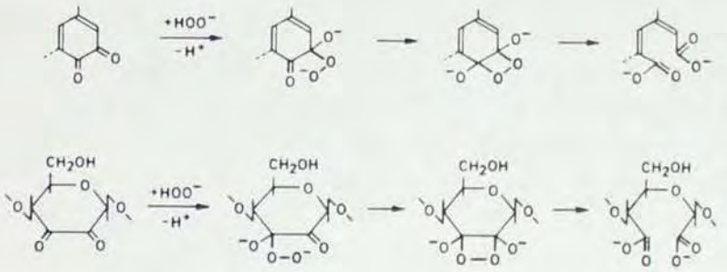


Fig. 10. Intramolecular nucleophilic attack of hydroperoxide intermediates

In the light of these mechanistic analogies between lignin and carbohydrate reactions, the selectivity problem encountered in current delignification processes will be briefly discussed.

COMPARISON OF PRETREATMENT METHODS FOR ENHANCING THE ENZYMATIC HYDROLYSIS OF WOOD

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ABSTRACT

Different methods of pretreating wood substrates to enhance enzymatic hydrolysis are discussed, and the effects on the recovery of lignin and hemicellulose components are compared.

Of the different pretreatment methods, those involving heating with steam appear, at present, to be the most economical. The principal mechanism of accessibility enhancement in all steaming processes appears to be the hydrolysis and dissolution of a significant part of the hemicellulose, which creates pores large enough to accommodate molecules of cellulase. Explosive decompression at the end of a steam treatment contributes virtually nothing to subsequent water extraction of xylan and to enzymatic hydrolysis. The products obtained after treatment with 240°C steam for 90 or 180 s, followed by steam explosion from the full steam pressure of 3.24 MPa, were compared with those obtained after similar steam treatments followed by bleed-down of pressure to only 0.69 or 0.34 MPa before explosive release. Similar yields of glucose were obtained on enzymatic hydrolysis, and similar yields of butanediol and of ethanol were obtained on combined hydrolysis and fermentation, regardless of the magnitude of the pressure drop on release. This was true even though the 90 s product was still in chip form after release from the bled-down pressure. The water-soluble fraction, of steam treated chips obtained without explosion, was easily extracted. Two-thirds of it was recovered as a 9% solution without concentration.

Steam temperatures above 200°C cause significant pyrolysis of the xylan, with formation of CO_2 (2% after 2 min at 240°C) and smaller amounts of CO, and with a significant decrease in the combined oxygen content of the resulting steam-exploded aspenwood (from 43.58 to 41.54%). Pyrolysis is undesirable in steam treatment and contributes little or nothing to hemicellulose solubilization and subsequent enzymatic hydrolysis. Pyrolysis for 6.5 min of aspenwood wafers in dry (superheated) steam at 276°C reduced the pentosan content to 66% of its original value - an identical reduction to that caused by saturated steam treatment at 240°C for 80 s followed by steam explosion. However, only 4% of the surviving pentosan from the pyrolysis was water soluble, compared with 85% of that from the steam explosion. Process variables such as impregnation with sulfuric acid of 0.2% concentration, which selectively accelerates hydrolysis relative to pyrolysis, improve the solubilization of xylan relative to its destruction, and improve enzymatic hydrolysis. Mass balances, with and without added acid, are compared.

High steam temperatures, such as 240 or 250°C, permit short treatment times but can result in uneven cooking of the chips. Air-dry, or partially dried aspenwood chips, even when thicker than 3 mm, heat rapidly as a result of steam passage into the wood through the vessels and release of the latent heat by condensation inside the chips. Aspenwood chips such as those impregnated with dilute acid, which have moisture contents (MC) greater than 100% (dry basis), become filled with water before reaching steam temperature. Further temperature rise of chip centers is then only effected by relatively slow heat conduction from the outer surface. Large wet chips of thickness greater than 3 mm are therefore unevenly cooked by 250°C steam. Lower temperatures lengthen required cooking time and promote more even cooking.

Moisture content has a major effect on consumption of high pressure steam with green wood (MC 100%) requiring twice as much steam to heat the moisture as to heat the wood substance. When small chips are used, MC (air-dry vs green) has little effect on solubilization of xylan, or on glucose yield on subsequent enzymatic hydrolysis.

Detection, Prediction, Synthesis and Confirmation of a Mutagen

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In 1980 a compound was detected by GCMS in the solution resulting from aqueous chlorination of acetovanillone, a model compound typical of some of the structural units of the softwood lignin molecule.

Acetovanillone contains the substituted guaiacol group present in lignin. It has been demonstrated that the mutagenicity produced by aqueous chlorination of acetovanillone is similar to that produced by the chlorination of kraft pulp.[1] The chlorination filtrates were characterized by extraction with ether and analysis of the extracts by GC-MS. Fewer products are obtained from chlorination of acetovanillone than from chlorination of kraft pulp. This simplifies the identification of products by GC-MS and the determination of their degree of mutagenicity.

Figure 1 is part of the total ion chromatogram (70 eV electron impact) of the ether extract of the solution of products of chlorination of acetovanillone. The chemical ionization mass spectrum (using methane as the reagent gas) of the gas chromatographic peak eluting at 18.2 minutes (Figure 2) shows a quasi-molecular M+1 ion (molecule plus a proton) of m/e 187, indicating a molecular weight of 186. The ratio of the isotopic chlorine atom cluster about the M+1 ion indicates that three chlorine atoms are present in the molecule. The electron impact spectrum of the same peak exhibits a very intense m/e 43 ion which indicates that the compound contains an acetyl group. The only formula which fits these data is $C_5H_5OCl_3$. From the fragmentation patterns (figure 3) this compound was assigned the structure 3,5,5-trichloropent-4-ene-2-one.

It was observed that filtrates from the chlorination of unbleached pulp were mutagenic, while filtrates from chlorine dioxide treatment of the same unbleached pulp were not mutagenic.[1] Analysis of the filtrates indicated that chlorine produced mutagenic -chlorocarbonyl group containing compounds, such as tetrachloroacetone, while chlorine dioxide did not produce such structures. Therefore it was predicted from its structure that 3,5,5-trichloropent-4-ene-2-one would be mutagenic.

The compound was synthesized by the method of Kiehlmann et al.[2] The product exhibited an identical EI mass spectrum and similar gas chromatograph retention time to the compound identified in the chlorination filtrate.

Using the Ames salmonella bioassay[3], strain TA100, the synthesized 3,5,5-trichloropent-4-ene-2-one was found to be a direct acting mutagen, as had been predicted.

Most direct acting mutagens are strong electrophilic alkylating agents.[4] Mutagenicity is caused by alkylation of the purine and pyrimidine bases of DNA. During cell replication DNA strands split and the separated strands are used as templates to synthsize new DNA. The correct sequence of bases in the strands being synthesized is determined by hydrogen bonding between the bases of the new and template strands. Alkylation of the bases disturbs the hydrogen bonding between bases and can cause inclusion of the wrong base in the new strand. This may change the genetic expression of the DNA in the new cell, resulting in a mutation.

Both carbonyl groups and chlorinated hydrocarbons are electrophiles. In chloroketones the inductive electron withdrawing properties of the chlorine make the carbonyl more susceptible to nucleophilic attack. Olefin and carbonyl groups make chlorine more susceptible to nucleophilic substitution. Thus 3,5,5-trichloropent-4-ene-2-one would be a strong electrophile and hence mutagenic, as found.

The importance of this work is that it led to an hypothesis concerning the types of chlorine containing structures in molecules which tend to make them direct acting mutagens. One such structure is chlorine atoms on a carbon next to a carbonyl group. Another mutagenic structure is chlorine atoms on a carbon of a carbon=carbon double or on a carbon next to one.

A systematic quantitative study is in progress of the direct acting mutagenicity of all aliphatic compounds containing from 2 to 5 carbon atoms, chlorine atoms, and either a carbonyl group or a double bond, or both. The ultimate goal is to be able to forecast from its structure the degree of mutagenicity possessed by any chlorinated aliphatic compound. The chlorinated acetones are now being studied.

Up to the present, the sum of the mutagenicity of all the many mutagens which have been identified in pulp chlorination filtrates does not account for as much as half of its total mutagenicity. Apparently many mutagens remain to be identified in such solutions.

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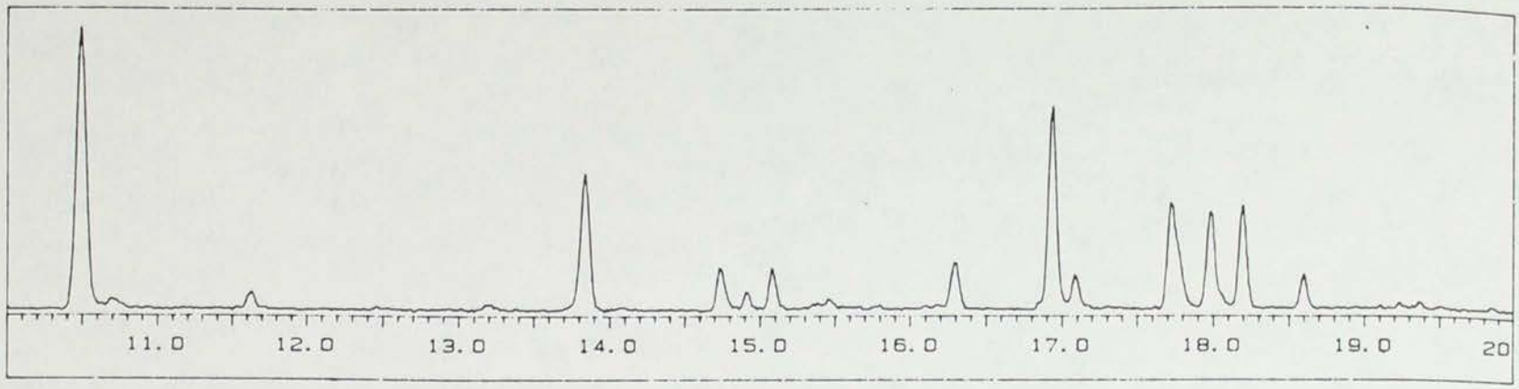

Figure 1

Total ion chromatogram of ether extract of aqueous chlorination filtrate from the aqueous chlorination of acetovanillone.

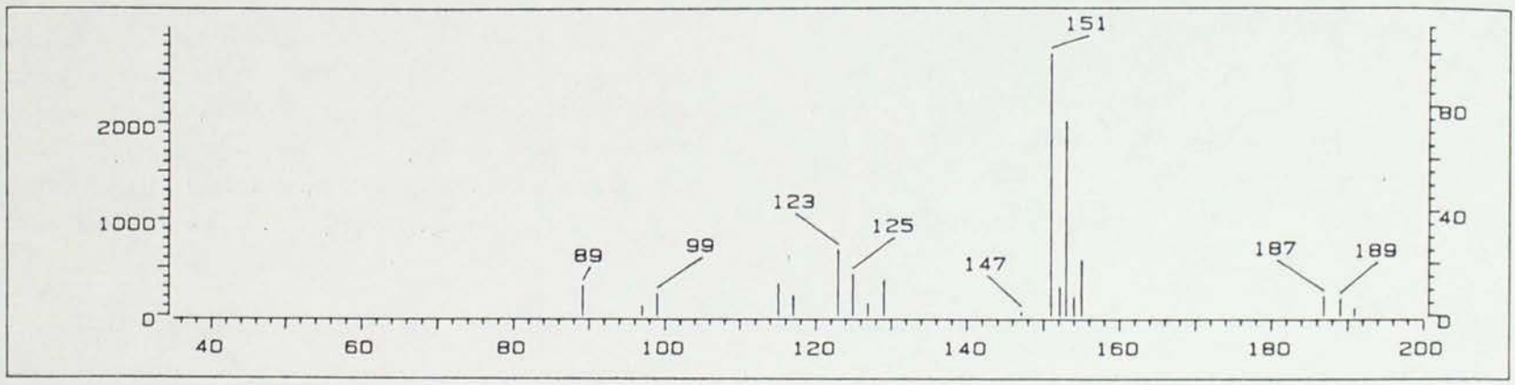

Figure 2

Chemical ionization mass spectrum from chromatogram (18.2 min) of the ether extract of the aqueous chlorination of acetovanillone.

