BIOMASS ASH-BASED HETEROGENEOUS CATALYSTS TO PRODUCE FATTY ACID METHYL ESTERS FROM WASTE COOKING OIL

by

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ABSTRACT

Biodiesel is widely accepted for blending with conventional fuels such as diesel and gasoline. The development of cheap, durable heterogeneous catalysts for its production is a rapidly growing field of scientific investigation. Two heterogeneous catalysts were prepared from ashes of wood gasification (GA) and wood pellet combustion (PBA). They were characterized and subsequently used in the transesterification of waste cooking oil (>1% FFA) to produce biodiesel. The methanol to oil ratio was 12:1 and 5 wt% catalyst was used over temperatures of 65 °C, 80 °C, 120 °C and 160 °C. ^{1}H-NMR was used to establish yield of the trans-esterification reaction. The maximum yield using PBA catalyst was 95% at 120 °C and 155 minutes, for GA catalyst, it was 95% yield at 120 °C and 160 minutes. The re-use of both catalysts was also investigated at 120 °C, 12:1 methanol to oil ratio and 5 wt% catalyst. The PBA catalyst upon reuse at 120 °C gave a yield of 75% at 160 minutes and fared better than the GA catalyst, which gave 60% yield after 300 minutes at 120 °C.

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Glossary

BET	Brunauer Emmet Teller theory for determining surface area of solid
1,2-DAG	1,2 - diacylglycerol
FAEE	Fatty acid alkyl ester
FAME	Fatty acid methyl ester
FAO	Food and Agriculture Organization
FFA	Free fatty acid
FT-IR	Fourier transform infrared spectroscopy
GA	Gasifier ash
GHG	Green house gas
ICDD	International Centre for Diffraction Data
ICP-MS	Inductively coupled plasma with mass spectrometer
1-MAG	1 - monoacylglycerol
^{1}H-NMR	Nuclear magnetic resonance (^{1}H)
PBA	Pellet burner ash
TAG	Triacylglycerol
TGA	Thermo gravimetric analysis
TMS	Tetramethylsilane
USDA	United States Department of Agriculture
WCO	Waste cooking oil
XRD	X-ray diffraction

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Co-authorship statement

I conducted all experimental work, data analysis and prepared all the drafts of manuscripts in this thesis. The manuscripts appear as separate chapters based on the research and its results. All drafts of the manuscripts and publications have been reviewed and strengthened through input given by my supervisor Dr. Ronald Thring. Other persons who have been instrumental in the successful completion and editing of the individual studies are:

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Adrian K. James

Chapter 1: Introduction[1]

1.1 Overview of the Biodiesel production process

Biodiesel has been used as an alternative energy source for the major part of the 20th century. It offers unique advantages as a fuel, with low sulphur content, emissions with lower particulate matter, and reduced greenhouse gas emissions over its life cycle. In particular, replacement of conventional fuels with biodiesel significantly reduces emissions such as CO_2, CO, SOx, volatile organic compounds (VOCs), unburned hydrocarbons, and particulate matter (Ozil et al. 2009; Pisupati and Bhalla 2008). Biodiesel is a biodegradable, non-toxic and environmentally friendly product, which may be blended with fossil based diesel fuel in any proportion to create a stable, useful fuel blend (Pinzi et al. 2009). Biodiesel has a higher flash point than conventional petroleum diesel and is safer to store, handle and transport (Morais et al. 2010). Because it possesses the properties of blending with conventional fuels, biodiesel has received great amount of scientific and social attention. It has been promoted by policy makers and governments across the world, and its use in the transportation sector has been mandated in countries such as those in the EU-27 and other parts of the developed world. To reduce Greenhouse Gas (GHG) emissions and promote a cleaner transport system, the European directive 2009/28/EC aims to achieve a 10% share of renewable energy in the transport sector by 2020 in EU (Redel-Macías et al. 2012).

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[1] Parts of this chapter have been previously published: James, Adrian K.; Thring, Ronald W.; Helle, Steve; Ghuman, Harpuneet S. 2012. "Ash Management Review—Applications of Biomass Bottom Ash." *Energies* 5, no. 10: 3856-3873.

Biodiesel is a mixture of fatty acid alkyl esters commonly produced from triglycerides and alcohol through transesterification reaction in the presence of alkali catalysts (Reed, Graboski, and Gaur 1992; Canakci and Van Gerpen 2001; Haas, Bloomer, and Scott 2002; Antolín et al. 2002; Haas 2005; Demirbas 2007) . Feedstock for biodiesel is mainly food grade vegetable oils (S. Lee, Posarac, and Ellis 2011). Because food grade vegetable oils are in demand in industries such as food production, restaurants and also for domestic consumption their availability and cost competitiveness is a major challenge for large scale industrial use to manufacture biodiesel. The costs of vegetable oils can be up to 75% of the total manufacturing cost, which makes biodiesel production costs approximately 1.5 times higher than those of diesel (Haas, Bloomer, and Scott 2002; Phan and Phan 2008). Therefore, the industry is influenced by the high cost, and also the limited availability of feedstock for biodiesel production (Morais et al. 2010).

Another important factor to be considered is the increase in consumption of edible oils which has a direct impact on production and availability of feedstock for biodiesel production (Morais et al. 2010). According to United States Department of Agriculture (USDA), the net consumption of edible oils in the top 15 countries and regions across the world will increase by 10.58 million metric tons between 2010 and 2013, which can be predicted from the past year trends in Figure1.1 (USDA 2013). This growth is seen primarily in emerging economies of China and India with approximately 9.7% and 11.7% increase in domestic consumption in the 3 year period, respectively. Similarly the United States shows an increase in domestic consumption, with an increase of 11.8% from 2010 to 2013 (USDA 2013) . China and the EU-27 remain the largest consumers of edible oils with estimates for 2012-13 pegged at 30.4 and 23.6 million metric tons respectively (USDA 2013). India and United States follow with consumption of 17.9 and 13 million metric tons, respectively for the same timeline. This increase in consumption of edible oils casts some doubt on the availability and the cost-competitiveness of feedstock such as refined vegetable oils in the near future. In the future, refined vegetable oils will have competing consumption patterns that will directly influence the cost of feedstock for production of biodiesel. It is evident from these developments that refined vegetable oils and similar agricultural products will be in high demand, both for human consumption, and for energy production. The percentage of vegetable oils used for food has steadily declined from 86% in 2002-2003 to about 74% in 2011-12, but it still remains the major application for using these vegetable oils (USDA 2013). It may be interesting to point out that the worldwide consumption of vegetable oil for food uses in 2002-03 was 83.1 million metric tons and it rose to about 114.2 million metric tons in 2011-12 (USDA 2013), and the net world vegetable oil production for 2001-2012 is shown in Figure 1.1. The overall share of food based applications is declining but the competition between food uses, industrial uses and energy production will only intensify in the future (USDA, 2013).

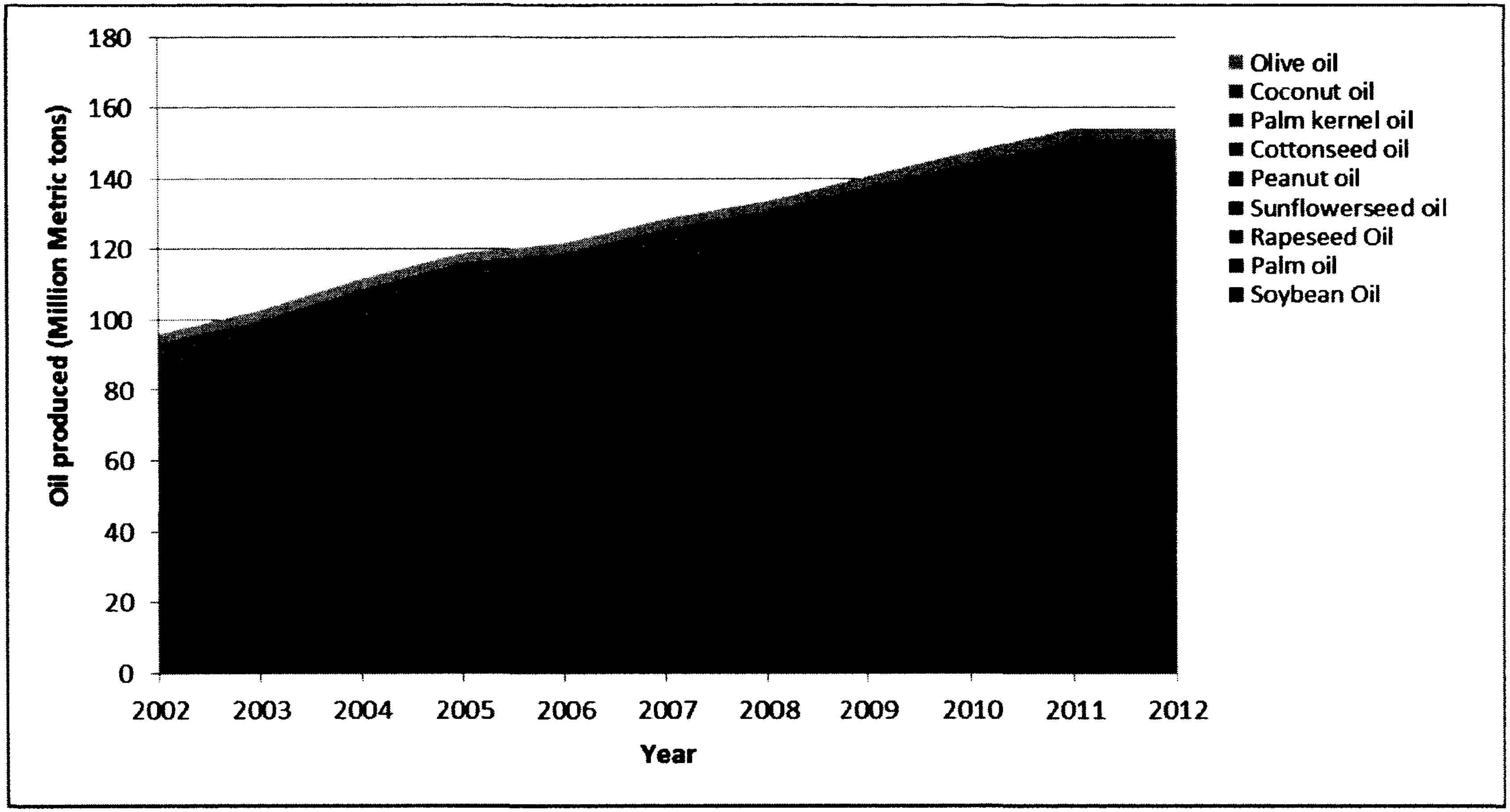


Figure 1.1. World Vegetable oil production, 2002-2012. Source: USDA 2013

1.1.1 Waste feedstock for Biofuel production

Biofuels from edible crops are not a long term solution. They do not have the potential to provide more than 10% of liquid fuel demand in developed economies (Huber and Dale 2009). The EU directive (2009/30/CE) states that GHG emission savings for biodiesel made from conventional feedstock such as refined vegetable oil is about 50% and this value increases to over 80% for waste vegetable oil, animal fats and other waste products which can be converted to biodiesel (European Commission 2013; Morales et al. 2011). The Renewable Energy Directive (RED) and article 17 of the EU directive also expresses support for promotion of renewable energies which are directly related to standards of sustainable biomass (European Commission, 2011). The RED specifically discourages the use of raw material which is cultivated on land which was previously a high carbon stock or of a high biodiversity value. The European Commission (EC) also encourages diversification of raw materials used for bio-fuel production and inclines towards biofuels from wastes, agricultural residues, lingo-cellulose and other such feedstock. These are healthy developments, both for the environment as well as for communities actively engaged in reducing their GHG emissions. Waste feedstocks are inexpensive materials with potential to be converted to biofuels. Because they are the by-products of industries or commercial operations, the most probable alternate fate for these wastes is disposal, landfilling or chemical treatment and refining.

Common wastes of vegetable origin are waste vegetable oils produced in restaurants. Other wastes of high free fatty acid (FFA) content are yellow grease, brown grease (Canakci and Van Gerpen 2001), chicken fat (Arnaud et al. 2006; K.-T. Lee and Foglia 2000), animal tallow (Öner and Altun 2009) etc.. The use of waste cooking oil (WCO) as a feedstock serves two purposes. It aids in decreasing the environmental impacts and costs of waste disposal and also reduces the production cost of biodiesel (Meng, Chen, and Wang 2008; Phan and Phan 2008). WCO has some amount of water and FFA which direct the conventional alkali catalyzed process to undesirable saponification. Using the conventional method, it is also difficult to remove the base catalysts after a reaction, and large amount of wastewater is produced during separation, cleaning of catalyst and products (Shu et al. 2010).

In 2004, the International Energy Agency (IEA) reported 2.63 billion pounds (1,192,947 tons) yearly average yellow grease production from 1993-1998 for the USA. This figure was sufficient to produce 344 million gallons per year of biodiesel, but only 100 million gallons per year could realistically be manufactured due to technological and economic limitations (IEA, 2004). Comparing these figures with the USDA figures for vegetable oil used for food purposes, we may establish an estimated percentage about WCO and yellow grease production related to vegetable oil consumed. The national food purpose vegetable oil consumption for 1993-1998 was 7,931,000 tons average per year (USDA 2013). The figures point to an approximate 15% yellow grease production from vegetable oil used for food purposes. To understand the situation better, we must consider that domestic households generate waste that is not collected, and does not contribute directly to available WCO or yellow grease. Commercial operations like restaurants, deep frying food manufacturing facilities, food processing industries use a more consolidated waste collection system, and contribute largely to this figure. If community waste collection programs are enforced, we may optimistically assume that this figure might likely double. Hence for the basis of further estimates, a range of 15% as the lower limit and 30% as the upper limit are established for calculations. Table 1.1 shows top 5 vegetable oil consuming countries and regions, and the amount of WCO and yellow grease that may potentially be generated for a range of 15%-30% of total vegetable oil consumed for food purposes. We may also estimate the potential for biodiesel production from these figures.

Table 1.1. Vegetable oil consumption (for food purposes) in top 5 regions of the world averaged from 2010/11 - 2011/12. Estimates of WCO produced within a range of 15%-30% from this consumed oil, and the potential for biodiesel production from the same.

Country	Vegetable oil consumed*	[1]Waste produced (a)	[2]Waste produced (b)	[3]Potential biodiesel produced from (a)	[4]Potential biodiesel produced from (b)
China	25860	3879	7758	1118.5	2237.1
India	15974.5	2396.2	4792.4	691	1381.9
EU-27	12457	1868.6	3737.1	538.8	1077.6
United States of America	10116	1517.4	3034.8	437.5	875.1
Indonesia	5091	763.7	1527.3	220.2	440.4

* for domestic food use, in 10^3 tons averaged for 2010/11 – 2011/12.(USDA 2013)

1 Using 15%, in 10^3 tons.

2 Using 30%, in 10^3 tons.

3, 4 In 10^6 gallons (each ton of waste producing 288.4 gallons biodiesel, (*IEA, 2004)*

1.1.2 Catalysts for biodiesel production from waste feedstock

The free fatty acid (FFA) and other impurities in WCO and other high fat wastes render the conventional alkali catalyzed biodiesel synthesis process open to saponification and gel formation that decreases the economy and yield, and increases the product separation and purification costs. The presence of water drives the reaction to an undesirable hydrolysis of esters and saponification. Commercial biodiesel operations usually employ a basic catalyst which is soluble in nature, like potassium or sodium methoxide. These operations also have an acid based pre-treatment step that esterifies the FFA if feedstock is not regulated for <1% FFA content (Santacesaria et al. 2007). Consequently, these homogenous acid and base catalysts are corrosive to process equipment in particular and pose a risk to fuel engines if not removed at the end of production. Their removal by aqueous quenching and neutralization is both energy and cost intensive and it directly increases the cost of production in a biodiesel processing facility. It also contributes to emulsions and gel formations in the product (Demirbas 2007). This section reviews some recently studied processes and their key features in processing waste feedstock and waste streams.