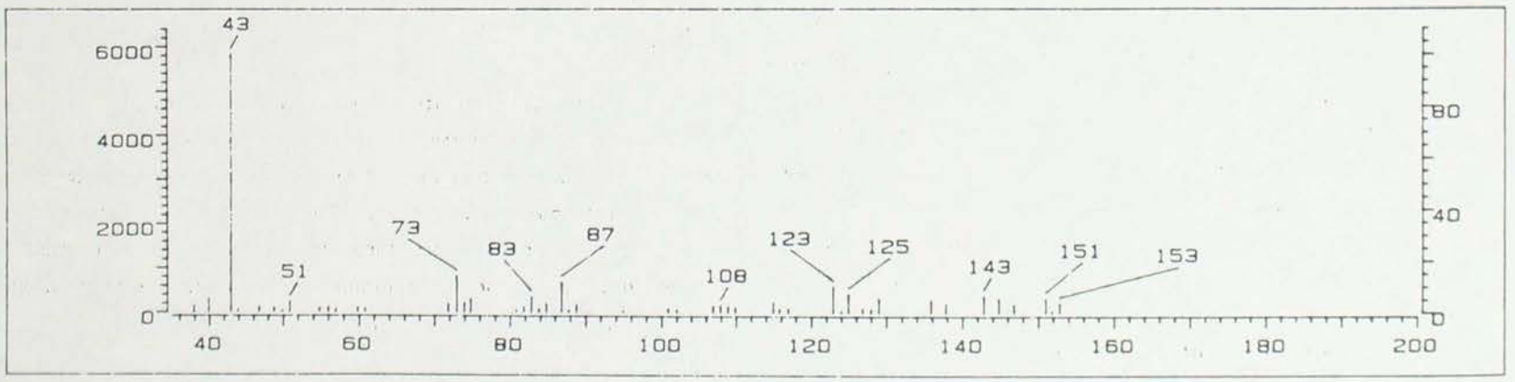

Figure 3

Electron impact mass spectrum from chromatogram (18.2 min) of the ether extract of the aqueous chlorination of acetovanillone.

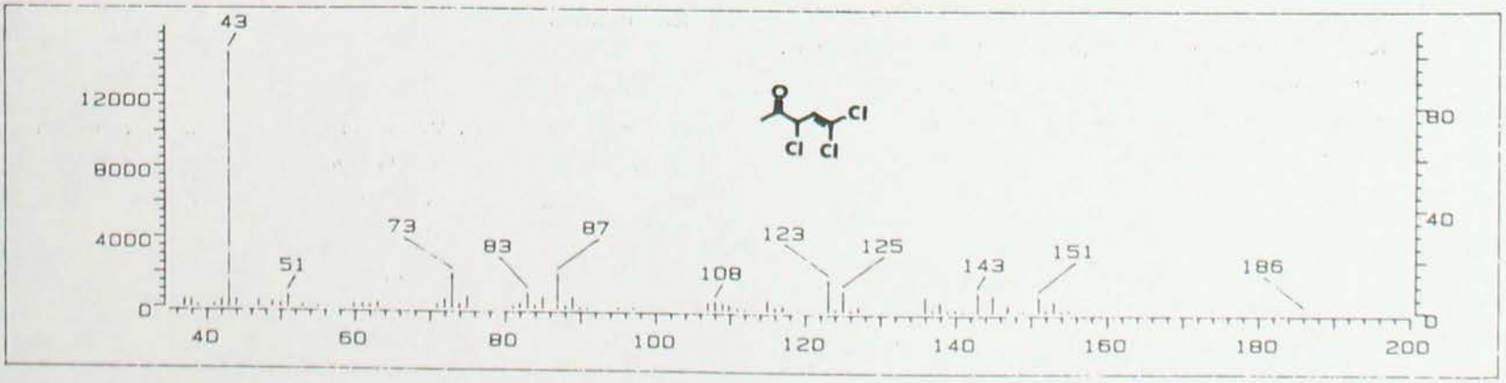

Figure 4

Electron impact mass spectum of 3,5,5-trichloropent-4-en-2-one.

THE KINETICS OF SULPHONATION REACTIONS ON NORWEGIAN SPRUCE*

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ABSTRACT

This study describes the kinetics of sulphonation at short reaction times (15 seconds to 15 minutes). The kinetics were studied at different temperatures, different sodium sulphite concentrations and different pH levels on wood meal in a specially designed reactor.

The results show that under normal conditions (2-4 % Na_2SO_3 charge, pH 8-11), about 75 % of the sulphonation achieved within 15 minutes has already taken place within 1 minute.

As expected, an increase in temperature and an increase in sodium sulphite concentration give a higher initial reaction rate.

The mechanism of the influence of pH at different temperatures and at different sodium sulphite concentrations in the alkaline region is at present not clear.

KEYWORDS: Sulphonation, kinetics, chemimechanical pulping.

INTRODUCTION

Important pulp and paper properties such as shives content, particle size distribution, handsheet tensile strength, dewatering capacity and resin content can be partly attributed to the degree of sulphonation of CTMP (1-5). Commercial CTMP mills now in operation in Sweden and other countries use low sulphite charges in the alkaline area and short preheating time. CTMP is in this paper defined as a pulp with a yield of about 95 per cent. This type of CTMP is mostly used in products such as carton board, fluff, tissue and to some extent in different printing grades.

Many studies on the sulphonation of wood have been reported earlier (6-10), but most of these works are devoted to the neutral and acidic regions. In addition, they evaluate only the longer reaction time region, i.e. from about 10 minutes to 3 days. This means that the information from these studies are not adequate for the control and optimization of the CTMP process now industrially used.

To be able to control this process from the kinetical point of view, an understanding of the sulphonation reactions at very short times is necessary. For this purpose cooking equipment was especially designed to permit the study of reaction times as short as 15 seconds under pressurized conditions.

EXPERIMENTAL

Preparation of wood meal

Fresh logs of Norwegian spruce (Picea abies) from the neighbourhood of Stockholm were debarked and the sapwood was separated from the heartwood. After chipping by hand, the chips were disintegrated to wood meal in a Wiley mill to a size that passed a 40 mesh screen. The wood meal was stored dry at 4°C. In this study wood meal from sapwood only has been used.

Preparation of cooking chemicals

The sulphite liquor was prepared from solid sodium disulphite of analytical grade and the different pH-levels were adjusted with sodium hydroxide. The pH-value and sulphite concentration were measured before and after each cooking trial. The pH-measurements were carried out at room temperature. Cooking liquors with pH 8.0, 9.5 and 11.0 have been used the sulphite concentrations of 0.02, 0.08 and 0.16 mol/l a each pH-level.

Cooking equipment

The cooking equipment used in these trials is designed in order to permit the study of the sulphonation reactions of wood at a period between 15 seconds and 15 minutes, in accordance with the sulphonation time applied in a CTMP manufacturing process.

The scheme of the reactor (cooking equipment) is outlined in Figure 1. The reactor consists of a double-walled pressurized vessel with a stirring device attached to it. The cooking liquor is placed in the vessel and is heated by ethylene glycol circulated between the two walls of the vessel. 30 g of wood meal is mixed with 200 ml deionized water and placed in the inner cylinder the upper end which is connected to a tube pressurized with nitrogen gas.

The wood meal suspension is shot into the preheated cooking liquor by opening the lower valve of the tube. Samples are extracted at various times by opening the valve at the bottom of the reactor. The sulphonation reaction in the sample was slowed down by collecting it in a bucket filled with ice prepared from deionized water.

Determination of sulphur content

The sulphonated samples were thoroughly washed with deionized water by means of a displacement washer for a period of 12 hours at room temperature. The amount of sulphur bonded to the wood was then measured by the Schöniger method and ion chromatography (11).

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* Conditions corresponding to the CTMP-processes in Scandinavia.

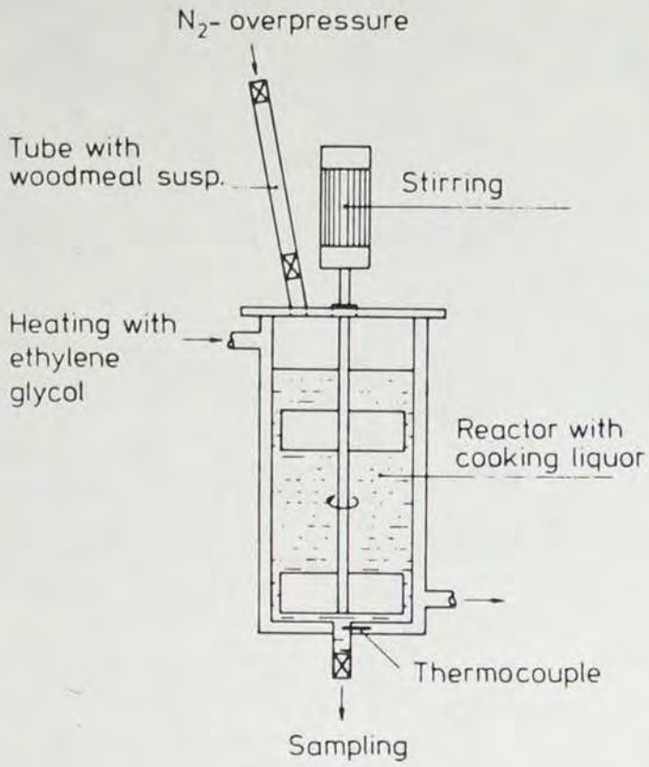

Figure 1. Reaction vessel designed for sulphonation studies during short reaction times under pressurized conditions.

RESULTS AND DISCUSSION

Sulphonation kinetics

A typical relationship between the degree of sulphonation (sulphur content) versus time is shown in figure 2 for samples treated with 0.08 mol/l Na_2SO_3 at 130°C and 15 minutes which corresponds to the process conditions used by most of the CTMP-producers of to-day. From a process point of view, it is interesting to observe that about 75 % of the sulphonation achieved in 15 minutes is already achieved in 1 minute.

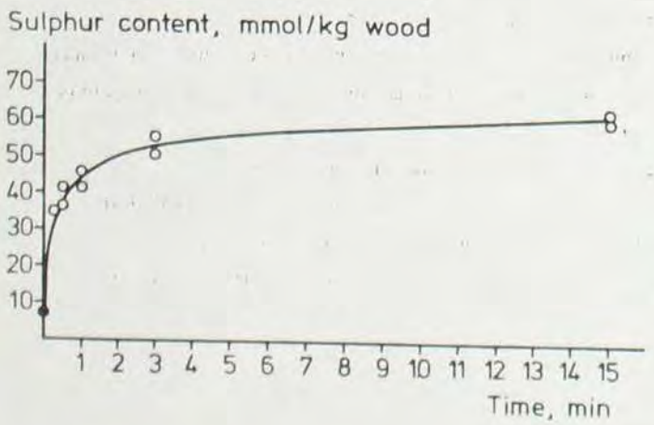

Figure 2. Degree of sulphonation as a function of time at a sulphite concentration of 0.08 moles/1, pH 9.5 and a temperature of 130°C.

In figure 3, the sulphur content is plotted against the logarithm of time. The results show that the reaction is not terminated at 15 minutes (though from a CTMP process point of view the sulphonation is very slow) but follows an exponential law within the time interval measured.

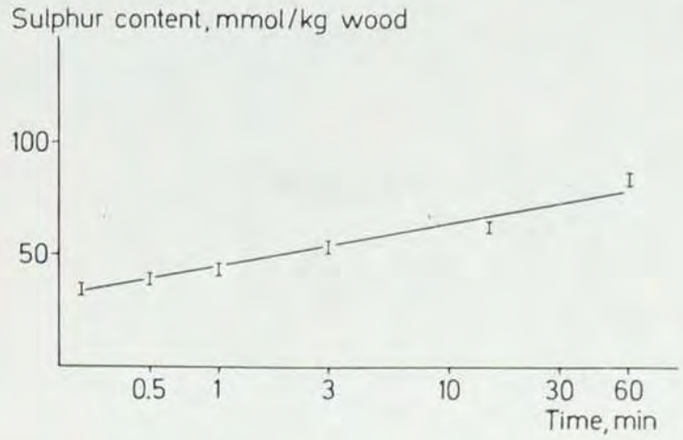

Figure 3. Degree of sulphonation as a function of log time at a sulphite concentration of 0.08 moles/1, pH 9.5 and a temperature of 130°C.

Effect of temperature

The effect of temperature (70 and 130°C) on the degree of sulphonation is shown in figure 4. The degree of sulphonation is increased two fold when the sulphonation is allowed to take place at 130°C instead of at 70°C. It is obvious that the reaction within the time range studied is thermally activated in accordance with the Arrhenius law, this statement is based upon 36 temperature curves like those in figure 4.

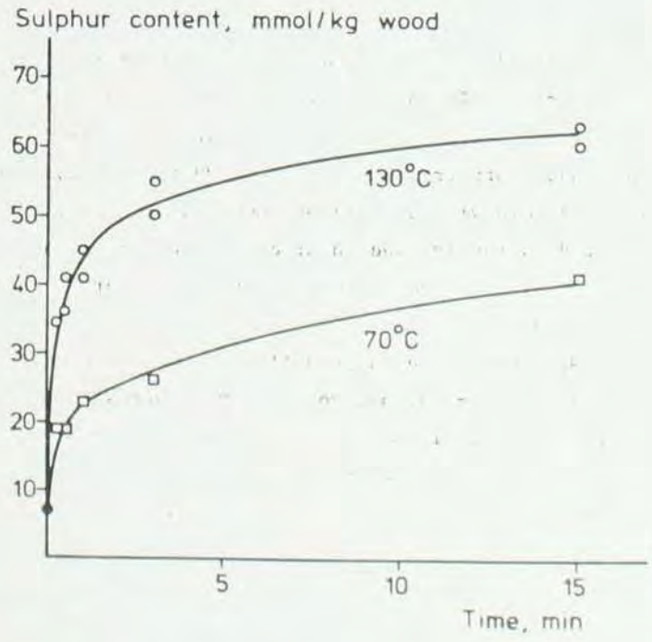

Figure 4. Degree of sulphonation as a funktion time at a sulphite concentration of 0.08 moles/1, pH 9.5, at temperatures of 70 and 130°C.

Effect of sulphite concentration

The effect of sulphite concentration on the sulphite process content is illustrated in figure 5. It is evident that the sulphite concentration has a significant influen- on the rate of the sulphonation reactions even at short eaction times. In terms of CTMP process conditions, a change in Na_2SO_3 charge from 2 % (0.08 mol/l initially to 4 % (0.16 mol/l) will increase the sulphur content by 40 %. Furthermore the results indicate that an increase in concentration from 0.02 mol/l to 0.08 mol/l gives relatively greater increase in sulphur content in the wood than when the concentration is increased from 0.08 mol/l to 0.16 mol/l, taking into account the fact that the concentration increase in the first case us four times and in the second case two times and that the sulphur content in the wood originally is 7 mmoles/kg wood.

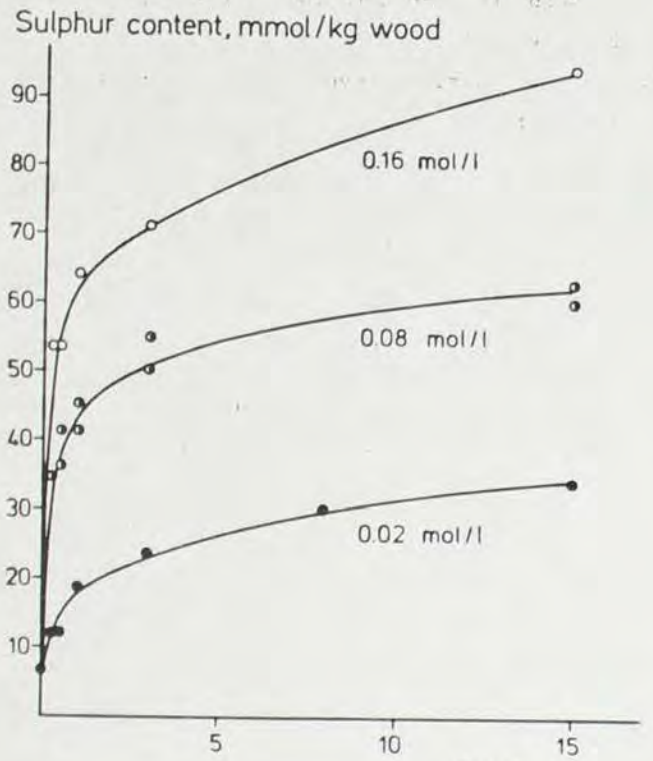

Figure 5. Degree of sulphonation as a function of time at 130°C, pH 9.5, at three sulphite concentration levels: 0.02, 0.08 and 0.16 (moles/l).

Effect of pH

The effects of pH on the rate of sulphonation at 130°C and a sulphite concentration of 0.08 moles/l are shown in Figure 6. There seems to be no significant difference between the rates obtained at pH 9.5 and 11.0, but the rate of sulphonation at pH 0.8 is significantly higher.

The pH dependence of sulphonation rate at longer reaction times has earlier been studied by Wennerås (12), observed that the rate of sulphonation is higher at pH ≥7 than the rate measured at a pH lower than 7. At pH 7 or higher (up to 9.5) no difference in sulphonation rate was observed, but the observations were made at much longer times than in the present case.

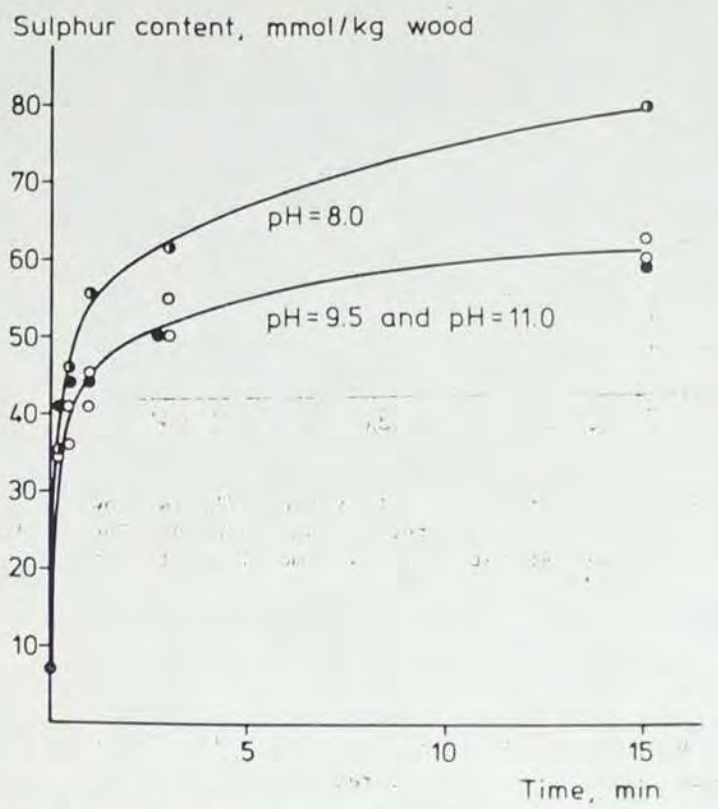

Figure 6. Degree of sulphonation as a function of time at 130°, 0.08 moles/l sodium sulphite and three pH levels; 8.0, 9.5 and 11.0.

Diffusion versus reaction kinetics

Since in this investigation, the kinetics of the reactions at short times are of primary concern it is essential to know whether there is any effect of diffusion on the reaction kinetics. In order to elucidate this, we have determined the activation energies at different degrees of sulphonation by using an Arrhenius plot. The results are shown in figure 7. It is evident that the slopes of ln (1/t) versus (1/T), where t is time to a certain degree of sulphonation and T is absolute temperature, are identical for all cases studied except for the case where the degree of sulphonation is 20 mmoles/kg wood. The activation energy obtained at 30 mmoles/kg wood or higher is 60 ± 4 kJ/mol whereas at 20 mmol/kg wood the activation energy is about 20 kJ/mol.

This indicates that the mechanism controlling the sulphonation is different when the degree of sulphonation is very low. The kinetics controlling the initial phase of the process may be due to diffusion rather than to the chemical reactions.

Time-temperature shift

For amorphous polymeric materials, the rate constant at one temperature may be related to the rate constant at other temperatures by simply shifting the time scale (13). From a master curve, the rate constant at very long times or at very short times can be approximated conveniently by the rate constant measured at any given temperature on

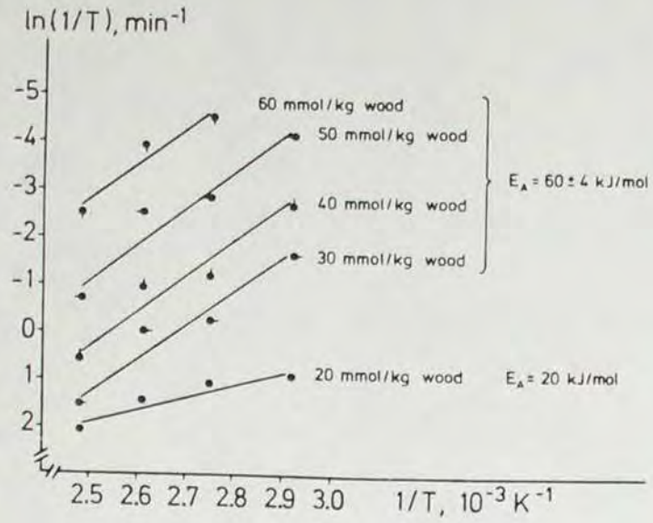

Figure 7. A plot of ln (1/t) versus 1/T, is shown for different degrees of sulphonation. The sulphite concentration is 0.08 mol/1 and the initial pH 9.5.

time scale. This method is in fact derived from the Arrhenius' law for chemical reactions.