Shu et al. (2010) used a carbon based solid acid catalyst to synthesize biodiesel from a high FFA content WCO. Simultaneous esterification and transesterification gave triglyceride conversion of 80.5 wt % and FFA conversion of 94.8%. Alptekin and Canacki (2011) used chicken fat as the waste feedstock and used an alkaline catalyst to obtain 88.5% ester yield after pre-treatment of the feedstock with H_2SO_4 to convert the

FFA content and reduce its interference with the alkaline catalyst. Noshadi, Amin, and Parnas (2012) used a heteropolyacid catalyst in a reactive distillation column to achieve a FAME yield of 93.9%. This reaction was a continuous operation with a methanol excess of 70:1, using 12-tungstophosphoric acid as a catalyst in a pilot scale plant. The feedstock was of low moisture content, of about 1% and the WCO had an acid value of 7.45 mg KOH/gm. The WCO was collected from domestic consumers and not commercial operations like restaurants or deep frying facilities. Guzatto et al. (2012) established that ethanol as a solvent in a transesterification double step process eliminates the need for anhydrous materials, low FFA content in feedstock and also deals with problems of emulsions and saponification that are experienced with using methanol. They obtained a high yield of Fatty Acid Ethyl Esters (FAEE), about 97% but also stated that the double step transesterification required longer reaction times and larger alcohol and catalyst amounts.

Toba et al. (2011) successfully applied a hydrodeoxygenation process to convert WCO, trap grease from industry to paraffins and iso-paraffins. They upgraded all these source wastes with Nickel-Molybdenum, Nickel-Tungsten and Cobalt-Molybdenum based catalysts with a solid acid B_2O_3-Al_2O_3 support, to achieve complete conversion at temperatures 300 ^{0}C – 350 ^{0}C. Corro et al. 2012 used zinc filings as catalyst and a setup to harness solar energy for the reaction's temperature control and produced biodiesel from non edible jatropha curcas oil. This process was again a two step process, the first step using the zinc catalyst to esterify the FFA and then using an alkali catalyst to transesterify the triglycerides to achieve 98% conversion using a 20% loading of zinc filings. Alptekin, Canakci, and Sanli (2012) investigated the conversion potential of leather industry waste as biodiesel feedstock. They used animal fat from leather industry waste and pretreated it with sulphuric acid and methanol to first convert the FFA, followed by alkaline catalysts for transesterification. The study achieved a greater than 90% conversion for the two step process using fleshing oil as a feedstock, which is a waste produced by the leather industry and has an FFA content of 5-25% (Canakci and Van Gerpen 2001). Bezergianni et al. 2011 used hydrotreatment of WCO as a process and optimized the Liquid Hourly Space Velocity (LHSV), H_2/oil ratio and pressure on a small scale pilot plant. They reported their results with using a Nickel-Molybdenum type industrial hydro treating catalyst, and obtained an 82% biodiesel conversion.

Morales et al. 2011 investigated the effects of impurities in WCO on sulfonic acid catalysts, and conversion of WCO to biodiesel using various catalysts. The yield with SBA-15 catalyst provided highest yields of 80% using an 8% catalyst and 30:1 methanol excess. They also stated that the catalyst was strongly deactivated due to strong interactions of unsaponifiable matter and impurities with the catalyst sites. Ramachandran et al. 2011 also used a heterogenous aluminium based sulphated catalyst, $Al(HSO_4)_3$ to convert WCO to methyl esters. They observed a conversion of 81% with an alcohol excess of 16:1 and 220 ^{0}C as the reaction temperature. Lei et al. (2011) used low quality rice bran waste and converted the FFA to FAEE using an in-situ process with an esterification yield of 98% and transesterification yield of 83%. The FFA content of the waste was reported at 73-80%, and the waste was a by product of a rice processing plant. Rice husk ash was applied by Manique et al. 2012 to purify biodiesel made from WCO. Azcan and Yilmaz 2013 used a microwave transesterification process with sodium methoxide as the catalyst, followed by molecular distillation to purify the product. The feedstock was WCO supplied from a local food facility. Molecular distillation was employed to separate and purify the products to avoid problems of toxicity and use of solvents for separation (Jiang et al. 2006; Martins et al. 2006). Al-Hamamre et al. 2012 used oil from spent coffee grounds and converted the FFA to FAME using a base catalyzed process.

It is evident that recent research and scientific endeavour has shifted to explore alternative sources of feedstock to ensure that biodiesel production is cost-effective, and has a minimal effect on the environment. Table 1.2 presents various aspects of some more research studies focused on employing waste feedstock, such as the type of catalyst, reaction conditions and nature of products obtained. The Table 1.2 is shown to draw attention to the heterogeneous catalysts and waste streams, and their proportions and reaction conditions used.

Table 1.2. *Brief summary of recent research on using waste feedstock to produce biodiesel. The table depicts the type of feedstock and catalyst, along with best yields and corresponding reaction conditions.*

Nature of feedstock	Type of catalyst	Reported Reaction conditions	Type of product
Waste cooking oil	Heterogeneous Potassium supported pumice	20 wt% catalyst, 21:1 Methanol excess, Reaction time of 4 hours(h), 60°C	90% FAME yield (Borges et al. 2011)
Brown grease	Heterogeneous Metal oxide-Zirconia catalyst	5 wt% catalyst, 6:1 Methanol excess, 7h, 200°C	>97% FAME yield (Kim et al. 2011)
Waste cooking palm oil	Heterogeneous Clay based catalyst	3.5 wt% catalyst, 15:1 Methanol excess, 5h, 150°C	96% FAME yield (Olutoye and Hameed 2013)
Waste cooking oil	Barium meliorated waste marble as Heterogeneous basic catalyst	3.0 wt% catalyst, 9:1 Methanol excess, 3h, 65°C	88% FAME yield (Balakrishnan, Olutoye, and Hameed 2013)
High FFA content oil	Functionalised porous carbonaceous materials	3.0 wt% catalyst, 32:1 Methanol excess, 6 h, 80°C	98 mol% FAME yield (Arancon et al. 2011)
Waste cooking oil	Metakaolinite clay mineral	3.0 wt% catalyst, 23:1 Methanol excess, 4 h, 160°C	95% FAME yield (Ramirez-Ortiz, Martinez, and Flores 2012)

1.1.3 Environmental and Economic Benefits of using waste feedstock

Biodiesel is an attractive substitute for use in diesel fuel based energy operations. One of the major challenges facing biodiesel production under current conditions is the cost competitiveness with fossil fuels and other fuel substitutes. The main external costs savings of biodiesel come from the reduction in depletion of fossil energy resources, and the mitigation of CO_2 emissions. Also, combining external and internal costs, B5 and B10 biodiesel blends are competitive to diesel on a per kilometre distance driven basis (Silalertruksa, Bonnet, and Gheewala 2012). Biodiesel combustion produces reduced particulate matter, hydrocarbons, carbon monoxide, sulphur oxide and poly aromatic hydrocarbons (PAH's) when compared to fossil fuel combustion (Lin, Hsu, and Chen 2011). One study used a public transit bus in Denver, Colorado to demonstrate that biodiesel blends reduce smoke opacity by almost 60% without any loss in power delivered by the engine (Reed, Graboski, and Gaur 1992). WCO based biodiesel emissions have been reported to have reduced content of particulate matter, hydrocarbons, PAH's and carbon monoxide (Antolín et al. 2002; Lin et al. 2006; Tsolakis et al. 2007). Haas et al. (2002) found that 88% of the costs in biodiesel production were associated with feedstock acquisition. The total costs of biodiesel are slightly higher than diesel (Van Gerpen et al. 2004) but the benefits of CO_2 emission reductions along with environmental benefits help justify the slightly increased costs. The use of biodiesel and its production has other social benefits such as stabilization of farmer's income and employment generation, as well as reduction of the country's dependence on oil imports leading to improved energy security and lesser economic dependence on oil exporting countries (Silalertruksa, Bonnet, and Gheewala 2012).

Using waste feedstock is a direct way to economize and reduce waste disposal costs and it helps produce a useful product from an otherwise obsolete material. Community programs for waste collection such as Trap the Grease implemented by the city of Tulsa, Oklahoma demonstrate that waste grease and associated types of domestic wastes are a significant cost in waste water treatment and maintenance of sewer systems. The initiative to collect them at source may not only offset these costs, but may also create potential to convert these wastes into upgraded and useful products such as bio-diesel with relative ease and efficiency.

1.1.4 Summary and Conclusions

Biodiesel is increasingly being recognised by industry and governments as an attractive alternate to reduce their net emissions. A brief summary of the policies influencing biodiesel production are reviewed in this section. These policies are the ones that directly impact availability and choice of feedstock, or promote the use of alternate fuels, in particular biodiesel. In recent years, mandates for blending have been implemented in countries all over the world.

The United States of America mandated targets (RFS-2) for national consumption of biomass based biodiesel at 0.65 billion gallons in 2010, about 1.1 % of total diesel sales for that year. The focus in this initiative was also laid on accounting for emissions from indirect land use changes (ILUC) when measuring the GHG reductions by using biodiesel. Lifecycle emissions according to this standard must account for a 50% reduction as compared to petroleum diesel for it to be considered sustainable. According to these RFS-2 standards, waste oils, fats and greases all comply with this requirement. Argentina has a mandate of 7% biodiesel blending as of August 2010. ILUC are a major concern when dealing with biofuels production, and increasing land use changes may decrease the environmental benefits offered by biofuels. Similar concerns were expressed by the European Union commission, and countries such as Germany, France and Netherlands speak in favour of certified sustainability criteria which may help determine the actual benefits of biofuels depending upon the source of feedstock and efficiency of production. In February 2011, Canada mandated a 2% blending of biodiesel with conventional diesel fuel across the country. The Chinese government in 2011 limited the use of all grains and edible oils for biofuel, alcohol or other non food applications, citing the aim to protect supplies of products for human and animal consumption. The European Union introduced the requirement for proof of sustainable production methods in the same year. The European Commission introduced seven voluntary certification schemes, aimed at evaluating and certifying the sustainable aspects of various bio fuels that are produced or consumed in the EU. As recent as May 2012, the EU was struggling to formulate concrete regulations to measure ILUC factored emissions for vegetable oil based bio fuels. Recent research carried out for the EU suggests that vegetable oil based biodiesel has higher GHG emissions if ILUC factors are considered.

Global developments and increasing concerns about land use changes, loss of biodiversity and food crisis has impacted the production of biodiesel from vegetable oil sources. This is reflected in the rapidly changing policies, reduction of subsidies and including of sustainability criteria in measuring the emission reductions and true environmental benefit of a renewable energy source. These influences are also observed in government action and decision making as regards to the biodiesel and renewable fuel sector. Waste feedstock such as waste cooking oil, animal fats, plant residue, leather waste, vegetable oil refinery waste have consistently exceeded and met these sustainability criteria. This is mainly because waste products are of low value, have been produced on completion of their primary purpose, and their alternate fate is landfilling or disposal. New technologies and processes to refine this waste feedstock have been evaluated in this chapter. It is imperative that the scientific focus be shifted to the feasibility of using waste feedstock in the production of renewable fuels especially biodiesel. The wide acceptance for biodiesel as a diesel fuel substitute and blend is evident from its global demand and production. The optimization of a process to balance the economic and environmental benefit in a sustainable manner is extremely important. The use of waste feedstock has driven us in the right direction, of minimizing waste disposal costs and upgrading low value wastes into high value products of both economic and environmental significance.

1.2 Biomass to energy

In recent years, technologies to harness energy from biomass have come to be widely used and accepted in a wide range of energy generation processes. District power and heating programs in Scandinavian countries, and utilization of biomass in co-combustion of coal in the Netherlands are such examples (Hoogwijk et al. 2005; Turkenburg 2000). Studies estimate the future contribution of biomass based energy to account for almost 15% - 25% of the worlds energy needs (Berndes, Hoogwijk, and van den Broek 2003; Hoogwijk et al. 2005). Investigations are also aimed at reviewing the potential of biomass to energy operations based on factors such as source feedstock, energy demand and supply, land use policy, population growth patterns and evolving technologies (Thrän et al. 2010; Batidzirai, Smeets, and Faaij 2012). Modern technologies to harness bioenergy are increasingly efficient and clean, contributing to the rising popularity and immense future potential of bioenergy obtained from renewable biomass (Hall 1997; Hall and Scrase 1998). The technologies are mostly thermo chemical processes that produce useful energy from biomass. They employ novel techniques such as combustion, gasification, pyrolysis and liquefaction to produce energy or liquid and gaseous fuels with a higher heating value (Oktay 2006; Suárez, Beaton, and Zanzi 2006).

In a unique initiative in 2009, the University of Northern British Columbia, Canada installed a 1.5 GJ/hr pellet boiler to heat the enhanced forestry laboratory using locally produced wood pellets. Combustion produces direct heat from biomass by rapid heating in an oxygen rich environment (Fryda et al. 2006; Bridgwater 2012). Pellet burners are devices used to achieve complete combustion of wood pellets to maximize energy output from biomass. Use of wood pellets for heating provides possibilities of more automated and optimized systems, with higher combustion efficiency and less products of incomplete combustion compared to traditional wood log firing (Öhman et al. 2004). Pelletized wood is more convenient than wood residue because it is energy dense, it can be easily stored and transported, and can be used in automated energy systems much like liquid fuels (Park et al. 2012). More than 2/3 of the annual pellet production of Canada comes from facilities located in British Columbia, specifically located closer to Prince George where these resources are found in close proximity (Magelli et al. 2009). The UNBC on-campus pellet boiler facility consumes approximately 150 tonnes/year of locally produced wood pellets to achieve a >90% fuel conversion efficiency. This entire setup offsets approximately 130 tons/year of fossil fuel CO_2, and consists of 400 kW pellet boiler accompanied with a 2500 L heat storage tank and a 50 ton fuel storage hopper. The 1.4 GJ/h KOB Pyrot rotary combustion pellet burner consumes 11 tonnes/month of pellets, generating 23 kg/month bottom ash and approximately 0.4 kg/month of fly ash. The bottom ash is collected from the bottom grate of the burner, while the fly ash is trapped in filters used to remove particulate matter from exhaust streams. The wood pellets are supplied by Wood Pellet Association of Canada and are produced primarily from softwood sawmill waste. The wood chips have varying ash content based on the bark content of the mixture. This is because the minerals are usually more concentrated in the bark region (James et al. 2012).