Analoguously the time-temperature equivalence principle may be applied to the kinetics of wood sulphonation. The time-temperature shift factor a_T can be approximated by the following semi-empirical equation

$$\log a_T = (E_A/2.303\ R) \cdot (1/T - 1/T_o)$$

where E_A is the activation energy and R is the gas constant. T is a reaction temperature at time t and T_o is the reference temperature at time t_o, both given in degrees Kelvin.

Figure 8 shows the relation between the degree of sulphonation and logarithm of the reduced time a_T/t. The master curve is constructed by shifting the curves measured at different temperatures horizontally along the time axis until the curves fit smoothly over one another using 130°C as the reference temperature. Master curves are cpmstructed for sulphite concentrations of 0.16, 0.08 and 0.02 mol/1 Na_2SO_3 at an initial pH of 9.5.

It can be seen that the curves fit smoothly and thus the time-temperature equivalence is applicable for the sulphonation reactions. The activation energy evaluated using the above equation is as expected identical with the one evaluated in figure 7, i.e. the activation energy for the process is 60 ± 4 kJ/mol.

FINAL COMMENTS

As shown in figure 6, the rate of sulphonation is higher at a sulphite concentration of 0.08 and a temperature of 130°C when the initial pH is 8.0 than when it is at 9.5 or 11.0. Earlier investigations have shown that the rate during the first hour of sulphonation at pH 6-10 is identical and that the rate is lower in the pH-range 3-6 (12). However over longer sulphonation times, cooking in lower pH range gives a higher degree of sulphonation (7, 9). It should be pointed out that in most of these studies only the initial pH of the cooking liquor is mentioned. It is well documented that when the initial pH of the cooking liquor is in the alkaline region the pH will be reduced during cooking and more so when the cooking time is extended.

It seems that the pH of the cooking liquor has a significant effect on the resulting degree of sulphonation.

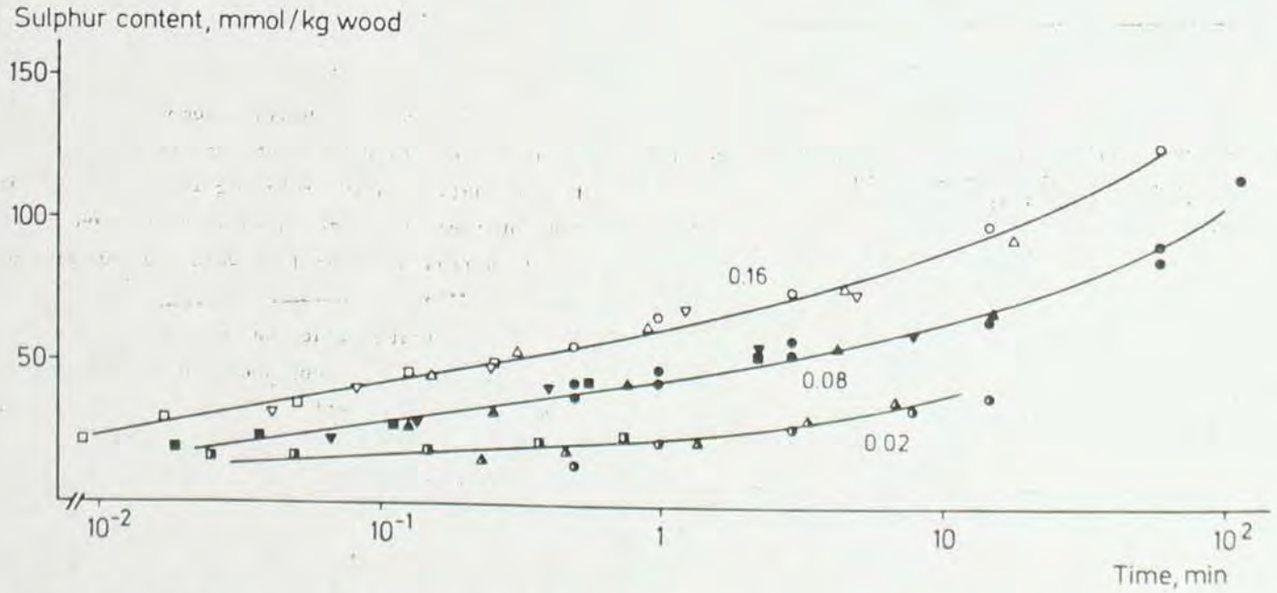

Figure 8. Master curves for the degree of sulphonation versus reduced time a_T/t for three sulphite concentrations. Symbols indicates temperature and sulphite concentration:

		70°C	90°C	110°C	130°C
0.16	moles/1	□	▽	△	○
0.08	"	■	▼	▲	●
0.02	"	◨	◬	◭	◑

Furthermore it is well known that the temperature and ionic strength affect the hydroxyl ion concentration in the liquor and the equiblibrium between sulphite and hydrogen sulphite ions, which would in turn affect the sulphonation rate (15). The degree of ionization of the phenolic and sulphite groups in lignin as a function of pH, ionic strength and temperature might also be of importance.

In order to achieve a complete understanding of the sulphonation reactions with wood, a further clarification of the effects of pH, ionic strength and temperature dependence of these three parameters is necessary. The changes in diffusion rates may also be of interest.

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ULTRA-HIGH YIELD PULPS FROM HARDWOOD

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INTRODUCTION

To give good chemimechanical pulps (CMP), high-density hardwood chips need an alkali treatment prior to refining. For adequate softening, without loosing to much in yield, about 3.5 to 4.0 wt.-% sodium hydroxide is preferred. Unfortunately, strongly colored chromophores are formed, resulting in low-brightness pulps.

During recent years, much effort has been directed to find pretreatment conditions which decrease the formation of chromophores. In this research, hydrogen peroxide has been used because it reduces chromophor production and is not harmful to the environment.

Hydrogen peroxide is known to readily decompose in alkaline solution at pH-values near its pKa-value. Penetration of a peroxide containing liquor into the chips is thereby substantially decreased. To overcome this problem, the available surface area of the chips has to be increased by using wafers, matchsticks or destructed chips in combination with silicate stabilizers.

Earlier results obtained in our department have shown that for maximum pulp brightness gained with a certain amount of peroxide, the peroxide charge has to be split between the pretreatment stage and a conventional pulp bleaching stage.

The work presented here has been concentrated on finding a method for production of CMP from European birch (Betula verrucosa). The aim was to use sodium hydroxide and hydrogen peroxide for the pretreatment and, after a single-stage refining, reach a high initial pulp brightness at a total yield above 90%.

By using a two-stage impregnation method for the pretreatment with NaOH and H_2O_2, the risk of peroxide decomposition should be minimized and, therefore, silicate stabilizers would not be needed. Normal-sized chips were to be treated in conventional equipment for chemimechanical pulping.

EXPERIMENTAL

The pretreatment of chips with sodium hydroxide and hydrogen peroxide respectivley, was carried out sequentially in two separate impregnation stages (fig. 1). Two different methods of performing the first-stage alkali impregnation were elucidated: cold impregnation and screw-press impregnation. Using cold impregnation, the atmospherically steamed chips were directly soaked in NaOH-solution for 10 min. at 20 °C. In the screw-press impregnation, the steamed chips were compressed in a screw-press, type Impressafiner, before being fed to the soaking bin. The chips were then soaked for 3 min. at 20 °C. The liquor uptake in the cold impregnation was about 600 L/ton, resulting in an average alkali charge of 3.8 wt.-%. For the screw-press impregnation, the corresponding values were 1100 L/ton and 4.8 wt.-%, respectively.

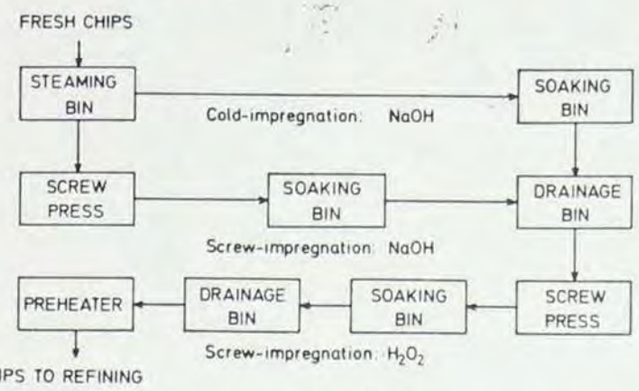

Fig. 1. Pretreatment flowsheet for the two different two-stage impregnation methods used in pilot-plant trials.

In the following treatment, applied to both methods of impregnation, the chips were first drained for 15 min., and then in a second impregnation stage fed through a screw-press and expanded in hydrogen peroxide solution. After soaking for 3 min. at 20 °C, the chips were drained for 3 min. The hydrogen peroxide charge was set by the concentration of the impregnating liquor. The preheating was carried out for 15 min. at 85 °C, followed by refining to different freeness values in a 36" double-disc refiner with atmospheric discharge. The pulp consistency was about 20 %.

RESULTS AND DISCUSSION

By using a screw-press in the second impregnation stage, excess alkali was removed from the chips and the pH of the chips before peroxide addition could be decreased below 11.5. Therefore, the peroxide charge could be chosen independent of the alkali charge, without risking penetration obstruction caused by peroxide decomposition.

The effect of the second stage screw-press treatment on pulp brightness after refining can be seen from fig. 2. For pulps A and D, the second-stage impregnation was omitted and the chips were brought to the preheater directly after the alkali charging and subsequent drainage. The other pulps were impregnated with water or hydrogen peroxide solution in the second stage. For pulp B, in which case reaction products such as soluble chromophores have been squeezed out (25 kg/ton COD on o.d. wood) and replaced by water, the initial brightness gain compared to pulp A was 4 units. By adding peroxide to a consumption of 0.5 wt.-% instead of water (pulp C), a further gain of 5 brightness units could be achieved.

Fig. 2. The effect of the first and second impregnation stage to pulp brightness before and after bleaching. NaOH-charges and H_2O_2-consumptions are given in the histogram.

To reach a very high initial pulp brightness, the chemical charges had to be optimized. With a charge of 2.5 wt.-% NaOH and a consumption of 3.2 wt.-% H_2O_2, 70% ISO was obtained, but at the expence of strength properties which were somewhat lowered.

The maximum brightness gained after a subsequent bleaching with 3 wt.-% H_2O_2 can also be seen from the figure. When compared to a single-stage impregnation with a mixture of NaOH and H_2O_2 and at a given total charge of hydrogen peroxide, the impregnation must be done in two stages to reach a final, maximum brightness.

By this method it was also possible to reach very high brightness values. For the earlier mentioned pulp with an initial brightness of 70 % ISO, a subsequent bleaching with 4 wt.-% of peroxide resulted in a final brightness of 85 % ISO, at a total pulp yield over 90%.

To increase pulp strength properties without risking a too high pH of the chips before the peroxide addition and, consequently, peroxide decomposition, some additional alkali was added through the refiner eye. No decreased energy requirement was found due to the higher, total alkali charge. Sodium hydroxide was twice as effective as sodium carbonate with regard to the development of strength properties. By adding 1 wt.-% NaOH or 2 wt.-% Na_2CO_3, tensile index and z-strength could be increased by 25 %, i.e. the same gain as if all the alkali had been added during impregnation. If the refiner charge was lower than 1 wt.-% NaOH, the bleachability was not affected.

Impregnation	Cold		Screw	
NaOH, wt.-%	3.8		4.8	
H_2O_2, wt.-%	0.5		0.5	
Freeness, mL CSF	100	350	100	350
Total energi, kWh/ton	1030+	600+	1320++	700++
Tensile index, kNm/kg	26	14	28	14
Scatt. coeff. m^2/kg	45	39	43	38
Fine fraction, P200, %	25	20	26	20

\+ Including 30 kWh/ton screw-press energy.
++ Including 60 + 30 kWh/ton screw-press energy.

Table 1. Effect of the two different first-stage impregnation methods on unscreened pulp characteristics and energy requirement.

As shown in table 1 by comparing the first-stage impregnation methods adopted, the screw-press impregnated chips consumed up to 30 % more energy to a certain freeness value or tensile index than the cold-impregnated chips did. According to the literature, undersized chips are known to consume less energy to a certain freeness value compared to normal or oversized chips. Furthermore, when the alkali charge is increased in the present interval, the energy consumption is lowered and the tensile index is increased compared at constant freeness. Since the chips which have been screw-pressed twice have a smaller size and have been subjected to a higher alkali charge, the energy requirement expected for these chips should thus be lower than that for the cold-impregnated chips. The opposite result obtained indicates that the way mechanical forces are applied to the chips is important and differs between the impregnation methods. One explanation of this result could be that when performing the first-stage impregnation by means of the screw-press, the chips are not chemically softened before the mechanical destruction. This might initiate an unfavorable fiber-fiber separation which requires increased refining energy to yield a low pulp freeness and a given tensile strength.

A Mathematical Model for the Ultrafiltration of Pulp Mill Effluent Liquors

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Abstract

A model of the batch ultrafiltration operations of diafiltration and concentration has been developed. The model accurately correlates available literature data and has been used to predict the size and operation of some possible batch ultrafiltration operations of pulp mill effluents.

Keywords: Ultrafiltration, kraft lignin, lignin sulphonate

Introduction

Ultrafiltration and similar membrane processes are energy efficient operations which are finding widening applications in the concentration and purification of macromolecular nd colloidal solutions. In the pulp and paper industry, the principal applications appear to be: 1] concentration of kraft bleach plant effluents (KBE) to reduce evaporator load, 2] purification and concentration lignin sulphonates from spent sulphite liquors (SSL), 3] production of high molecular weight kraft lignin (HMKL) from weak or strong kraft black liquor (KBL), and reducing color, BOD, and COD from eftluent streams (1).

At relatively low pressures, 134 kPa and above, the flux rate through the membrane is independent of the trans-membrane pressure. This phenomena has been attributed to the existance of a gel layer with a resistance to flow similar to a packed bed of solids (2). A semi-empirical relationship, shown in Equation 1, describes the concentration dependence of the flux rate. Work in this laboratory has determined that the empirical constant C_g for kraft lignins and lignin sulphonates is 320 g/l and 260 g/l, respectively. The mass transfer coefficient is best determined from the Deissler correlation (3) and is typically about 50 $L/m^2/hr$ for plate and frame modules and about 150 for tubular units.

$$J = k_m \ln C_g/C_B \quad (1)$$

The rejection coefficient is an experimentally obtained parameter which describes the amount of solute which is retained by the membrane as is shown in Equation (2). For multi-component solutions, a rejection coefficient can be determined for each solute or for groups of solutes. In the ultrafiltration of pulp mill liquors, rejection coefficients have been defined in terms of total solids, total lignin, each lignin species, BOD, COD, sugars and organic acids, and inorganic salts. The rejection coefficient is primarily a function of the membrane pore radii and the solute size, but operating conditions such as temperature, pH, and trans-membrane pressure have been shown to play an important role (4).

$$R = 1 - C_p/C_B \quad (2)$$

Model Description

Two major ultrafiltration operations are batch concentration and diafiltration, a washing procedure which removes small solutes from large solutes. These operations are inherently non-steady state since the solute concentration and solution volume constantly change with time.

These operations are typically performed in a variety of apparatus which all have a block diagram similar to Figure 1. The overall material balance of this system is shown in Equation 3a in differential form and Equation 3b in integrated form with the assumption that in any small time interval, Δt, the flux rate is constant. A material balance can be written for each solute in the system as shown in Equation 4.

$$\frac{dV}{dt} = Q - JA \quad (3a)$$

$$V(t) = V(t-1) + (Q-JA)\ \Delta t \quad (3b)$$

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$$\frac{dC_B V}{dt} = C_B \frac{dV}{At} + V \frac{dC_B}{dt} = JA\ (1-R)C_B \qquad (4)$$

Equation 3a can be substituted into Equation 4, and integrated again assuming that the flux rate within each differential time step Δt is constant. This operation yields Equation 5.

$$C(t) = C(t-1)\ \exp\ [(\frac{JAR}{V} - Q)\ \Delta t] \qquad (5)$$

The assumption of constant flux rate within a time step is usually valid if the concentration change within that time step is small.

In the computer program, all initial values and calculational parameters are entered as well as limiting conditions. Initial values are the solution volume, solute concentrations, and solvent addition rate. Calculational parameters are the membrane area, the mass transfer coefficient, C_g, the rejection coefficients, and the time step size. The program iterates on Equations 5, 1, and 3b at each time step until two successive calculations of C(t) are within .1% of each other. The program then calculates the concentration of each material in the permeate using Equation 2. The time since the beginning of the run, the remaining solution volume, the flux rate, and retentate and permeate concentrations are written into a file at each time step. The program continues to run until one of the limiting conditions are obtained. Final values are specified for the maximum run time, maximum solute concentration, and the maximum volume reduction.

Model Applications

The model has been successfully used to simulate data available in the literature for batch concentration, diafiltration, and mixed mode operation. A previous publication (5) demonstrated the ability to model KBL operations. The ability to simulate SSL batch concentration is shown in Figure 2 using the data provided by Bottino (6). Some initial conditions and rejection coefficient had to be assumed to obtain an acceptable fit to the data.

The model has been applied to the batch concentration of a kraft bleach plant effluent. A base case was assumed at 416,666 L of effluent at a lignin concentration of 15 gL^{-1} and 30 gL^{-1} of non-lignin solids with rejection coefficient of 0.9 and 0.0 respectively. A tubular ultrafilter unit with 1200 m^2 of membrane with a mass transfer coefficient of 150 L/m^2hr will concentrate this solution to 40,000 L and lignin concentration of 140 g/L in one hour.

Several schemes to produce a concentrated purified lignin sulphonate from SSL have been simulated. The initial volume of SSL was assumed to be 100,000 L at a lignin concentration of 60 gm/L and non-lignin concentration of 40 gm/L with rejection coefficients of 0.9 and 0.0 respectively. A tubular UF unit with 500 m^2 of area and k_m = 150 L/m^2hr was assumed. The results of these simulations are shown in Figure 3 and demonstrate that the highest purity and lowest volume can be obtained by a flow management which alternates concentration and diafiltration, with the first and last steps being batch concentration. These results suggest that the best fluid management to maximize purity and minimize volume may be obtained with continuous addition of solvent at a flow rate less that that of the permeate.

The production of one ton per hour of HMKL from weak black liquor has also been examined and is presented in Figure 4. Different membrane areas have been examined to increase the purity of the HMKL. The increase in membrane area from 60 m^2 to 125 m^2 produces a higher purity, lower volume product. Similar results are not exhibited when the membrane area is increased from 125 m^2 to 200 m^2, indicating an optimal area may exist.

Notation

A	membrane area	m^2
C(t)	concentration at time step t	g/l
C(t-1)	concentration at time step t-1	g/l
C_B	concentration in bulk solution	g/l
C_g	concentration of gel layer	g/l
C_p	concentration of permeate	g/l
J	flux rate	$l/m^2/hr$
k_m	mass transfer coefficient	$l/m^2/hr$
Q	solvent addition rate	l/hr
R	rejection coefficient	--
V	solution volume	l
Δt	time step size	hr

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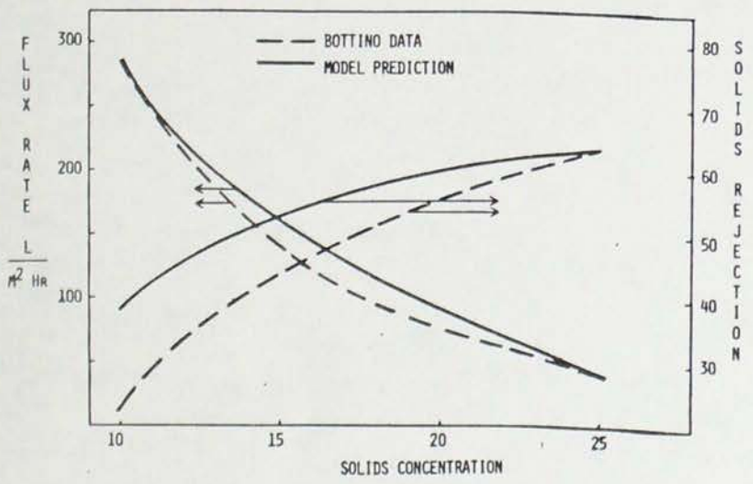

Figure 2. Model Fit to Batch Concentration Data of Bottino. Initial Values: 10,000 L of 60% lignin SSL at 100 g/l total solids on a .69 m^2 of membrane with a k_m=180 $L/m^2/hr$. R(lignin)=.75 R(non-lignin solids)=0.0.

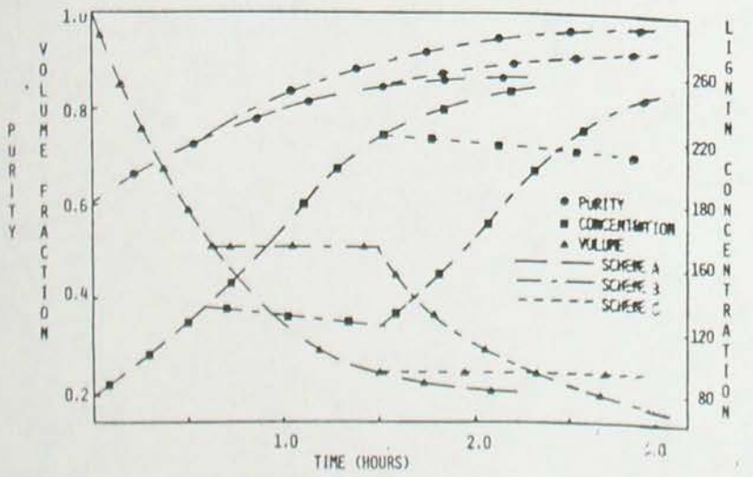

Figure 3. Model Fit of SSL production. Scheme A- Batch Concentration. Scheme B- Batch concentration to 1/2 initial volume followed by diafiltration to 90% purity then concentrate.