A gasification system has also been operational since January 2011 at the campus of University of Northern British Columbia to harness energy from sawmill residue such as shavings, sawdust, chips etc from local mills. Gasification is the controlled heating of biomass in oxygen deficient, reducing conditions to produce producer gas (Malkow 2004; Bridgwater 2012). Fuel gas that is produced may be combusted in a conventional burner, connected to a boiler and a steam turbine, or in a more efficient energy conversion device, such as gas reciprocating engines or gas turbines (Arena 2012). The gasification system is a reducing environment gasifier located on campus at the University of Northern British Columbia, Prince George, Canada. The biomass gasification system uses wood residues or other clean residues to produce energy in an oxygen deficient environment. The gasifier has a diameter of 4.3 meters and the accompanying flue gas boiler has a capacity of 4.4 MW. The plant based on biomass gasification has an energy output of 16 GJ/h and offsets approximately 85% of the campus heating needs. It also reduces CO_2 emissions, registering a decrease of 3500 tonnes annually when compared to using fossil fuels for the equivalent energy production.

These initiatives are relevant in a socio-economic setup which is rapidly shifting towards more sustainable practices. The prime focus is to supplement current energy production and provide cleaner sources of energy that are renewable and environment friendly. The initiatives reflect the exponentially growing sectors of bioenergy and their appeal to a large section of the world's developed nations, united in their common goal of lowering CO_2 emissions. These steps to reduce pollutants are consistent with various international pollution and emission control agreements and objectives and goals outlined by the Intergovernmental Panel on Climate Change (IPCC). While bioenergy continues to rise in popularity and market value, there are particular concerns that arise from current practices. An example of these is land use change and its effect on the environment along with including it in sustainability accounting. Of particular concern in biomass to bioenergy operations is the generation of residues. Most processes produce an ash residue rich in inorganic content in varying volumes depending upon feedstock, type of process, operating conditions and process efficiency.

1.2.2 Ash production and utilization

Ash is the incombustible part of wood fuel and biomass left after complete combustion, and contains the bulk of the mineral fraction (Khan et al. 2009). The ash containing part is an integral component of the plant structure and consists of a wide range of elements (Quaark, Knoef, and Stassen 1999) . The ash content varies from less than 2% for wood, to about 5%-10% for crop residues and 30% - 40% for rice husks, milfoil (Quaark, Knoef, and Stassen 1999). Ash is produced upon the thermochemical degradation of biomass based products such as sawdust, shavings, wood pellets etc. Finer ash particles are trapped in filters, precipitators and comprise the fly ash fraction of the ash. Coarser and larger particles are collected as bottom ash. These types of ash vary in properties due to the difference in feedstock biomass, operating process and conditions and system efficiency. High ash content significantly reduces the energy output derived from that biomass source (James et. al, 2012). The current scenario of ash production, and future potential may be estimated by assessing the amount of woody biomass available for energy operations. Wood residue forms a significant input for energy uses such as in gasification, pyrolysis and combustion. The Food and Agriculture Organization (FAO) describes wood residue as by products which have not been reduced to small pieces. This consists of industrial generated wood wastes such as sawmill rejects, slabs, edgings and trimmings, veneer log cores, veneer rejects, sawdust, bark (excluding briquettes), residues from carpentry and joinery production etc. Residues produced at industrial processing sites such as bark and sawdust from sawmills are the largest commercially used biomass source (Thrän and Kaltschmitt 2002). According to the Food and Agriculture Organization (FAOSTAT), approximately 98.2 $x10^7$ m^3 of wood residue was generated globally, as a yearly average from 1992 to 2010. In this period, the top five wood residue generating countries were China, Brazil , United States of America the Russian federation and France which can be seen in Table 1.3. These residues have potential in the near future to supplement growing demands from wood and biomass based energy. The coniferous wood fuel used is a good means to estimate current ash generation. The top five users of coniferous wood fuel in the year 2010 were United States of America, China , Brazil , Russian federation and France which may be seen in Table 1.3 . The bulk density of residual woody biomass varies for different categories. Some of these varieties of residues are hardwood chips (0.23 ton/m^3), softwood chips (0.18-0.19 ton/m^3), sawdust (0.12 ton/m^3) and planer shavings (0.10 ton/m^3) (McKendry 2002). The approximate bulk density of wood residue is considered equivalent to 0.16 ton/m^3, and for wood fuel this is estimated at 0.21 ton/m^3. The product of the bulk density (ton/m^3) and amount of wood fuel (m^3) gives us an estimate of the mass of wood currently used in ash generating processes. Similar calculation of product of bulk density (ton/m^3) of wood residue and amount of wood residue (m^3) generated can give us an approximation of the wood residue for potential use in energy processes, which has been done in the last two columns of Table 1.3. The ash content of wood varies widely depending upon the type of wood. Clean wood without bark (<1%), bark (3%-4%), contaminated bark (5%-15%), contaminated reject wood (0.5%-19%), clean reject wood (0.5%-3%) are some examples of varying ash content. The ash is fixed at 10% (dry basis) for wood fuel, to account for inefficiencies in the variety of processes used, and 15% for wood residue to accommodate contaminated feedstock and mineral rich parts such as contaminated bark etc.

Table 1.3: Estimate of potential ranges of net ash production based on complete wood residue utilization in global leaders of wood residue generation, and complete wood fuel utilization (FAOSTAT, 2012)

Country	Wood residue (10^7 m^3)	Wood fuel (10^7 m^3)	Ash from wood residue (10^6 tons)	Ash from wood fuel (10^6 tons)
China	15.3	91	2.45	28.7
Brazil	14	13	2.24	4.1
United States of America	13	9.5	2.1	3.0
Russian federation	7.9	19	1.3	6.0
France	7.7	2.7	1.2	0.9

The European Union produced 56 x 10^6 tons of ash in 2005, and this is expected to double by 2020, leading to an estimated 155 x 10^6 tons of ash in the EU-27 (Obernberger and Supancic 2009). Our estimate for the 140 x 10^7 m^3 of fuel wood produced in the region puts the ash generation at 44.1 x 10^6 tons of ash. The imports of fuel wood and pellets, industrial utilization of wood residues are not included in our estimate as these parameters vary from country to country and over time as well. An accurate calculation is difficult to determine and may only be achieved by monitoring ash generation processes and measuring the final generated ash quantities. The current use compared to potential varies from 12% in Latin America, 16% in North America, 22% in Europe and 108% in Asia (Thrän and Kaltschmitt 2002; Thrän et al. 2010). There is immense potential for developing biomass to bioenergy technologies in countries in North America and Europe (Parikka 2004). These figures will likely rise in the future which will be accompanied by an increase in total ash generation. The alternate fate for majority of wood residues not being used for power generation is landfill or disposal (Morris 1999).

Some alternative applications for these biomass ashes have been suggested by recent scientific studies. Agricultural and construction use are two main applications that have been studied (Holt and Raivio 2005; Holt and Raivio 2006; Gómez-Barea et al. 2009; Rajamma et al. 2009; Cheah and Ramli 2011). With the increased use of biomass to produce energy, the ash and residue volumes will increase in the future. Major challenges will arise relating to the efficient management of these products (James et al. 2011).

The alternate useful utilization of these wastes as catalysts in bio-diesel production is the focus of this thesis and discussed in the following chapters. Residues from previously described biomass to energy operations were collected, characterized and prepared as catalysts for use in a chemical process. The transesterification of WCO was done using the catalyst to demonstrate the process utility of the inorganic content in ash. The catalytic activity was tested in a batch process over a set of different temperatures to evaluate the highest yields possibly achieved by the two catalysts.

CHAPTER 2: **Pellet burner bottom ash as a heterogeneous catalyst for fatty acid methyl ester production**

2.1 Introduction

Biodiesel is defined as a mixture of fatty acid alkyl esters which are commonly produced from triglycerides and alcohol through transesterification reaction in the presence of alkali-catalysts. Methanol is the most widely used alcohol; and the resulting esters are known as fatty acid methyl esters (FAME). Feedstock for biodiesel is mainly food grade vegetable oils (Lee, Posarac, and Ellis 2011). The costs of these vegetable oils can be up to 75% of the total manufacturing cost, which makes biodiesel production cost approximately 1.5 times higher than those of conventional diesel (Haas, Bloomer, and Scott 2002; Phan and Phan 2008). Therefore, the biodiesel industry is influenced by the high cost, and limited availability of vegetable oil for biodiesel production (Morais et al. 2010). Also, biofuels from edible crops are not a long term solution as they do not have the potential to provide more than 10% of liquid fuel demand in developed economies (Huber and Dale 2009). The EU directive (2009/30/CE) states that Green House Gas emission savings for biodiesel made from conventional feedstock such as refined vegetable oil is about 50% and the value increases to over 80% for waste vegetable oil, animal fats and other waste products that may potentially be converted to biodiesel (Morales et al. 2011; European Comission 2013). Common wastes of vegetable origin are waste vegetable oils produced in restaurants. Other wastes of high Free Fatty Acid (FFA) content include yellow grease, brown grease (Canakci and Van Gerpen 2001), chicken fat (Lee and Foglia 2000; Arnaud et al. 2006) and animal tallow (Öner and Altun 2009). The use of waste cooking oil (WCO) as a feedstock serves to decrease the environmental impacts and costs of waste disposal and decreases the production cost of biodiesel significantly (Canakci and Van Gerpen 2001; Meng, Chen, and Wang 2008). WCO has some amount of water and FFA which direct the conventional alkali catalyzed process to undesirable saponification. Using the conventional method also makes it difficult to remove the base catalysts after a reaction, and large amount of wastewater is produced in separation and cleaning of catalyst and products (Shu et al. 2010). FFA impurities in WCO and other high fat wastes render the conventional alkali catalyzed biodiesel synthesis process open to saponification and gel formation that decreases the economy and yield, and increases and increases the product separation and purification costs (Santacesaria et al. 2007). The presence of water drives the reaction to an undesirable hydrolysis of esters and saponification. Commercial biodiesel operations usually employ a basic catalyst which is soluble in nature, like potassium or sodium methoxide. These operations also have an acid based pre-treatment step that esterifies the FFA if feedstock is not regulated for <1% FFA content (Santacesaria et al. 2007). Consequently, these homogenous acid and base catalysts are corrosive to process equipment in particular and pose a risk to fuel engines if not removed at the end of production. Their removal by aqueous quenching and neutralization is both energy and cost intensive and it directly increases the cost of production in a biodiesel processing facility. It also contributes to emulsions and gel formations in the product (Demirbas 2007).

The near future requires economic growth with sustainable environmental benefits from the use of low cost renewable energy sources (Grammelis et al. 2006; B-M. Steenari, Karlsson, and Lindqvist 1999). The increased shift to biomass use for energy may potentially generate upwards of 400 million tonnes of ash. The ash is harmful if not properly disposed. Such concerns arise from findings that nutrients largely considered useful for land application are unavailable as they are water insoluble, but dangerous trace elements such as As, Bi, Cd, Co, Hg, Mn, Se, Pb and V are present in water soluble forms (Obernberger et al. 1997; Narodoslawsky and Obernberger 1996; Callesen, Ingerslev, and Raulund-Rasmussen 2007; Reimann et al. 2008). There is a high probability of large quantities of ash becoming a source of heavy and toxic metals especially during storage and disposal or application to soils (George, Dugwell, and Kandiyoti 2007; Gogebakan and Selçuk 2009; Llorente et al. 2006; Meij and te Winkel 2007; Vamvuka, Zografos, and Alevizos 2008; Pandey, Abhilash, and Singh 2009). In the light of these findings, the proper disposal and useful utilization of this waste is very important (Vassilev et al. 2013a; Loo and Koppejan 2008; Obernberger, Brunner, and Bärnthaler 2006). Alternate uses of ash such as application to chemical processes are yet to be explored.

The production of FAME from oil via transesterification is a well studied process, as previously mentioned. The yield of the transesterification reaction is estimated by techniques such as gas chromatography, infrared spectroscopy, gel permeation and ^{1}H-NMR among others. In recent years, various studies have focused on using ^{1}H-NMR to monitor the transesterification reaction progress, kinetics and FAME yield among other parameters (Gelbard et al. 1995; Gerhard Knothe 2000; Suppes et al. 2001; Neto et al. 2004; Morgenstern et al. 2006; F. Jin et al. 2007; Ghesti et al. 2007; Cabeça et al. 2011; Anderson and Franz 2012). High-resolution NMR is fast compared to conventional analytical techniques for assessing FAME yields, such as chromatographic (GC), or gel permeation methods. Also, it is easily adapted in routine process analysis, and allows non destructive measurements of the samples (G. Knothe 2001). High-resolution ^{1}H NMR spectroscopy has been used to monitor the transesterification reaction (Cabeça et al. 2011), based on the areas of the methoxy signal at 3.7 ppm, the α-carbonyl methylene signal at 2.3 ppm (Morgenstern et al. 2006), and the areas of the glycerides signal from 4.04 to 4.25 ppm (Ghesti et al. 2007).

There are different formulae suggested in various studies to estimate the progress of reactions (Gelbard et al. 1995; Knothe 2000; Morgenstern et al. 2006; Anderson and Franz 2012). There seems to be a consensus among studies (Morgenstern et al. 2006; Cabeça et al. 2011; Anderson and Franz 2012) that the formula suggested by Knothe (2000) had incorrectly assigned five protons to the glyceryl methylenes in the range 4.10-4.33 ppm. The equation put forth by Gelbard et. al (1995) on the other hand is susceptible to interference at 2.31 ppm by FFA signals (Satyarthi, Srinivas, and Ratnasamy 2009; Anderson and Franz 2012). Recent studies (Morgenstern et al. 2006; Cabeça et al. 2011; Anderson and Franz 2012) have shifted to different assignments and formulae. The formulae listed below have varying integrations for different peaks of the ^{1}H- NMR spectra to arrive at the final yield of the reaction, but the assignment of the methyl signal is consistent across studies at approximately 3.70 ppm.

$$C_{Knothe} = \frac{5I_{ME}}{5I_{ME} + 9I_{TG}} \times 100$$

$$C_{Gelbard} = \frac{2I_{ME}}{3I_{CH2}} \times 100$$

$$C_{Morgensten} = \frac{2I_{ME}}{2I_{ME} + 9I_{OIL}} \times 100$$

$$C_{Anderson} = \frac{I_{ME}}{I_{ME} + 9I_{TM}} \times 100$$

The equation of Anderson and Franz, is precise for high resolution ^{1}H-NMR with accurate results from 400 Mhz and higher rated equipment (Anderson and Franz 2012). These high resolution techniques involve relatively expensive equipment which was not available. For the current work, the expression derived by Morgenstern et al. is used. This equation has recognized the incorrect integration by Knothe, and does not consider the 2.31 ppm integration either (Anderson and Franz 2012). It has also been used by Cabeca et al. to monitor the progress of the reaction. The use of pellet burner bottom ash as a heterogeneous catalyst for the production of FAME using waste cooking oil in a batch reactor is presented. This chapter investigates the use of a heterogeneous catalyst made from pellet burner bottom ash to produce FAME from waste cooking oil, and its efficiency at different working temperatures.

2.2 Experimental

2.2.1 Materials and Methods

Waste cooking oil was collected from both domestic and commercial cooking operations. The cooking oil was filtered using whatman (number 4) filter paper and mixed prior to use so as to ensure homogeneity of the sample. The ash (PBA) used in the experiment was obtained from a pellet burning facility that utilizes wood pellets, and is located in northern British Columbia, Canada. Methanol (> 95 %) was obtained from Fisher Scientific. Chloroform-d (> 98.9 %) with 0.03 % (v/v) TMS as internal standard for use as a solvent in the ^{1}H-NMR analysis was purchased from Sigma Aldrich. Thermo-Scientific 7500 inductively coupled plasma with a mass spectrometer (ICP-MS) was used to evaluate the elements present in ash. The samples were microwave digested in a Milestone MLS 1200 Mega digestion system using concentrated nitric acid prior to ICP analysis. The X-ray diffraction (XRD) pattern for the ash (< 150 μm) after sieving and after treatment, were taken on a Bruker D8 Advance Series II to evaluate the different phases of the inorganic content on a moisture free basis. The XRD was done using Cu-Kα1 radiation at a wavelength of 1.5406 Å with 2Θ being varied from 10° to 90°. The Scanning electron micrograph (SEM) was obtained on a Philips XL30 series microscope at an accelerating voltage of 20.0 kV and 2500x magnification. The BET surface area was determined using a Micromeritics HS 112300 machine using a 30 % Nitrogen and 70 % Helium atmosphere at 77 K. Thermo gravimetric analysis (TGA) was done on a TG 50 instrument and 10 mg of sample. The temperature was increased at 10° C/min in Nitrogen with a gas flow rate of 20 mL/min. The sample was heated to a maximum temperature of 900 °C and held there for 5 minutes.

2.2.2 ^{1}H-NMR Method

^{1}H-NMR spectra were obtained using a Bruker Fourier 300 MHz instrument. Solvent used was chloroform-d ($CDCl_3$) with 0.03 % v/v Tetra Methyl Silane (TMS) and the number of scans was set at 32. The integrated intensities of the methyl peak were considered between 3.63 - 3.69 ppm chemical shift, and 4.25 - 4.35 ppm for the oil signal (Morgenstern et al. 2006; Cabeça et al. 2011). A ^{1}H-NMR sample was prepared by dissolving 10 µL of each sample was dissolved in 800 µL of chloroform-d.

2.2.3 Catalyst Preparation

The ash was sieved through a 150-µm sieve, and the fraction < 150 µm was used to prepare the catalyst. The <150 µm fraction was dried at 105 ^{0}C for three hours and subsequently heated in a muffle furnace to prepare the catalyst. The temperature was increased to 500 °C in 30 minutes, and then ramped up from 500 – 800 ^{0}C at a heating rate of 10 ^{0}C/ min, and then maintained at 800 ^{0}C for four hours. The catalyst was then stored in a desiccator until further use.

2.2.4 Experimental Procedure for transesterification

A 300 mL EZE Seal reactor from Autoclave Engineers, USA was used for all the reactions. One hundred mL of the Waste Cooking Oil (WCO), 12:1 molar ratio of methanol to oil and 5% (wt% of oil) of solid catalyst were added into the reactor. The reactor was pressurized with N_2 before starting the reaction to ensure that methanol remained in the liquid state at the different working temperatures, followed by turning on the heater and mixer. The ramp up rate was specific to each temperature and the heat-up time was ~ 20-25 minutes for each reaction. Samples were collected over different time intervals as soon as the heat source was introduced. A valve type liquid sample outlet was used to collect liquid samples of ~1.5 mL each. The samples were collected in 2 mL borosilicate vials. The application of heat to the system and starting of mixer was considered as zero minutes for all the reactions. These liquid samples were then analysed by ^{1}H-NMR.

2.3 Results and Discussion

2.3.1 Catalyst Characterization

The ash (PBA) was particularly rich in Calcium and Potassium (Table 2.1). The concentration of Calcium was approximately 250 mg/g, and Potassium was 95 mg/g in the ash. Magnesium and Manganese were also present in relatively high concentrations, present in 50 mg/g and 26 mg/g of ash respectively. The high concentration of alkaline metals justifies the exploration of PBA as a catalyst for processes catalyzed by the metals and their carbonates and oxides. FAME production is a process that performs well with basic catalysts. The variation in particle sizes affects the physical and chemical properties displayed by the ash (Table 2.1).

Table 2.1: *Elemental concentrations in ash and catalyst from the wood pellet burner for the top six elements in decreasing order of concentration as found by ICP-MS.*

	Ash (As received)	Ash (< 150 μm)			PBA Catalyst
Element	(mg/kg)	(mg/kg)	Difference (mg/kg)	Increase (%)	(mg/kg)
Calcium	246185	262727	16542	6.7	288735
Potassium	95231	95659	427	0.4	107087
Magnesium	50910	56532	5622	11.0	68158
Manganese	25845	28114	2269	8.7	33562
Aluminium	7688	7555	-133	-1.7	9412
Iron	6659	6168	-491	-7.4	5980

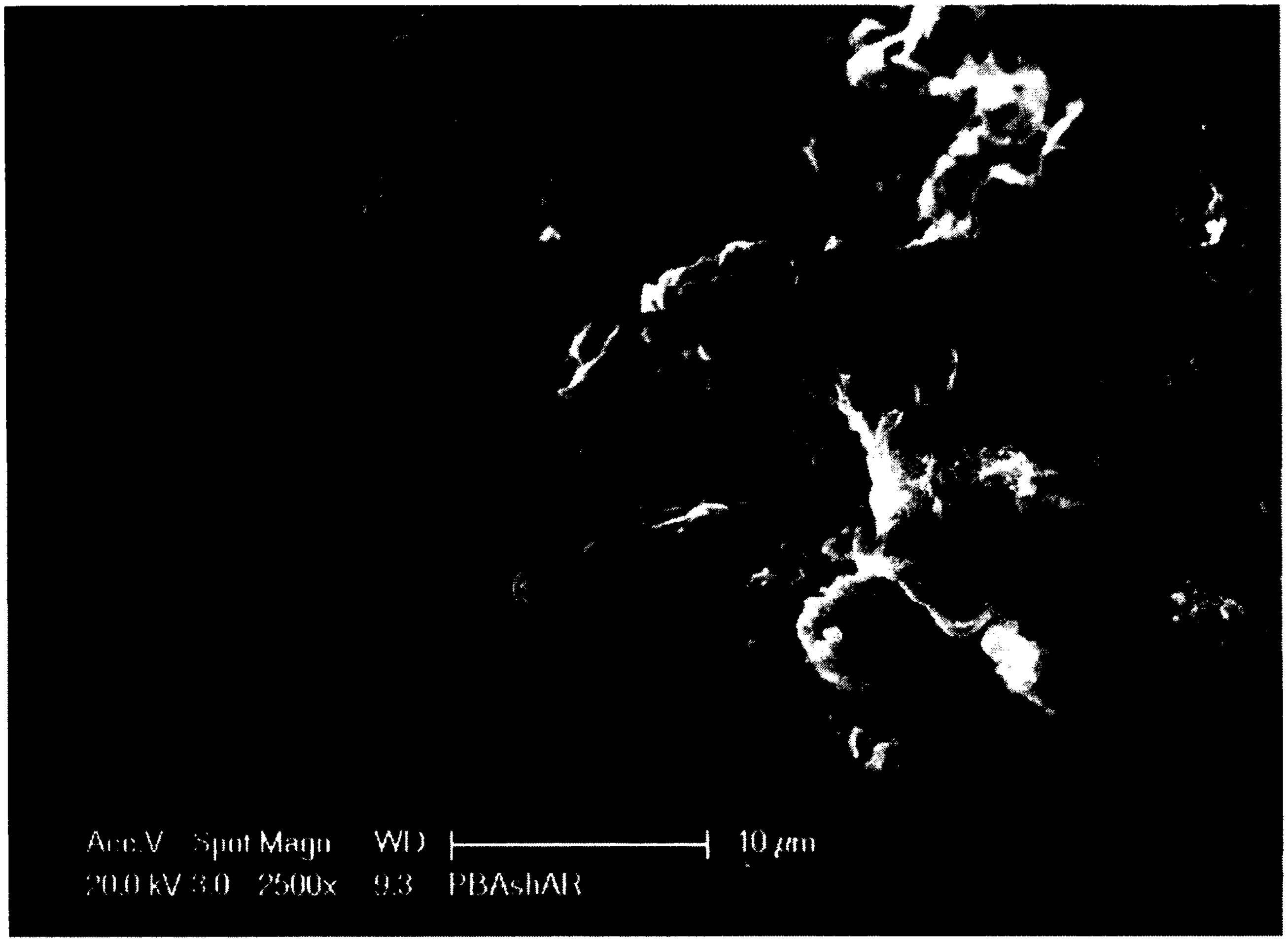


Figure 2.1: *Scanning electron micrograph at 2500x magnification for Pellet burner ash after sieving through <150 µm*

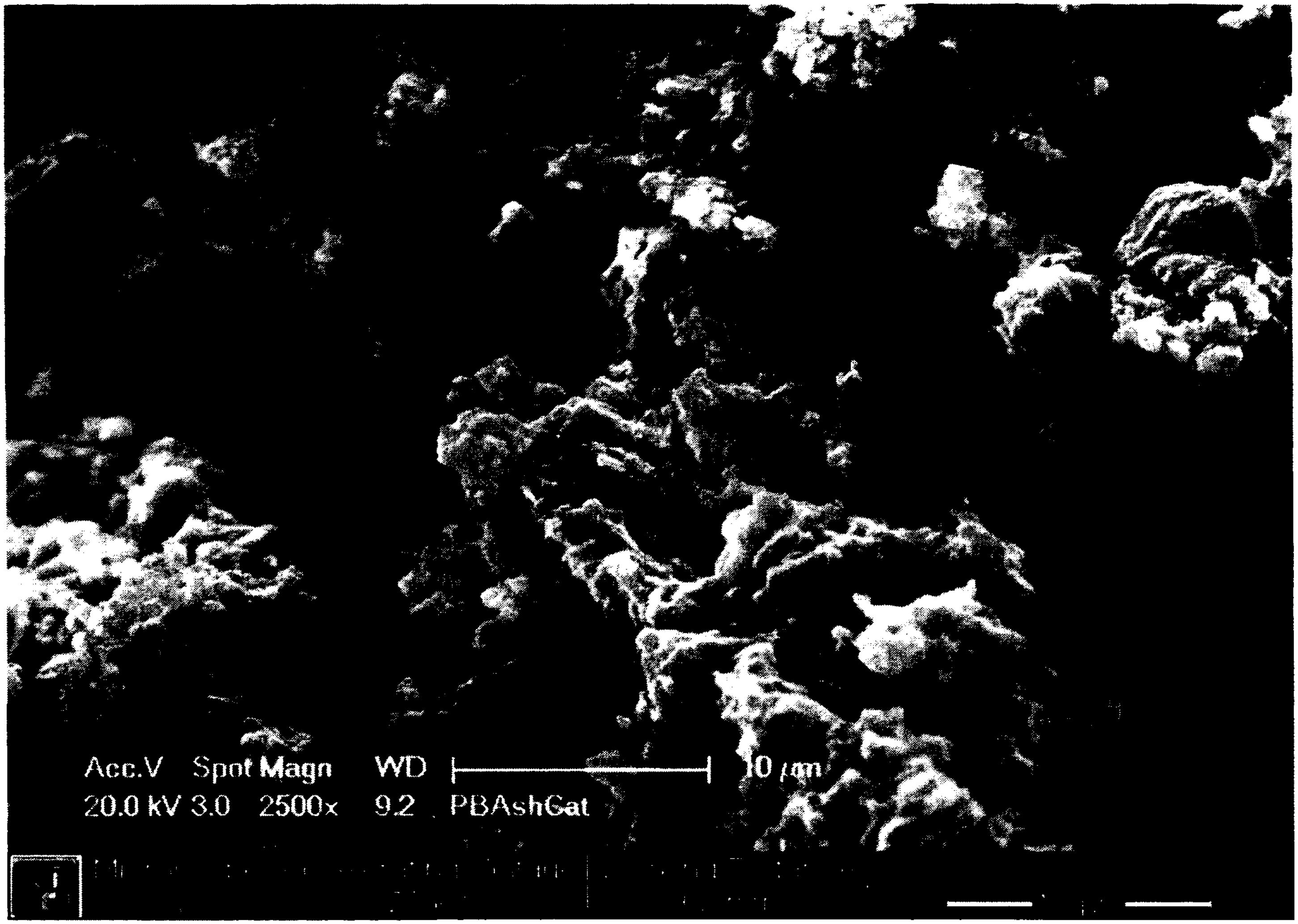


Figure 2.2: *Scanning electron micrograph at 2500x magnification for PBA catalyst.*

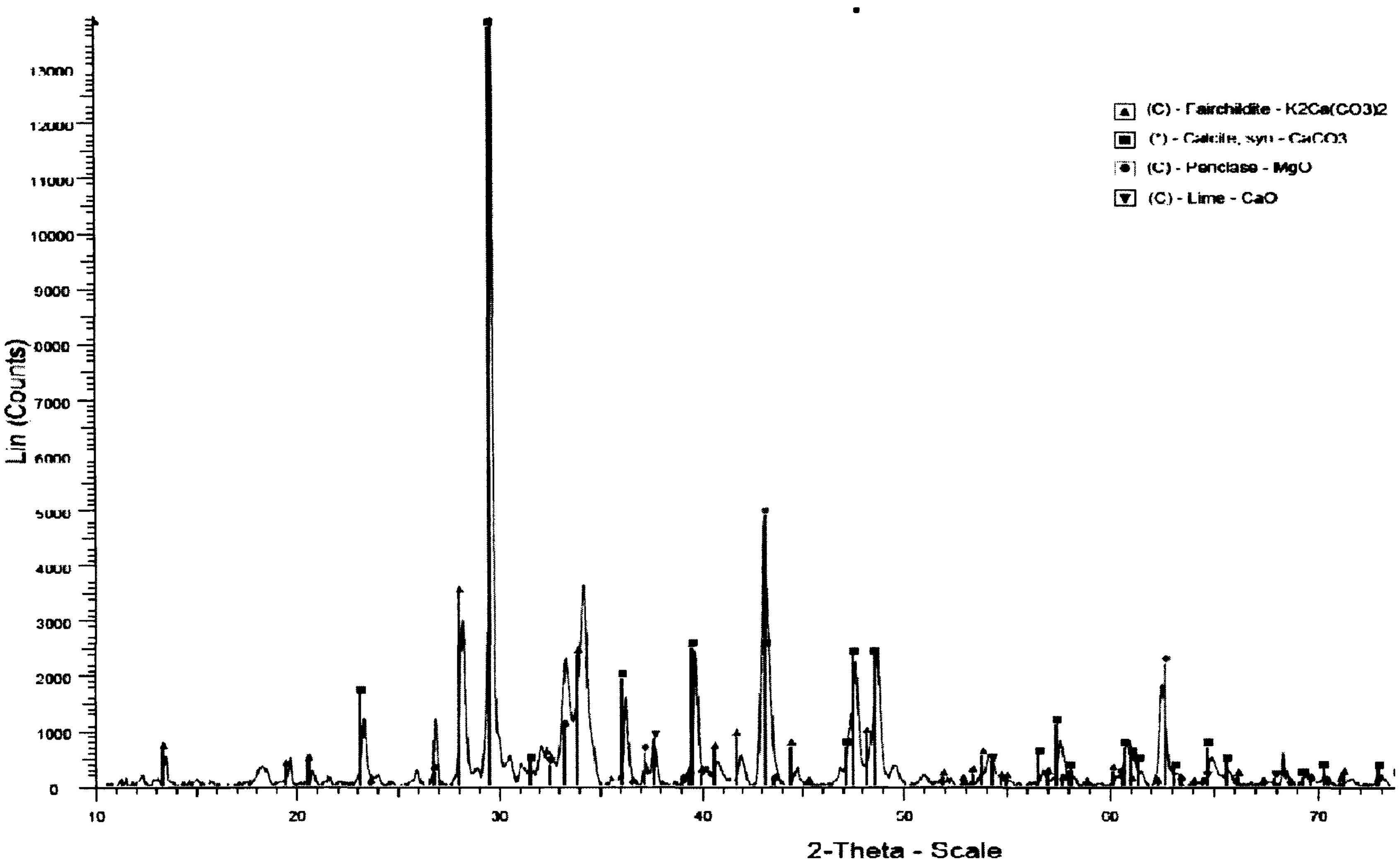


Figure 2.3 *: X-ray diffraction pattern of sieved ash (<150 μm) for* 2Θ 0° *to* 70°*. The peak markers show the relation between experimental data and best fit patterns for the identified materials.*