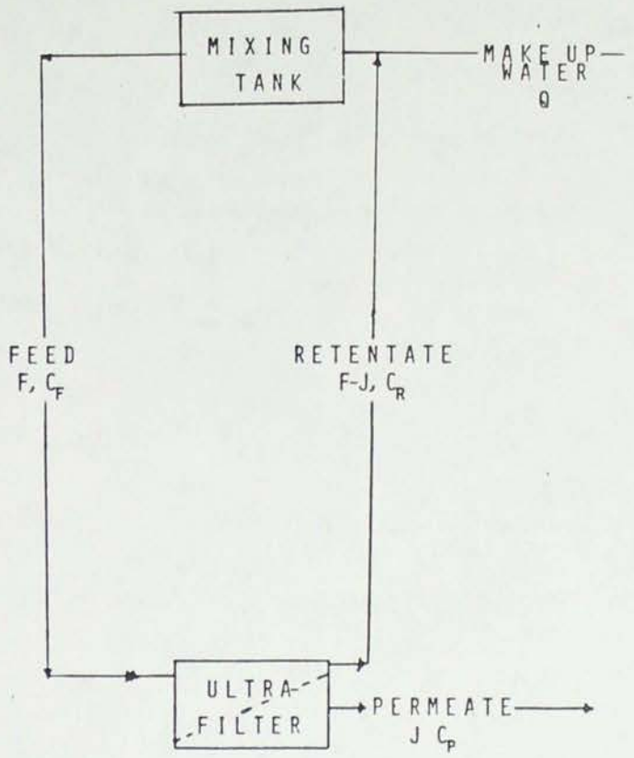

Figure 1. Typical Block Diagram of Ultrafiltration Batch Operation.

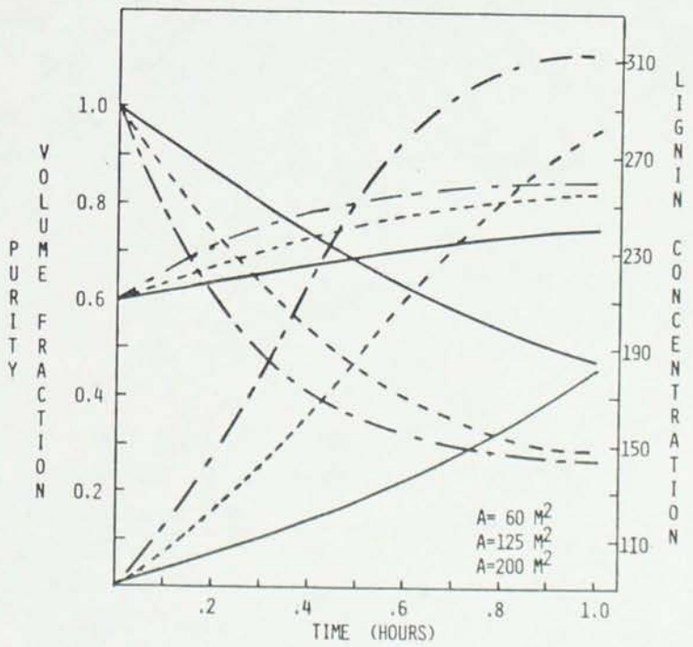

Figure 4. Production of HMKL by Batch Concentration. Effect of membrane area.

THE CATALYTIC HYDROGENOLYSIS OF WOOD AND ISOLATED LIGNINS

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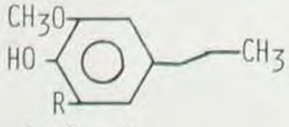
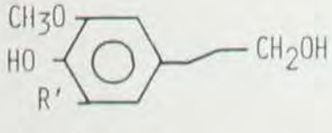
Lignin, a polypropylphenolic bipolymer is an abundant resource whose potential as a source of aromatic (phenolic) chemicals has received only minimum attention. It would appear inevitable that, in time, biomass will replace fossil hydrocarbons as the primary source of carbon for the organic-based chemistry industry. It is therefore imperative that methods be found whereby the lignin raw material, either as a secondary product of the pulping industry or other biomass conversion processes, can be converted into compounds which can be used directly or for which new applications can be found or which may serve as starting material for further synthesis.

The objective of this research was to initiate a study to determine the appropriate reaction conditions whereby a degree of selective degradation of the lignin may be achieved to produce a variety of products. Catalytic hydrogenolysis in a dioxane-water medium was the degradation technique used. Chloroform extraction of the resulting organo-aqueous phase separated the lignin products which were analyzed by gas chromatography and mass spectrometry. Reaction parameters studied included: lignin source (native poplar wood or an isolated lignin), amount of catalyst, effect of agitation and the effect of the addition of alkali both with and without added anthraquinone.

Under previously published (1) "standard" conditions: [aspen wood meal (10 g)(containing ~ 1.8 g lignin); dioxane-water (1:1)(150 mL); Rh-C (5%) (1.0 g); H_2 (initial pressure 500 psi, heated in a rocking stainless steel bomb for 5 hours] the major monomeric products were I → IV.



I R = H
II R = OCH_3

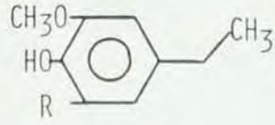


III R' = H
IV R' = OCH_3

They were isolated by $CHCl_3$ extraction of the filtrate and by analysis shown to have yields of 5.4, 14.0, 4.3 and 18.0% respectively of the chloroform-dioxane extract and which had been shown previously to consist of essentially only lignin degradation products.

The following studies were monitored on the basis of the yields of these four compounds.

1. Similar treatment of isolated lignins (Iotech, Stake and dioxane lignin) led to markedly reduced total yields (~ 12% vs ~ 40%) indicating that the isolation treatment had caused significant structural changes.
2. The degree of agitation was important: decreased agitation led to an increased abundance of the aryl-substituted propanes (I and II) and a corresponding decreased abundance of the aryl-substituted propanols (III and IV).
3. Consecutive five hour periods of either agitation followed by no agitation or visa versa showed that the more highly reduced products (I and II) did not arise by the initial production and subsequent reduction of the alcohols (III and IV).
4. The catalyst was required but the ratio to wood was important: the amount of the chloroform-dioxane soluble fraction decreased as this ratio increased; the total yields of compounds I → IV maximized at a wood-catalyst ratio of 10:1 and the relative abundance of the propanols (III and IV) over the propane derivatives (I and II) increased as the ratio increased.
5. Studies under initially alkaline conditions (addition of NaOH (4.5 g)/10 g wood meal in 150 mL solvent) gave rise primarily to the ethyl derivatives (V and VI).



V R = H
VI R = OCH_3

The following experiments were monitored on the basis of the abundance of compounds V → VI.

i) As before isolated lignins gave reduced yields over wood itself.

ii) Compounds V and VI were also obtained without added hydrogen but the yields were reduced.

iii) Subsequent treatment of the black liquor from an alkali-anthraquinone pulping (170°C) in the presence of Rh-C (5%) catalyst, without added hydrogen, at 195°C gave rise to monomeric lignin degradation products.

Mechanisms are proposed for the production and relative abundance of the lignin derivatives.

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NITROBENZENE OXIDATION OF GROUND WOOD LIGNIN

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KEYWORDS: GP bleaching, Alkali darkening, Reflectance, Nitrobenzene oxidation, Vanillin yield.

1. INTRODUCTION

Though it is generally believed that some mechanochemical conversions of lignin molecules must have occurred during ground wood pulping, there is almost no information about what kinds of conversion occur and how they participate in pulp bleaching. In the present report, therefore, changes in vanillin yield on oxidation of GP with nitrobenzene were compared as an indicator to find out the difference between GP lignin and wood lignin. Changes in reflectance of a sheet of treated GP were also compared by using $\Delta(-\log R_\infty)$ to find out the cause for alkali darkening in GP bleaching.

2. RESULTS AND DISCUSSION

2.1. An origin of alkali darkening in the GP bleaching.

Though consumption of H_2O_2 in GP bleaching increased with running up the temperature, brightness of the resultant pulps leveled off as shown in fig.1. After the treatment of GP with H_2O_2, $NaBH_4$, and NaOH, reflectance R_∞ were measured, and $-\log R_\infty$ and the difference before and after treatment, i.e. $\Delta(-\log R_\infty)$ were shown in fig.2(A) and (B), respectively. When GP was treated with NaOH, $\Delta(-\log R_\infty)$: (d-a) afforded a predominant peak near 420 nm indicating that the treatment produced a chromophore having λ_{max} near here. Degradation of chromophores by GP bleaching appeared as the negative curves of (b-a) and (c-a), of which a slight shoulder near 420 nm seemed to be caused by co-existing NaOH. When GP(a) was treated with enough amounts of NaOH(d'), $\Delta(-\log R_\infty)$ of (d'-a) increased as high as 0.135, similarly to $\Delta(-\log R_\infty)$ of (d'-b) as shown in fig.3(A). When GP was bleached with $NaBH_4$, consecuting treatment with NaOH did not produce the peak near 420 nm as shown in fig.3(B). Therefore, the origin of the chromophore was stable to alkaline H_2O_2 but easily reducible with $NaBH_4$ and might be one of the significant causes of alkali darkening. This is also the case for a sheet of TMP. Production of the similar chromophore with λ_{max} near 420 nm by alkaline treatment of wood section was reported by C. Heitner et al. It is suggested, therefore, that an origin of the chromophore is common to lignin in GP, TMP, as well as wood section.

2.2. Nitrobenzene oxidation of GP lignin.

Taking into considerration that formation or degradation of chromophores in GP lignin might give considerable influences on nitrobenzene oxidation, vanillin yields were determined before and after the treatment. Fig.4 showed remarkable differences in the yield among treated samples of GP, TMP, and wood meal, in spite of very little difference among unterated ones. This suggested the significance of mechanochemical conversion of lignin occurred in GP production. Not much deviation of TMP lignin from wood meal lignin was also indicative from the point of view.

S. Hosoya et al. mentioned about importance of α-carbonyl group as a reaction site with H_2O_2, where Dakin-type splitting took place at either C_1-C_α or C_α-C_β depending on the nature of para-substituents as shown in fig.5. At least a part of the great decrease in vanillin yield after the H_2O_2 treatment might be caused by the type of splitting. However, treatment of GP with either $NaBH_4$ or NaOH also brought about remarkable decrease in vanillin yield. This might imply the presence of special atomic groups formed in GP lignin requiring more investigations.

To find out the relationships between chemical characteristics of these treatments and vanillin yield, treatment with H_2O_2 for 30, 60, and 90 min and consecutive treatment with either $NaBH_4$ or NaOH under certain conditions were followed by nitrobenzene oxidation. As shown in fig.6, gradual decrease in vanillin yield was observed. When treatment with $NaBH_4$ of 0.5% was followed by H_2O_2 treatment, an unusual increase in vanillin yield was found as shown in fig.7. However, this is not the case for the consecutive NaOH treatment. A partial reduction of carbonyl groups with $NaBH_4$, therefore, resulted in considerable stability of the product against H_2O_2. The order of decrease in vanillin yield due to single treatment was $H_2O_2 > NaOH > NaBH_4$ as shown in fig.4. However, any of double treatments lowered vanillin yield in comparison with single treatment of either H_2O_2 or $NaBH_4$ as shown in fig. 6 and 7.