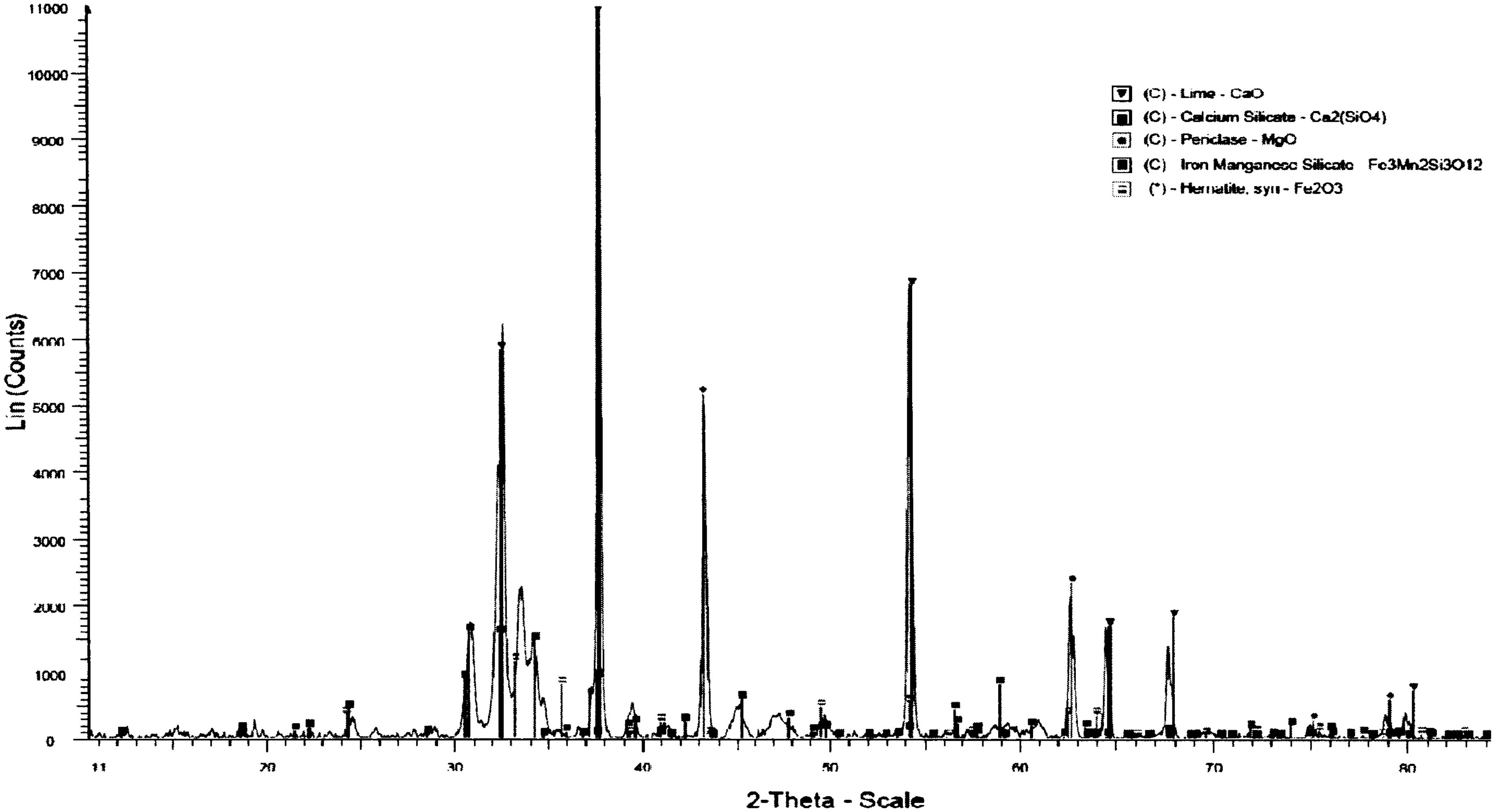


Figure 2.4. *X-ray diffraction pattern of PBA catalyst for 2Θ from 0° to 80°. The peak markers show the relation between experimental data and best fit patterns for the identified materials.*

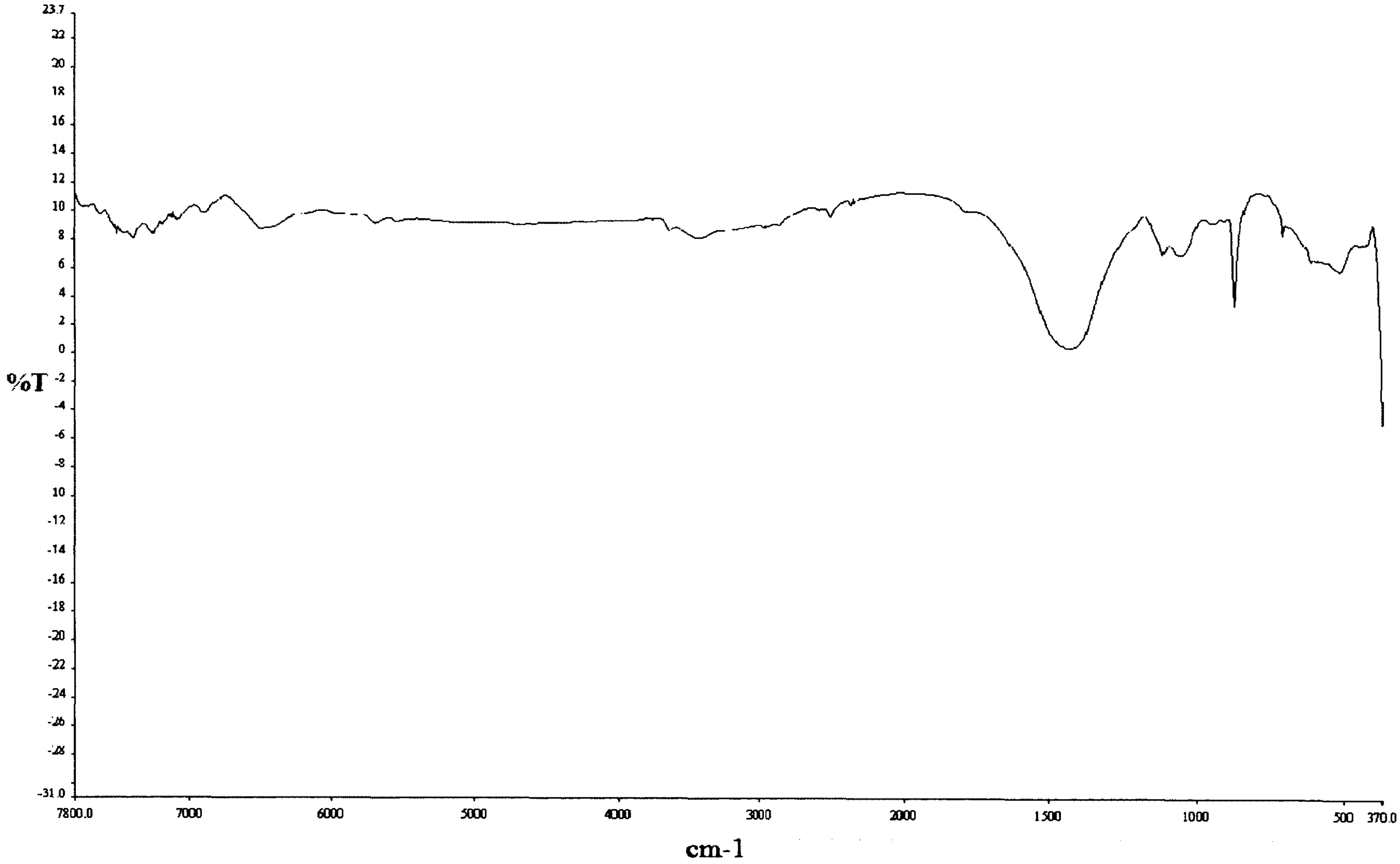


Figure 2.5 FT-IR spectroscopy of pellet burner ash (<150 μm)

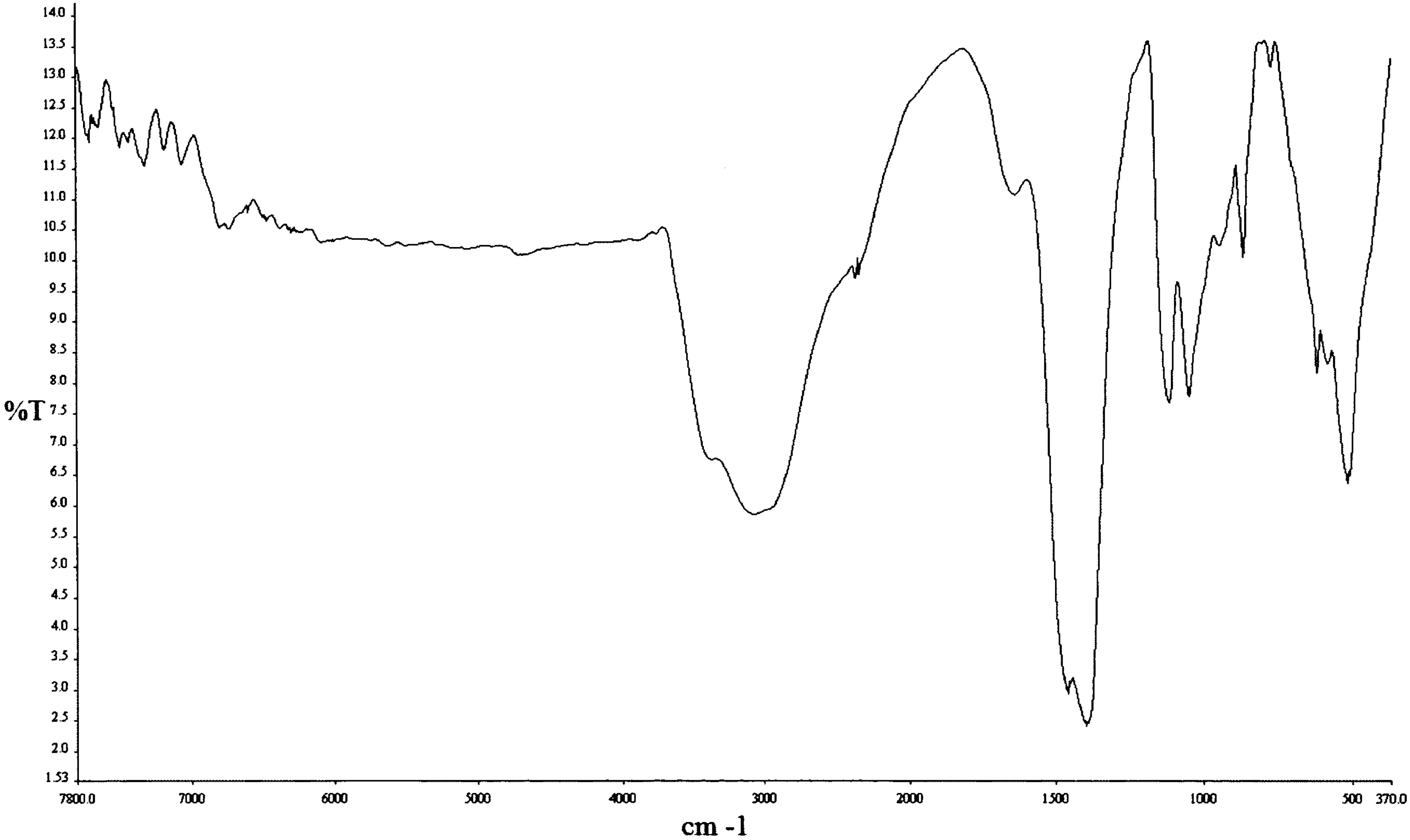


Figure 2.6 FT-IR of catalyst prepared from pellet burner ash

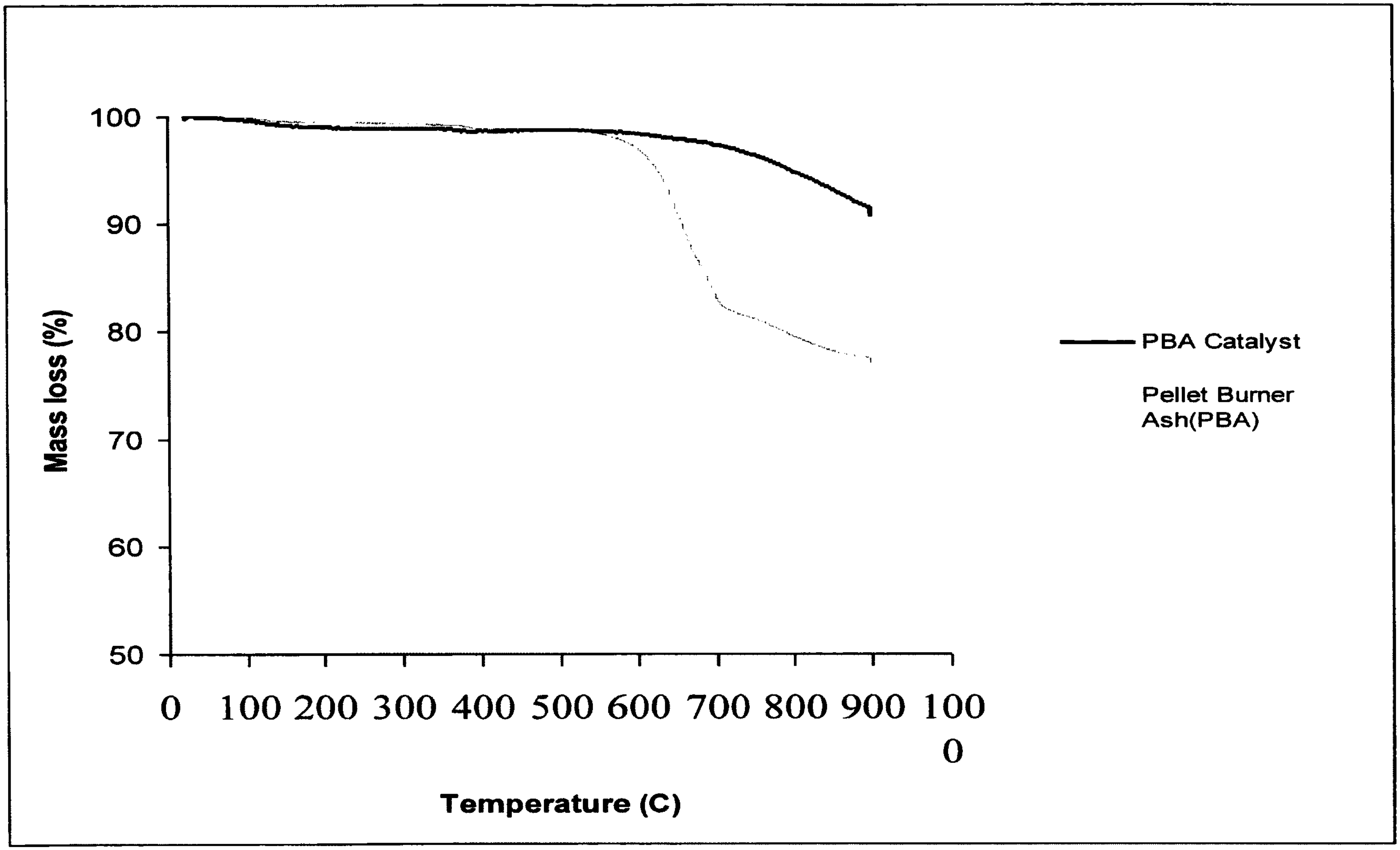


Figure 2.7 *TGA curves of catalyst and ash at heating rate of 10°C/ min. The mass losses in ash after 650°C are observed due to loss of carbonates.*

Figure 2.1 shows the SEM of the ash (< 150 μm), and catalyst after treatment. The post treatment image in Figure 2.2 displays layers of solid in a well ordered arrangement. This may be explained as the formation of calcium oxide upon treatment, present as a uniform crystal system in the material. The earlier image consisting of different metal carbonates has different phases; hence, the well ordered solid layers are absent.

The XRD pattern obtained for PBA in Figure 2.3 is in good agreement with the ICP analysis. Calcium, Magnesium and Potassium are the major elements in the ICP analysis are also found by the co-relation of the experimental XRD pattern to the reference database from the International Council of Diffraction Data (ICDD). The ash, as a waste product, is rich in inorganic content but sieving the ash improved the relative concentration of calcium as may be seen from Table 2.1. Fairchildite and Calcite are found in wood ash, and are commonly known as wood ash stones (Milton and Axelrod, 1947). The presence of Calcite, Periclase, Fairchildite and Calcium oxide is in agreement other similar studies done on XRD analysis of wood ash (Dawson and Sabina 1958) and specifically ash from biomass combustion (Steenari and Lindqvist 1997; Steenari, Karlsson, and Lindqvist 1999; Steenari and Lindqvist 1997). The FT-IR of the PBA displayed characteristic peaks at 500 cm^{-1}, 875 cm^{-1}, 1431 cm^{-1}, 3440 cm^{-1} as seen in Figure 2.5. While the peaks at 880 cm^{-1} and 1400 cm^{-1} – 1500 cm^{-1} are characteristic of $CaCO_3$ (Pouchert 1997; Kleiner et al. 2002), the other peaks at 500 cm^{-1} and 3400 cm^{-1} – 3500 cm^{-1} are attributed to MgO (Jin et al. 2009; Xie et al. 2011). The PBA catalyst in Figure 2.6 displays peaks at 519 cm^{-1}, 868 cm^{-1}, 1051 cm^{-1}, 116 cm^{-1}, 1400 cm^{-1} and 3080 cm^{-1}. The disappearance of the carbonate peaks observed in the ash is indicative of loss of the carbonates. The formation of peak at 519 cm^{-1} is attributed to CaO (Granados et al.

2007) and MgO displays peaks at 1400-1600 cm^{-1} (Jin et al. 2009; Xie et al. 2011) and 1025 – 1100 cm^{-1} (Jin et al. 2009).

Table 2.2: Semi-quantitative *composition of PBA and PBA catalyst as determined by XRD.*

Pellet Burner Ash (<150 μm)		PBA Catalyst	
Mineral	%	Mineral	%
Lime, syn	3.6	Calcium Silicate	15.2
Periclase	12.6	Lime	44.4
Fairchildite	12.9	Periclase	24.6
Calcite, syn	70.9	Iron Manganese Silicate	8.9
		Hematite, syn	6.8

The concentration of alkaline metals such as Calcium, Potassium and Magnesium increased after sieving the ash (Table 2.1) Upon treatment, the mass loss in the range of 700 – 900 °C, as seen in the TGA curve in Figure 2.7 were associated with the loss of carbonates of Calcium.

The catalyst is a solid, formed after calcination of ash from biomass combustion operations. The BET surface area of the catalyst was determined to be 2.75 m^2/g. The ash

(< 150 μm) was rich in calcite and related metal carbonates as may be seen in the XRD pattern in Figure 2.3. The phases identified by FT-IR are also in agreement with XRD results. The presence of carbonates in the ash, and oxides in the catalyst was observed by IR spectroscopy. After treatment, the XRD pattern also shows the presence of oxides as may be seen in Figure 2.4. The calcination process gives a solid with approximately 44 % Calcium oxide, and 25 % Magnesium oxide as observed by XRD. The use of these oxides in different forms for producing FAME has been studied (Kouzu et al. 2008; Xu et al. 2010; Díez et al. 2011; Olutoye and Hameed 2013). The presence of these oxides in the solid calcined ash is useful in the application of this solid as a heterogeneous catalyst.

2.3.2 Reaction yield and catalyst performance

The methyl peak is obtained at ~3.70 ppm, and the solvent peak for methanol is observed at ~3.50 ppm. TMS (0.03 % v/v) was used as an internal standard, and its peak was at 0 ppm chemical shift. The integrated intensities of the methyl peaks and triacylglycerol (TAG) in all the samples were used to calculate the yield and progress of reaction. Figure 2.8 shows the time based overlap of different spectra from 35 minutes to 95 minutes at specified reaction conditions. As the reaction progressed, the characteristic methyl peak increased in intensity. Figure 2.8 shows that the TAG signal at ~4.25 ppm decreases in intensity relative to the characteristic methyl ester peak at ~3.7 ppm, as the reaction proceeds. The TAG signal is employed for calculating the yield and is observed at 4.27 - 4.33 ppm as a doublet of doublets. The overlap from intermediates such as di and monoglycerol may lead to incorrect yield calculations based on wrong integration of peaks (Anderson and Franz 2012). The multiplet of 1,2-diaclyglycerol at 4.17 – 4.29 ppm or doublet of doublets of 1-monoacylglycerol at 4.15 – 4.25 ppm were not observed in the NMR. Figure 2.9 shows the ^{1}H-NMR of the samples at different times in the region of 4.0 - 4.5 ppm chemical shift. Figure 2.9(a) displays the region for sample collected after 35 minutes of reaction at 120 °C and Figure 2.9(b) displays the same region for the sample collected at 60 minutes of reaction at the same temperature. Interference or overlap from intermediates and other species were not observed, and the peaks of the TAG are the two doublet of doublets, ranging from 4.11 – 4.17 ppm and 4.27 – 4.35 ppm.

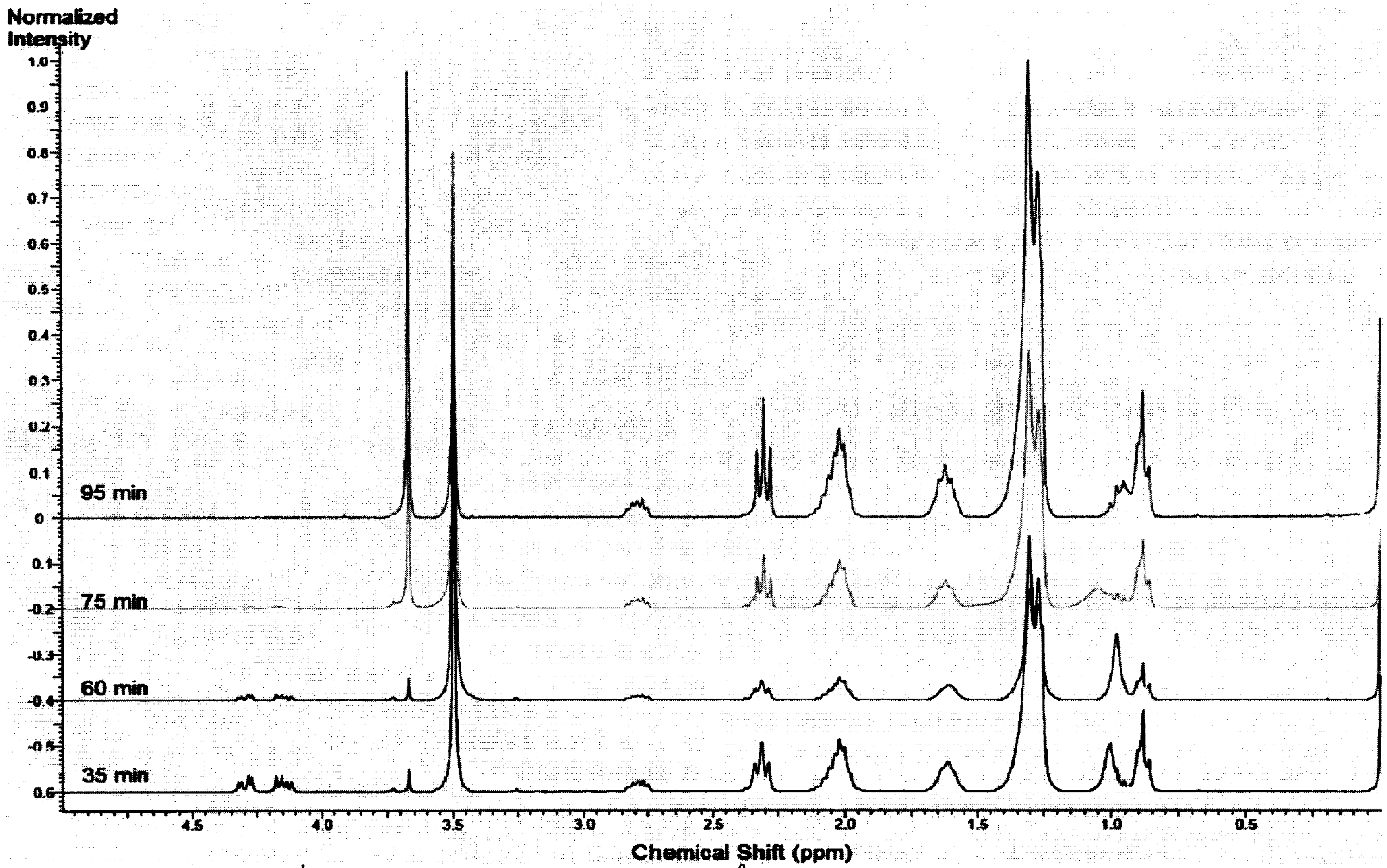
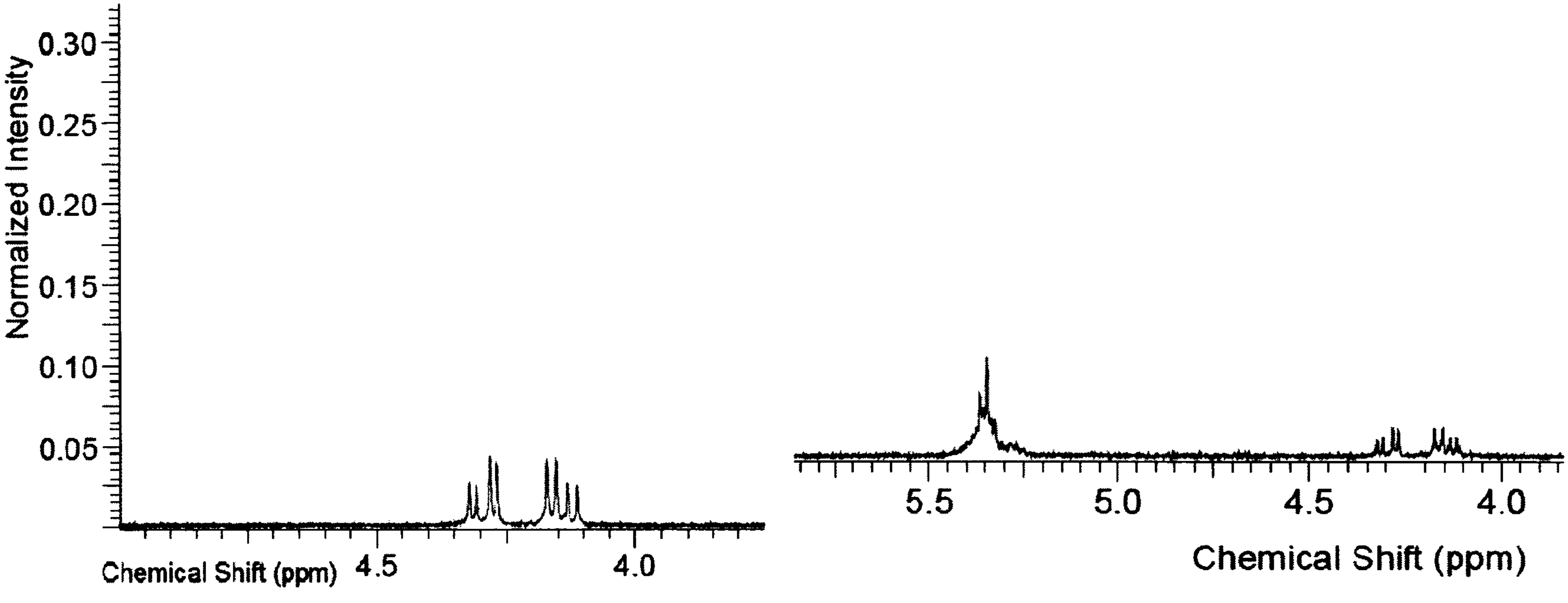


Figure 2.8. *Time based overlap* ^1H*-NMR of samples for the reaction at* 120^0C*, 12:1 Methanol to oil molar ratio and 5 wt% catalyst.*



(a)

(b)

Figure 2.9 : *^{1}H-NMR region showing Triacylglycerol (TAG) as a doublet of doublets with no overlap or interference by reaction intermediates for (a) 35 minutes and (b) 60 minutes of reaction at 120° C.*

The reaction yields at various temperatures are shown in Figure 2.10 - 2.12. The figures show that the reaction is temperature dependent. The lowest yield and rate of reaction were observed at temperature of 80 °C, seen in Figure 2.10. Approximately 25 % of the reactants were converted after an extensive period of 8 hours. At 160 °C, the reaction yield was 95 % or higher after 45 minutes. The reaction at 120 °C gave a yield of 90 % or higher in approximately 90 minutes of reaction time.

The reaction at 120 °C proceeded at a moderate rate and takes significantly lesser time than the reaction at 80 °C. Also, there is lesser risk of damage to the catalyst or lower quality of product due to excessive heating of the reactants. It is evident from the graphs in Figure 2.11 and 2.12 that the reaction achieved a stable FAME conversion after different periods of time relative to the process temperature. These plateaus indicate that the reaction has gone to the full extent and all the TAG has been utilized in the production of FAME. Governed by the conditions of the reaction, these are achieved fastest for the highest temperature in Figure 2.12, while the reaction at 80 °C did not go to completion as may be seen from Figure 2.10. The reaction at 80 °C is not feasible over extended periods of time, as the heating and constant stirring of the process medium consumes energy, which renders the process inefficient.