G. Gellerstedt et al. reported that coniferyl aldehyde [I] and its methyl ether [II] were effectively destroyed with H_2O_2. Calibration curves for these compounds in terms of $-\log R_\infty$ were prepared by the use of phloroglucin-HCl reaction. As shown in table 1, coniferyl aldehyde structure was efficiently converted with either H_2O_2 or $NaBH_4$ but not with NaOH. However, the most of [II] but a few of [III], coniferyl alcohol methyl ether, were converted with H_2O_2 in homogeneous state under the conditions shown in table 2. Difference in vanillin yield between the two products was too small to account for the unusual increase shown in fig.7. At present, therefore, this would be better explained by the α-carbonyl structuer as mentioned above.

3. CONCLUSION

One of the major causes of alkali darkening in GP bleaching was shown to be the chromophore with λ_{max} near 420 nm. An origin of the chromophore seemed to be common to lignin in GP, TMP, as well as wood section. Broad and significant mechanochemical changes of lignin occurred during ground wood pulping were discussed from the view point of vanillin yield.

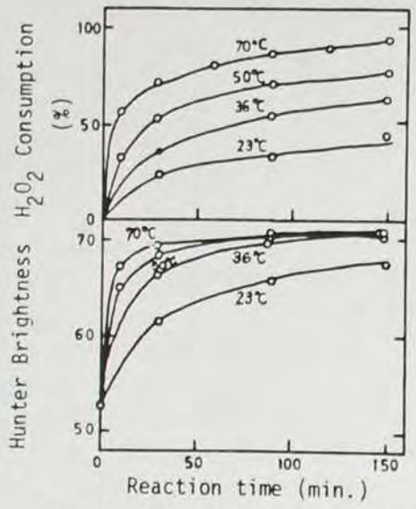
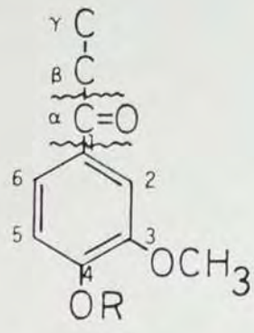


Fig. 1. Consumption of H_2O_2 by GP at different temperature and brightness of the resultant GP.



R = H or CH_3

Fig. 5

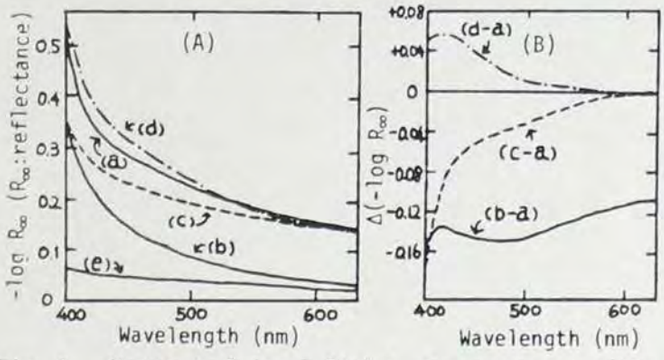


Fig. 2. Change in [-log R_∞](A) by the treatment of GP (a) with H_2O_2(b), $NaBH_4$(c), and NaOH(d), and the difference curve(B). (e): BKP.

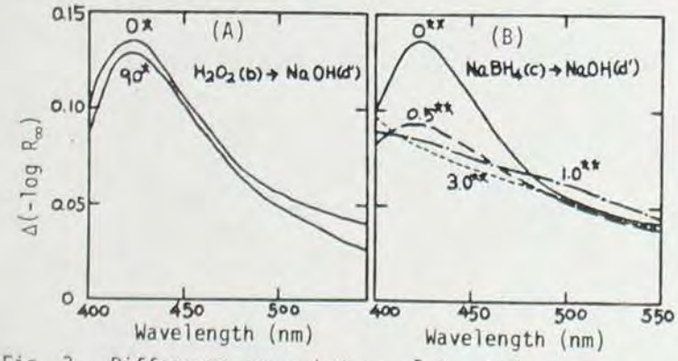


Fig. 3. Difference curve between [-log R_∞] after bleaching of GP with either H_2O_2(A), or $NaBH_4$(B) and that after the post-treatment of bleached GP with 20% NaOH. * Treatment time with H_2O_2 (min.). ** Added amount of $NaBH_4$(% to pulp).

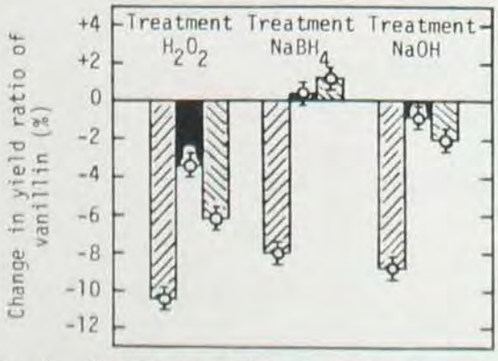


Fig. 4. Change in vanillin yield after the treatment of GP, TMP, and wood meal with H_2O_2, $NaBH_4$, and NaOH, respectively.
Notes: GP, TMP, wood meal.

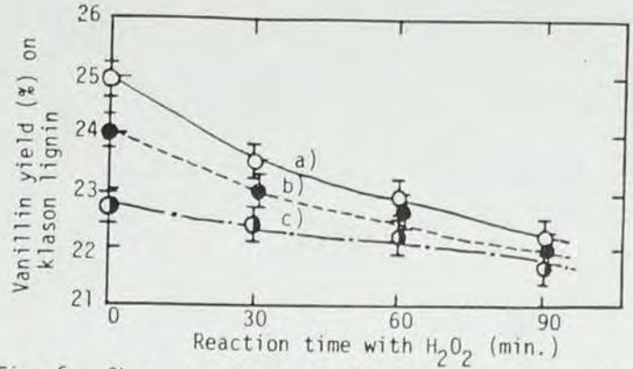


Fig. 6. Change in vanillin yield from treated and untreated GP.
Notes: a) Treatment with H_2O_2(-○-) for different time. b) Treatment(a) as a pre-treatment followed by treatment with 1% $NaBH_4$(-●-) for 60 min. c) Treatment(a) sa a pre-treatment followed by treatment with 2% NaOH(-◑-) at 70 °C for 90 min.

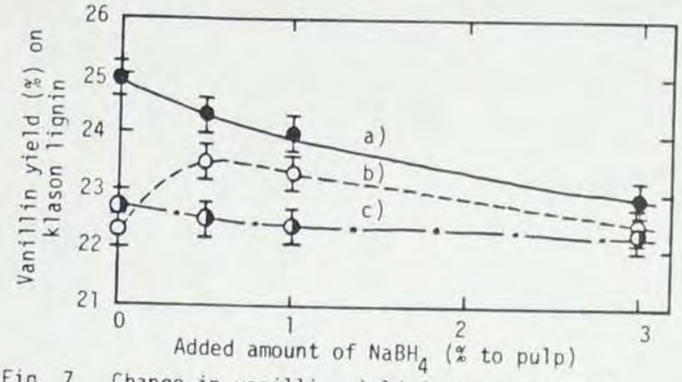


Fig. 7. Change in vanillin yield from treated and untreated GP.
Notes: a) Treatment with different amount of $NaBH_4$(-●-) for 60 min. b) Treatment(a) as a pre-treatment followed by treatment with 3% H_2O_2(-○-) at 60 °C for 90 min. c) Treatment(a) as a pre-treatment followed by treatment with 2% NaOH(-◑-) at 70 °C for 90 min.

Table 1. Change in content of coniferyl aldehyde structure in GP lignin.

Treatment	% on pulp	Temp. (°C)	Residual coniferyl aldehyde [A][d] μmol/g(lignin)	%	[B][e] μmol/g(lignin)	%
Untreated	-	-	65±11	(100)	110±42	(100)
H_2O_2[a]	3	35	30±6	(46)	38±9	(35)
H_2O_2[a]	3	70	10±4	(15)	12±2	(11)
H_2O_2[a]	6	70	3±1	(5)	5±2	(5)
$NaBH_4$[b]	0.5	RT[c]	24±6	(36)	27±5	(24)
$NaBH_4$[b]	1	RT[c]	10±4	(16)	15±4	(13)
$NaBH_4$[b]	3	RT[c]	9±5	(14)	7±3	(7)
NaOH	2	70	65±11	(100)	110±42	(100)
NaOH[f]	20	70	74±15	(114)	120±50	(109)

Notes: a) Treated for 90 min. b) Treated for 60 min. c) RT; Room temperature. d) Calculated as free coniferyl aldehyde [I]. e) Calculated as coniferyl aldehyde ether [II]. Pulps were treated in 10% conc. except (f), 1%.
Number in parentheses are based on untreated pulp to be 100%.

Table 2. Vanillin yield from the model compounds and those reaction products with H_2O_2.

Compound	Treatment with H_2O_2* Residual H_2O_2 (%)	Residual model compound (%)	Recovery ratio of the product (%)	Nitrobenzene oxidation Vanillin (%;W/W)	Relative vanillin yield (%)
Model [II]	–	–	–	48±2	100
Reaction product from model [II]	0	3±0.5	108	24±2	50
Model [III]	–	–	–	48±2	100
Reaction product from model [III]	27	85±5	94	35±2	73

* Conditions: Model compound concentration 0.005 mol/l. H_2O_2 concentration 0.01 mol/l. Solvent, EtOH:H_2O=1:1. Temperature 70 °C. Reaction time 90 min. Alkali; Na_2SiO_3. Initial p. 10.5 (without EtOH).

EFFECT OF ETHANOL ON SODA-ANTHRAQUINONE PULPING

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ABSTRACT

The catalytic effects of various derivatives of anthraquinone (AQ) in soda pulping of Norway spruce have been studied with varying proportions of ethanol and water. In general, it was found that the most prominent effect of the solvent was an enhancement of carbohydrate stabilization, notably in the case of insoluble 2,3,6,7-tetramethyl AQ. The influence of ethanol on delignification efficiency was complex and varied widely with different additives. It was clearly shown that a high alcohol concentration (>50%) drastically reduced the effectiveness of additives. The observed solvent effects did not display any simple relation with increased solubility reflecting the importance of other factors involved.

KEYWORDS: Soda Pulping, AQ, Ethanol, AQ Derivatives, Delignification, Carbohydrate Stabilization.

INTRODUCTION

The relative effectiveness of various anthraquinone (AQ) derivatives (1) are known to be influenced by both chemical and physical factors, notably solubility (2, 3), redox potential (4, 5), hydrophilicity (6, 7) and xylophilicity (6). It is intriguing that the performance of AQ does not seem to be seriously limited by its low solubility in aqueous alkali. However, it has been shown that base-catalyzed oxidation of simple sugars by AQ is accelerated substantially by the addition of ethanol (8). Moreover, the inability of 2,3,6,7-tetramethyl AQ to promote the delignification reaction in aqueous alkali has been ascribed to its insolubility (3).

Conceptually, there are potential advantages in adding an organic solvent to soda-AQ cooks, as this would facilitate the dissolution and penetration of AQ into the wood chip, which have been shown to be a factor of critical importance (9).

The present study was undertaken to determine the effect of ethanol on the overall performance of AQ additives in alkaline pulping. After completion of this study, some related work along this line has been reported by Abbot and Bolker (10). They showed that presence of ethanol in soda-AQ cooks significantly enhanced the initial phase of delignification, but severely reduced the effectiveness of AQ during the later stage of pulping. Our study has also included a variety of AQ derivatives ranging from soluble AQ-2-sulfonate (AMS) to insoluble 2,3,6,7-tetramethyl AQ. The role of ethanol is discussed with respect to both delignification efficiency and carbohydrate stabilization.