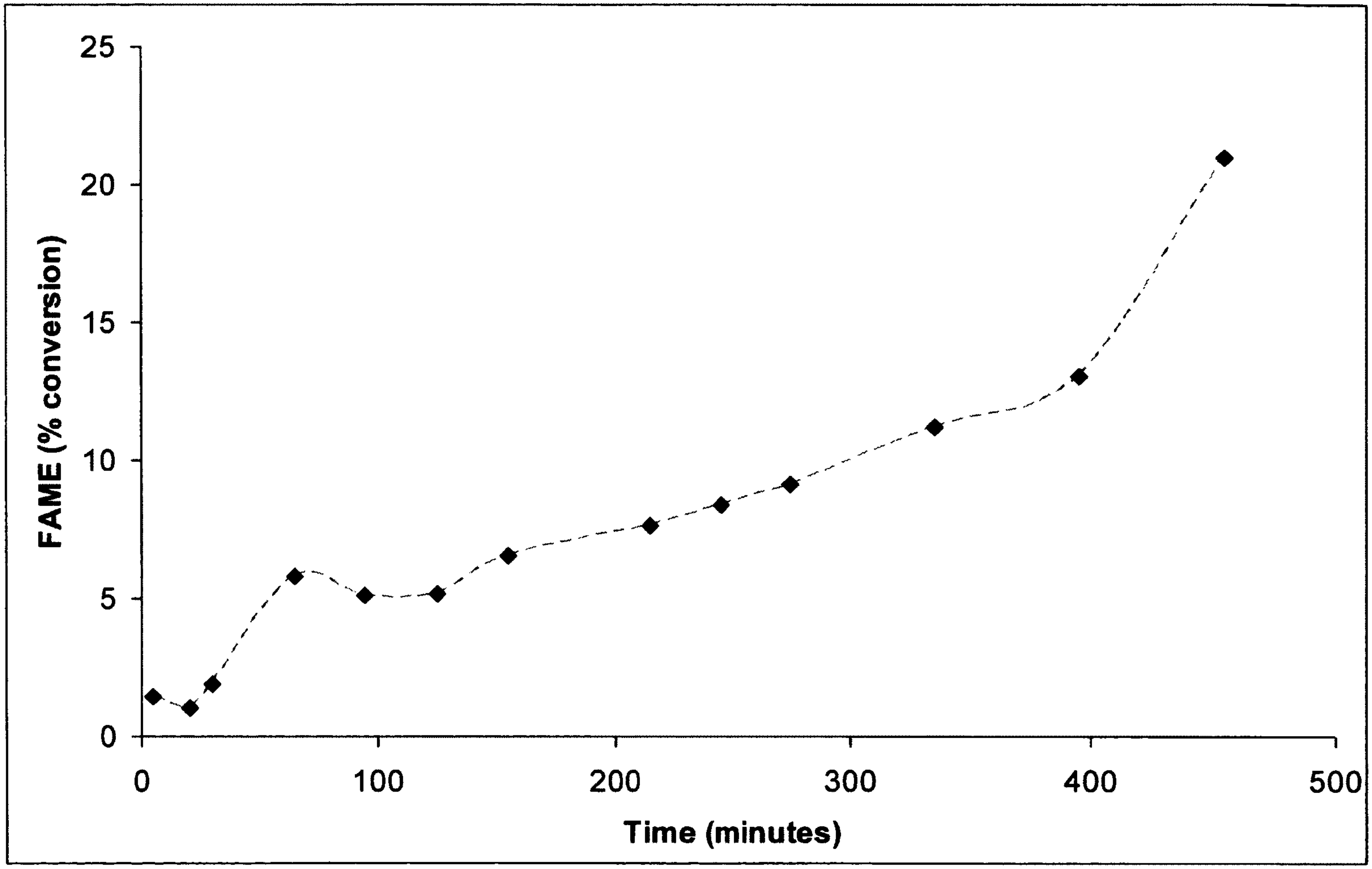


Figure 2.10 *The conversion of oil to methyl ester using calcined ash as catalyst. The reaction conditions were 5 (wt %) catalyst, 80^0 C and a 12:1 molar ratio of methanol to oil. The higher yields (≈20 %). were obtained after 300 minutes of reaction at 80^0C. The ramp up time for the reaction was 25 minutes*

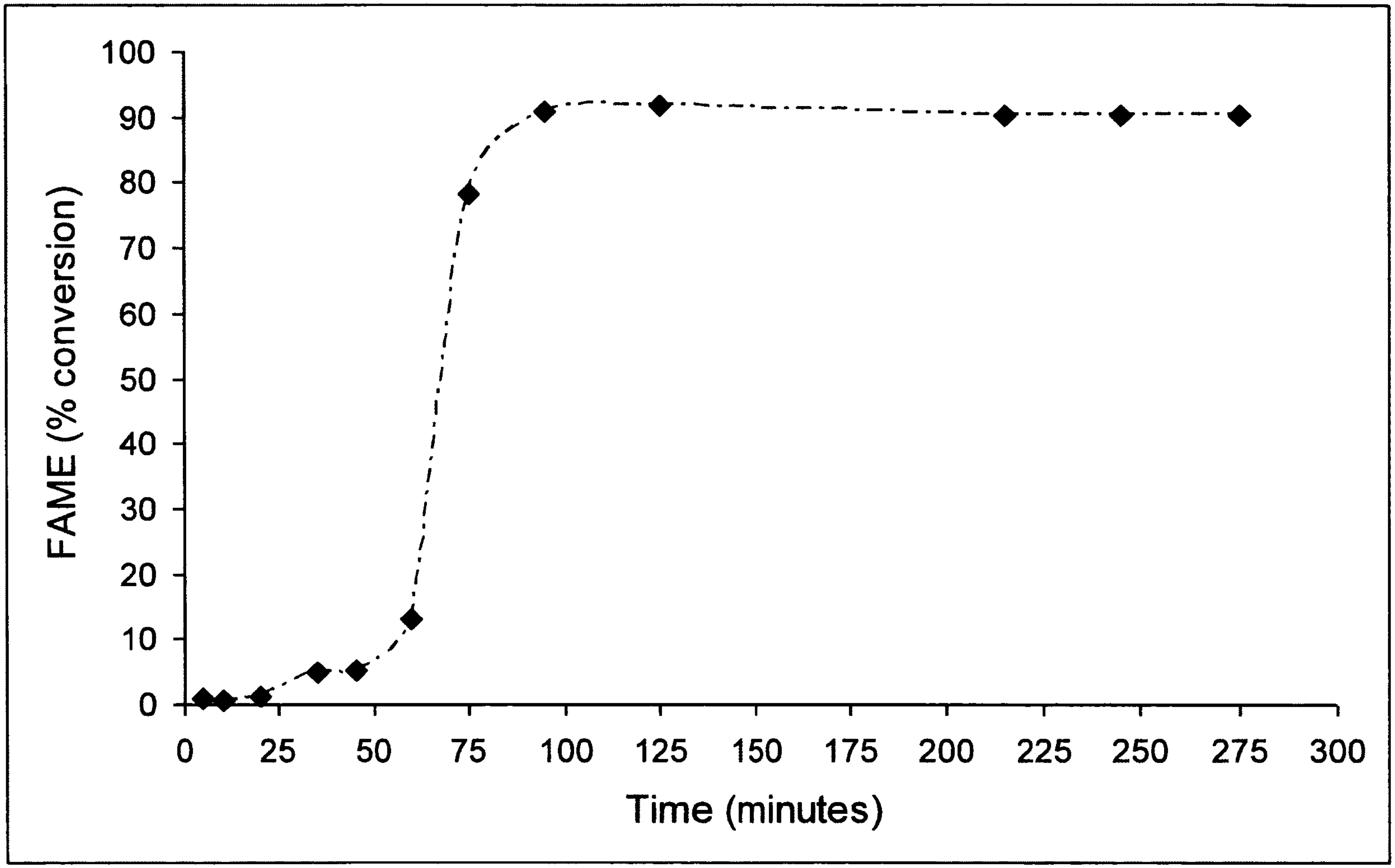


Figure 2.11 *The conversion of oil to methyl ester using PBA catalyst. The reaction conditions were 5 (wt%) catalyst, 120^0 C and a 12:1 molar ratio of methanol to oil. The highest yields (≈90 %). were obtained after 95 minutes of reaction. The ramp up time for the reaction was 25 minutes.*

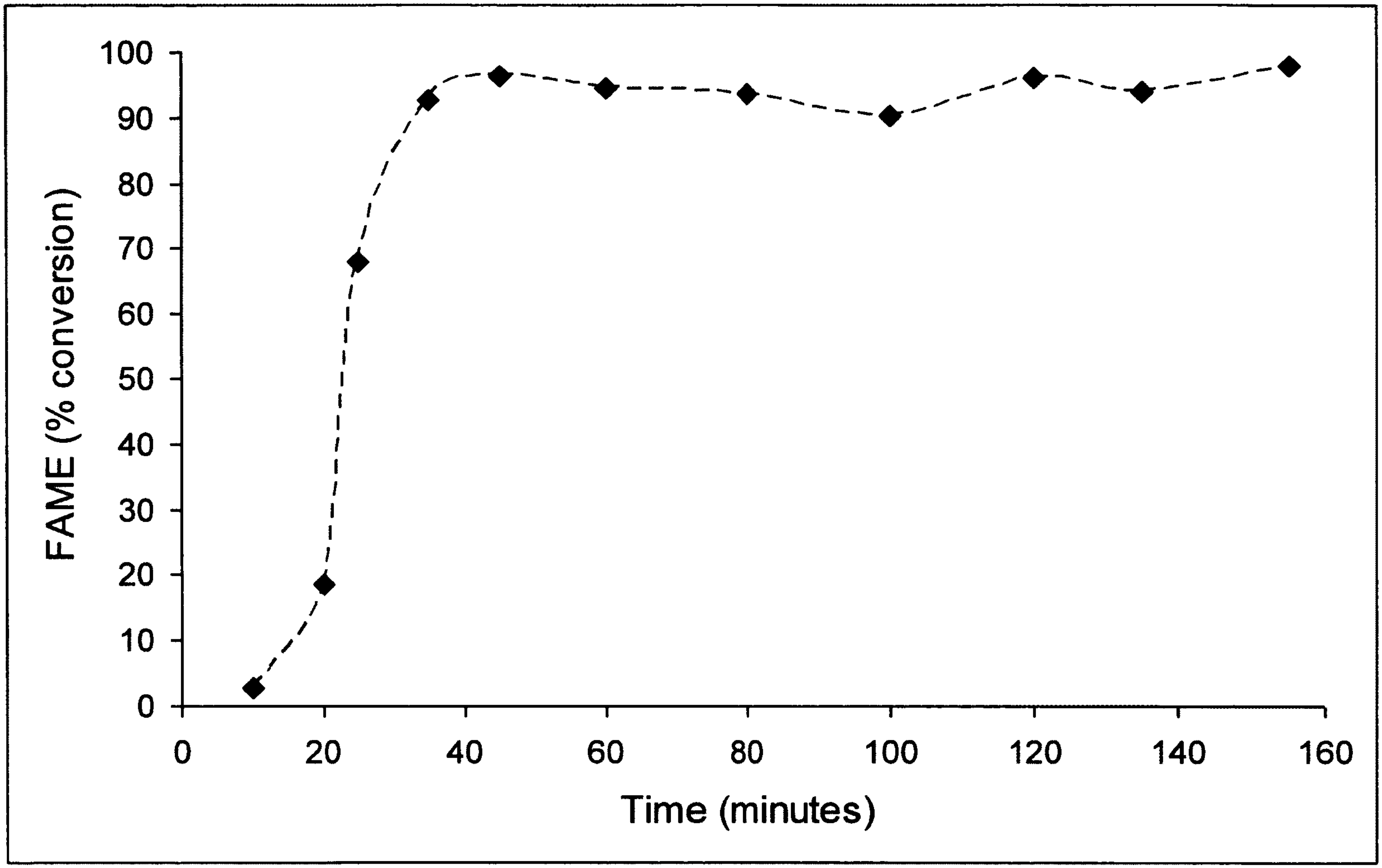


Figure 2.12 *The conversion of oil to methyl ester using PBA catalyst. The reaction conditions were 5 (wt%) catalyst, 160^0 C and a 12:1 molar ratio of methanol to oil. The highest yields (≈95 %) were obtained after 45 minutes of reaction. The ramp up time for the reaction was 25 minutes.*

2.3.3 Catalyst Reuse

To investigate the re-use capability of the catalyst the separated catalyst was washed with methanol and dried at 105 ^{0}C for 2 hours. This was then heated to 500 ^{0}C at heating rate of 10 °C/min and maintained at 500 ^{0}C for 4 hours to burn all organic content that might be present from residual reactants. This catalyst was then used at the reaction conditions of 120 ^{0}C, 5 (wt %) catalyst and 12:1 Methanol to oil molar ratio. The catalyst showed some decrease in activity. Under similar reaction conditions, it gave a decreased FAME yield, and took longer to achieve the higher yields. The reaction yield curve for the re-use is shown in Figure 2.13.

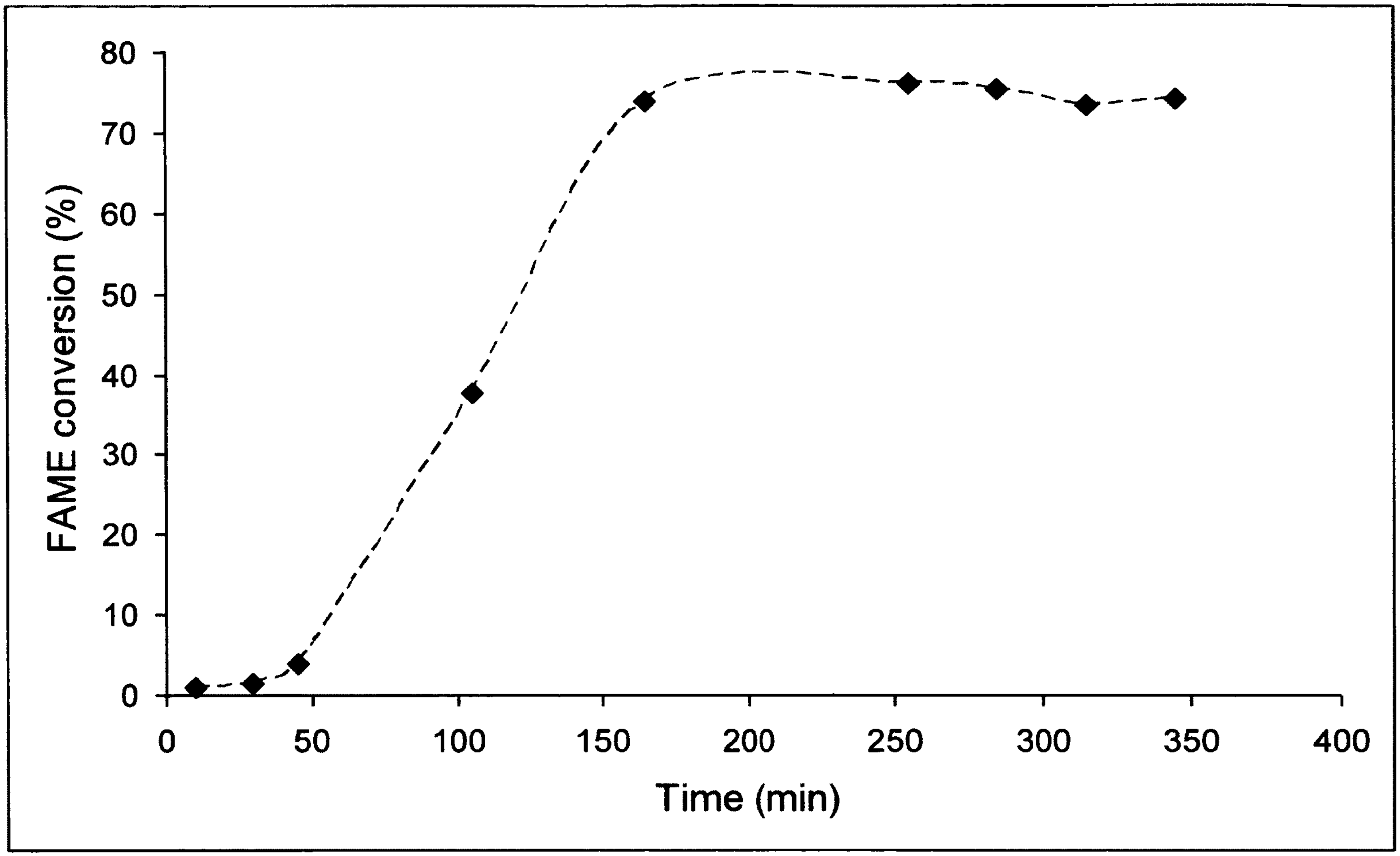


Figure 2.13 *The conversion of oil to methyl ester using recycled PBA catalyst. The reaction conditions were 5 (wt%) recycled catalyst, 120^0 C and a 12:1 molar ratio of methanol to oil. The highest yields (≈75 %) were obtained after 160 minutes of reaction. The ramp up time for the reaction was 25 minutes.*