EXPERIMENTAL

Two series of soda pulping of air-dried Norway spruce wood were made.

Extractive-Free Wood

Alkaline pulping of extractive-free woodmeals or chips was carried out in small autoclaves (75 mL) in sodium hydroxide solution (1N) containing varying proportions of 95% ethanol, ranging from 0 to 75% by volume at a liquor-to-wood ratio of 40:1. The cooking temperature was at 160°C for 1 h. Cooks with various derivatives of AQ were made at a level of 5% by weight on dry wood. The additives studied were AQ, a series of 2-substituted AQ including the t-butyl, ethyl, methyl, chloro, amino and sulfonate group, as well as 2,3,6,7-tetramethyl AQ which was generously provided by Dr. R.C. Eckert.

Unextracted Wood

Air-dried chips (~300 g) were pulped in an M & K digester with a charge of 20% NaOH containing an equal mixture of water and ethanol at a liquor-to-wood ratio of 5:1 with 0.1% AQ charge and at 170°C for different periods of time. Similarly, another series of cooks were made with different AQ charge (0.01-5%) at 170°C for 90 min.

RESULTS AND DISCUSSION

Effect of Ethanol on Effectiveness of AQ

Figure 1 illustrates the beneficial effect of ethanol on soda-AQ pulping. It is clearly shown that the delignification in a solvent system is much more responsive to an increase in the AQ addition, and levels off at a higher AQ charge (1% vs. 0.5%). Presence of ethanol increases the slope of the initial portion of the curve by a factor of 2. Thus, AQ is more effective in a solvent system probably attributed to

an increase in the solubility of additive. For some reasons, Abbot and Bolker (10) observed a much smaller effect of ethanol on soda-AQ pulping of black spruce matchstick-sized chips conducted at a lower temperature of 150°C.

Effect of Ethanol on Soda Cooks with 5% Additives

Delignification

The complex pattern shown in Figure 2 indicates a strong interaction among the solvent, additive and alkali. First, the extent of alkaline delignification is strongly enhanced by the addition of ethanol. There is an almost linear relationship between the lignin content of the pulp and the alcohol concentration.

Second, the addition of ethanol to soda cooks with various derivatives of AQ produced some rather interesting results. The delignification efficiency of tetramethyl AQ, which is practically ineffective in aqueous alkali, increases very distinctly with the alcohol addition up to 50%. This observation strongly supports the contention that solubility can be a limiting factor for an additive with low solubility (2, 3).

Third, it is very intriguing that the alkaline delignification of woodmeals with both AQ and 2-butyl AQ is essentially unaffected by the alcohol addition. In contrast to the behavior of woodmeals, ethanol is shown to greatly accelerate the delignification of chips with soda-AQ (Figures 1 and 2). It is noteworthy that delignification for woodmeals is higher than that for chips in the aqueous system, while the reverse is true in the solvent system.

Fourth, a similar pattern was obtained for 2-ethyl, 2-methyl, 2-chloro and 2-amino AQ; the extent of delignification increased significantly with the initial addition of ethanol, and tended to level off at about 25% alcohol concentration. It was also indicated that the delignification reaction gradually slows down as the alcohol concentration went above 50%.

Fifth, a close examination of the data in Table 1 and Figure 2 clearly indiates that solubility is not the only dominant factor in a solvent system. Interestingly, tetramethyl AQ, the least soluble additive, is the most effective one in the solvent system. Also, AQ, the most active additive in the aqueous system, becomes the least effective in the presence of alcohol. Thus, it appears that presence of ethanol also exerts some side effects which retard delignification. It is likely that the relative effectiveness of various AQ derivatives in a solvent system is also controlled by the xylophilicity (6).

Additive	Solubility, μmol/L			
	Ethanol, %			
	0	23.75	47.5	71.25
AQ	0.96	3.37	240	552
Me_4 AQ	0.19	0.77	3.89	18.29

Table 1. Approximate Solubility of AQ and 2,3,6,7-tetramethyl AQ in Ethanol-NaOH Solution (1 N)

Carbohydrate Stabilization

The effect of solvent on the extent of carbohydrate-stabilization catalyzed by the AQ additives can be seen clearly in Figure 3, which represents the net change in carbohydrate content with respect to the control soda and soda-ethanol cooks. The effectiveness of all the additives tested, with the exception of AMS, was substantially enhanced by the addition of ethanol, notably, tetramethyl AQ, and 2-chloro AQ. These two additives gave a distinct maximum near 50 and 25% alcohol concentration respectively.

On the other hand, the solvent had a negative effect on AMS, and the carbohydrate stabilization decreased steadily with increasing alcohol concentration. This finding is in line with a previous report (11) that the presence of ethanol reduced the rate of oxidation of D-glucose by AMS in aqueous alkali. Thus, the maximum stabilization of carbohydrate requires an optimum balance between the solubility of the additive and the rate of oxidation of carbohydrate end-groups.

Effect of AQ (0.1%) on Soda-Ethanol Cooks

To assess the potential of soda-ethanol pulping with the AQ additive, a series of experiments were made in 50% ethanol with 0.1% AQ at 170°C for different periods of time, and compared to control cooks without the additive. It was found that the rate of delignification was substantially increased by a small amount of AQ, a 66% increase in the rate of bulk delignification. Also, the transition from bulk to residual delignification took place earlier (90 vs. 150 min) and at a slightly lower lignin content. The use of AQ in this solvent system also resulted in higher pulp yields at a given Kappa number. The most beneficial effect (2-3%) was found between the Kappa number of 40 and 70 (Figure 4). Preliminary data indicated that the addition of

AQ to soda-ethanol cooks practically has no effects on the strength property of pulp produced.

CONCLUSIONS

The above data clearly show that the addition of ethanol has a complex influence on the performance of various derivatives of AQ in alkaline pulping. The main features observed are briefly outlined in the following.

First, the most prominent effect of the solvent is on the insoluble 2,3,6,7-tetramethyl AQ as reflected in an enhancement of both delignification (Figure 2) and carbohydrate stabilization (Figure 3). Such an enhancement was mainly due to an increased solubility of the additive in a solvent system.

Second, the solvent effect on the stabilization of carbohydrate is also very pronounced for other additives with the exception of AMS (Figure 3). It appears that ethanol exerts some negative effect by reducing the oxidation efficiency of carbohydrate end-groups. Thus, the maximum carbohydrate stabilization requires a proper balance between solubility and rate of oxidation, which seems to occur in the range of 25-50% alcohol concentration.

Third, the solvent effect on the delignification efficiency of 2-substituted AQ derivatives was mixed. A positive effect was observed with a small addition of ethanol, but a high solvent concentration (>50%) in fact hinders delignification. The striking difference between soda-AQ cooks of chips and woodmeals in response to the alcohol addition suggests the importance of some physical factors involved. The potential role of preferential alkali sorption and imbibition of organic components in a solvent system by the cell wall polymers need to be explored further.

Finally, the remarkable effects of AQ additive observed in the aqueous system have been shown to be applicable to the solvent system.

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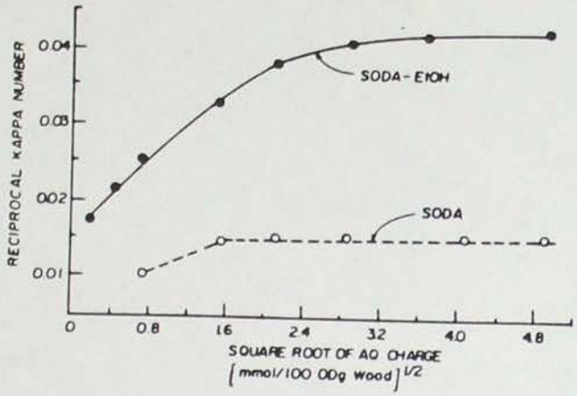

Figure 1. The effect of ethanol (50%) on soda-AQ delignification of unextracted Norway spruce chips at 170°C for 90 min using a 20% alkali charge at a 5:1 liquor-to-wood ratio

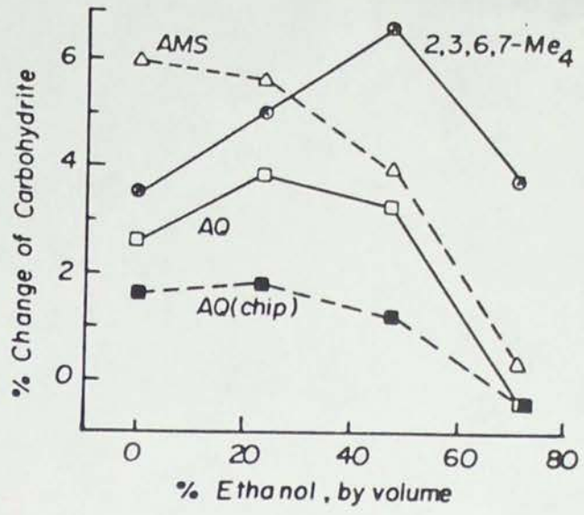

Figure 3. Effect of ethanol and AQ derivatives on carbohydrate stabilization from extracted Norway spruce woodmeals in 1N NaOH at 160°C for 1 h. Data of soda-AQ cooks of chips are also included

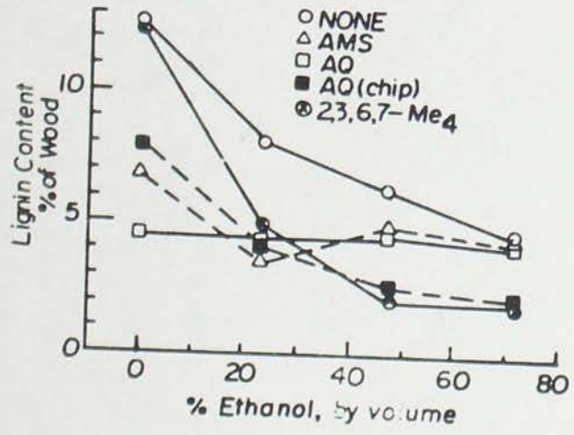

Figure 2. Effect of ethanol concentration and AQ derivatives on the lignin content of pulp from extracted Norway spruce woodmeals in 1N NaOH at 160°C for 1h. Data of soda-AQ cooks of chips are also included

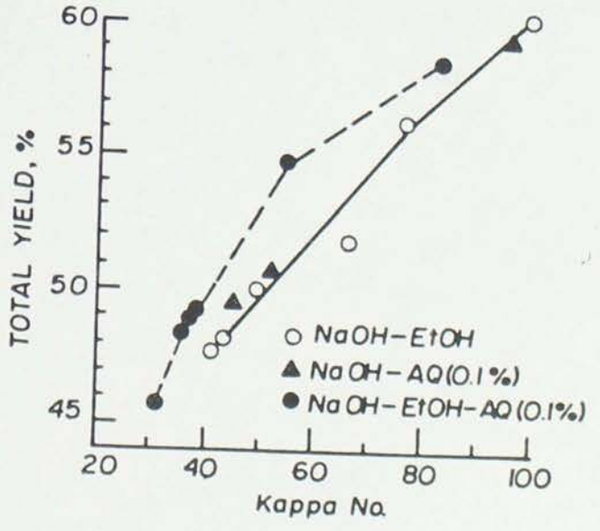

Figure 4. Effect of ethanol (50%) on the delignification selectivity from soda-AQ pulping of Norway spruce at 170°C