2.4 Summary and Conclusions

Recent developments in harnessing biomass based energy in developed countries have led to the increase in production of ash as residual waste. For highly efficient processes such as pellet burners, the bottom ash produced is rich in inorganic compounds such as metal carbonates and oxides. These inorganics existing in different states in the ash may be applied to a variety of uses such as forest fertilizers, land applications, soil amendments and other known techniques. The production of ash is predicted to increase as the energy demands from renewable and sustainable sources grows and biomass is used to produce clean efficient energy. Wood pellets form a significant fuel source for small scale power facilities that utilize efficient combustion technologies and wood pellets prepared from waste wood to generate energy with lower particulate and carbon emissions. Harnessing biomass to create bioenergy is a fundamentally accepted technique to utilize waste generated by logging, pulp mill and other wood based operations. In recent years, efficient combustion techniques and waste treatment methods have led to the use of waste wood to manufacture wood pellets that are used in pellet burners, gasifiers and boilers. The resulting final product, ash is rich in inorganic content as seen from the ICP-MS and XRD analysis. The presence of inorganic carbonates was observed by characteristic powder diffraction patterns of Calcite, Fairchildite and Periclase (MgO) commonly associated with ash from woody biomass. Sieving the ash to particle sizes less than 150 μm improved the relative concentrations of inorganic content and also gave finer particles for use as a heterogeneous catalyst. After calcination, the solid analysis by XRD was done to identify the useful metal oxides and justify the application of the ash as a heterogeneous catalyst. The work presents a reliable method and sufficient proof of a process to re-use the bottom ash from wood combustion in a pellet burner facility as a potential heterogeneous catalyst for the synthesis of FAME from waste cooking oil. The highest yield of 95 % was obtained for 160 °C, 12:1 methanol to oil molar ratio, 5 wt% catalyst and 155 minutes of reaction by using this ash as a heterogeneous catalyst in the reaction. The ash and waste cooking oil have associated disposal and handling costs and pose significant issues to the operations that produce them. Waste cooking oil has been considered as a better alternative to refined vegetable oil in the production of biodiesel owing to its lower cost and reduced carbon emissions. To increasingly reduce our impact on the environment, the exploration of unique applications and alternate utilization of these waste streams is vital. The concept of utilizing two low value by-products to produce upgraded and useful products is a step in the right direction. The treatment of a readily available biomass waste and using it in a heterogeneous catalyzed process for manufacture of Fatty acid methyl esters from waste cooking oil was demonstrated.

CHAPTER 3: Biomass gasification residue as a heterogeneous catalyst for biodiesel production

3.1 Introduction

In recent years, vegetable oil based biofuels such as straight vegetable oil and biodiesel have emerged as renewable, carbon neutral alternatives and supplements to petroleum fuels (Gerpen et al. 2004; Mondal, Basu, and Balasubramanian 2008). Biodiesel is a mixture of mono alkyl esters resulting from the transesterification reaction between an alcohol and vegetable oil in the presence of a catalyst (Gerpen 2005). These esters are usually prepared by the reaction of methanol with the vegetable oil, resulting in production of fatty acid methyl esters (FAME). Biodiesel is considered as an alternative fuel due to a significant decrease in greenhouse gas emissions, particulate emissions, total hydrocarbon emissions, sulphur content, and volatile organic content as compared to petroleum diesel (Hill et al. 2006).

Fatty acid methyl esters produced from waste cooking oil by heterogeneous catalysts have been found to be cost competitive with conventional methods of biodiesel production. These relatively low costs are due to a cheaper feedstock as well as less energy intensive neutralization and cleaning of the finished product (Demirbas 2007). Waste feedstock has been found to reduce environmental impact, waste disposal costs and production costs of biodiesel (Lee and Foglia 2000; Canakci and Van Gerpen 2001;

Arnaud et al. 2006; Phan and Phan 2008; Meng, Chen, and Wang 2008; Öner and Altun 2009; Borges et al. 2011). Heterogeneous catalysts have been used in a wide number of studies, to further decrease product cleaning costs and steps to neutralize homogeneous catalyst at the end of the process (Borges et al. 2011; Kim et al. 2011; Arancon et al. 2011; Olutoye and Hameed 2013; Balakrishnan, Olutoye, and Hameed 2013).

Gasification of biomass is a simple process to convert solid material to a gaseous fuel (Bridgwater 1995). It produces a fuel gas suitable for co-firing in existing boilers, or feeding gas engines and turbines to generate electricity (Fernández-Pereira et al. 2011). Focus on utilizing biomass based ash from gasifier operations is limited to a few studies, which have explored the potential use of ash as an additive to building materials (Holt and Raivio 2005; Holt and Raivio 2006). Gasification occurs at a temperature of about 750 – 900 °C in a reducing environment; the product gases are cleaned and the purified gas is burned together with coal, oil or natural gas (Moilanen et al. 1996).

Small scale gasifier power plants have recently become commercially available to produce electricity with locally available biomass resources (Eberhardt and Pan 2013). Gasifier based energy generating operations produce solid by-products that are concentrated in inorganic constituents and unburned carbon (Gómez-Barea et al. 2009; Fernández-Pereira et al. 2011). To improve process efficiency and application, re-use of gasifier ash is recommended. Furthermore, it is important that the process conditions be optimized to achieve maximum carbon conversion.

The increase in the use biomass consumption for energy has led to an increase in ash production (Loo and Koppejan 2008). Current methods of ash disposal and utilization include landfilling, soil amendment, fertilizer for agricultural and forest land (Loo and Koppejan 2008; Vassilev et al. 2013b). Due to the presence of heavy metals, land application has associated risks with possible leachate of contaminants such as heavy metals (Izquierdo et al. 2008). Alternate applications such as using ash in construction material (Rajamma et al. 2009; G. Wang, Shen, and Sheng 2012), and as an adsorbent for pollutants (Umamaheswaran and Batra 2008; Mansha et al. 2011; Cheah and Ramli 2011) have also gained interest. The alternate application of ash in the field of heterogeneous catalysis is yet to be explored. As discussed earlier, the presence of a catalyst in biodiesel production via transesterification offers improved efficiency in production and yield. The measurement of FAME yield is done by tools such as gas chromatography, infrared spectroscopy, ^{1}H-NMR, gel permeation techniques among others.

In this study, the real time yield of the transesterification reaction for FAME production was monitored by ^{1}H-NMR. Previously, high-resolution ^{1}H NMR has been used to monitor reaction progress for transesterification of biodiesel among other parameters like degree of unsaturation, and reaction intermediates (Gelbard et al. 1995; Gerhard Knothe 2000; Suppes et al. 2001; Neto et al. 2004; Morgenstern et al. 2006; Ghesti et al. 2007; F. Jin et al. 2007; Cabeça et al. 2011; Anderson and Franz 2012). ^{1}H-NMR is a fast and reliable tool that can be easily adapted for routine non-destructive analysis of samples (Knothe 2001). Previous studies have monitored the yields by comparing the methoxy signal at 3.7 ppm (Cabeça et al. 2011), the α-carbonyl methylene signal at 2.3 ppm (Morgenstern et al. 2006) and the glyceride signal ranging from 4.04 to 4.25 ppm (Ghesti et al. 2007). As the reaction progresses, the relative intensity of the methoxy signal increases and therefore can be compared with the α-carbonyl methylene signal or the glyceride signal to confirm the conversion of FFA to biodiesel.

To determine the extent of conversion, various studies have suggested relationships based on integration of different peaks (Gelbard et al. 1995; Knothe 2000; Morgenstern et al. 2006; Cabeça et al. 2011). In these studies different formulae have been developed and reviewed. The formulae listed below show the percent conversion by using different regions for integrations. Though the integrations are of different regions in different formulae, the signal assignments are consistent throughout and detailed descriptions of each assignment may be found in the original articles (Gelbard et al. 1995; Knothe 2000; Morgenstern et al. 2006; Cabeça et al. 2011; Anderson and Franz 2012). These assignments and some details have been described previously in Chapter 2.2.1.

The various equations from these studies are listed below. For all studies, the integration of methyl ester is approximately at 3.70 ppm.

$$C_{Gelbard} = \frac{2I_{ME}}{3I_{CH2}} \times 100$$

$$C_{Knothe} = \frac{5I_{ME}}{5I_{ME} + 9I_{TG}} \times 100$$

$$C_{Morgensten} = \frac{2I_{ME}}{2I_{ME} + 9I_{OIL}} \times 100$$

$$C_{Anderson} = \frac{I_{ME}}{I_{ME} + 9I_{TM}} \times 100$$

In this study, the bottom ash from a gasifier was used as a heterogeneous catalyst in the production of FAME from waste cooking oil. The ash and the catalyst were characterized using ICP-MS, XRD, FT-IR, BET Surface area, TGA and SEM. Based on the results of XRD, ICP-MS and FT-IR the main elements and their phases were identified. The catalyst was developed and used in a batch reactor to produce FAME from waste cooking oil. The trans-esterification reaction progress was monitored by ^{1}H-NMR.

3.2 Experimental

3.2.1 Materials and methods

Waste cooking oil was collected from both domestic and commercial cooking operations and the determined acid value of oil was 3.32 mg KOH/g of sample. The cooking oil was filtered using a Whatman (number 4) filter paper, and mixed prior to use so as to ensure homogeneity of the sample. The gasifier bottom ash (GA) used to prepare the catalyst was obtained from a gasification system located on campus at the University of Northern British Columbia, Prince George, Canada. The biomass gasification system uses wood residues from a local sawmill to produce energy and has been operational since January 2011. The gasifier has a diameter of 4.3 meters and the accompanying flue gas boiler has a capacity of 4.4 MW. The bioenergy plant based on biomass gasification has an annual energy output of 61,000 GJ, and is used for campus heating.

For the solid characterization and analysis, inductively coupled plasma with mass spectrometry (ICP-MS) analysis on the ash was conducted using an Agilent Series 7500 ICP-MS machine. All samples were digested in concentrated nitric acid before analysis. The BET surface area determined by nitrogen adsorption was done on a Micromeritics HS112300 machine. The atmosphere was 70 % Nitrogen and 30 % Helium at 77 K. The thermo gravimetric analysis (TGA) was done on a TG50 instrument with 10 mg of sample. The heating rate was set at 10 °C/min, using Nitrogen gas at a flow rate of 20 mL/min. The maximum temperature was 900 °C, and the sample was held at this temperature for 5 minutes. The X-ray diffraction (XRD) analysis to determine the mineralogy of the ash was done on a Bruker D8 Advance Series II machine. The radiation used was Cu- Kα1 with wavelength of 1.5406 Å, and 2Θ was varied from 10° to 90°. The scanning electron micrographs (SEM) were obtained on a Philips XL30 series microscope operated at an accelerating voltage of 20 kV. Methanol (>95%), for use in the reaction was acquired from Fisher Scientific. The FT-IR spectra of the ash and catalyst were obtained on a Perkin Elmer 2000 system using KBr to prepare the pellets. A total of 8 scans were taken between the wavenumbers 400 cm^{-1} to 7800 cm^{-1}.

3.2.2 ^{1}H-NMR Method

The samples were analysed using ^{1}H-NMR spectroscopy to determine the yield of the reaction. The ^{1}H-NMR was taken using Fourier 300 equipment from Bruker, USA. The solvent used for ^{1}H-NMR was chloroform-d (>98.9%) with 0.03% (v/v) tetramethylsilane (TMS) as an internal standard. The number of scans for each sample was set to 32. The two peaks used to evaluate the yield were the methyl ester peak, from 3.63 – 3.69 ppm and the oil signal from 4.25 – 4.35 ppm [37, 38]. To prepare the sample, 10 μL of each sample was dissolved in 0.8 mL of solvent in an NMR tube immediately before analysis.

3.2.3 Catalyst Preparation

The gasifier ash catalyst was prepared in a two step process. The ash was sieved to obtain particle sizes <150μm which were then dried at 105 °C for 3 hours, followed by calcination in a muffle furnace. The temperature was increased from 500 °C – 800 °C at a heating rate of 10 °C/min. The material was then kept at 800 °C for four hours before being cooled to room temperature. The final catalyst was stored in a dessicator until further use.

3.2.4 Experimental Procedure

All the reactions were carried out in a batch reactor from Autoclave Engineers, USA. The EZE Seal reactor had a volume of 300 mL and was equipped with a liquid sampling outlet. The reactor was charged with 100 mL of waste vegetable oil, 12:1 molar ratio of methanol to oil and the catalyst loading of 5 % by weight of oil. The heating element was controlled by a PID controller and the ramp up time of each reaction temperature was set to 25 minutes. Nitrogen was used to pressurize the reactor to reduce the formation of a gaseous phase by methanol. The initial application of heat was considered as time t=0 and samples were collected over various elapsed times. The liquid samples were analysed using ^{1}H-NMR procedure described earlier.

3.3 Results and Discussion

3.3.1 Catalyst Characterization

A summary of the ICP-MS results is shown in Table 3.1. This includes the gasifier bottom ash (GA), sieved ash fraction and the catalyst. The ash is rich in calcium, potassium, magnesium and manganese. All these metals are residual plant nutrient metals left after biomass gasification. The high concentration of the metals justifies the application of gasifier bottom ash to processes that are catalyzed by basic catalysts. The particle size has an effect on the chemical and physical properties displayed by the ash. Table 3.1 also represents the chemical composition of sieved ash. As can be seen in Table 3.1, there was a significant improvement in the inorganic content of GA after sieving as determined by ICP-MS. The Calcium content was increased by 33 % and Magnesium by 27 % on segregating the GA to <150 μm particle size. The inorganic content is vital as it provides the possibility of catalytic properties. The BET surface area of the GA catalyst was 7.1 m^2/g. The major mass loss observed in the sieved bottom ash is initiated at approximately 650 °C, losing about 25 % of the sample mass by 700 °C (Figure 3.1). Mass losses in this range are associated with release of carbon dioxide from metal carbonates such as calcium carbonate (Fernández-Pereira et al. 2011). The increase in inorganic content of the catalyst noted in the ICP-MS may be explained by this mass loss.

Table 3.1: *Elemental concentrations in GA, GA <150μm, and GA catalyst from the wood waste gasifier for important elements in decreasing order of concentration as determined by ICP-MS.*

	Gasifier Bottom Ash (As received)	Gasifier Ash (<150 μm)	Relative increase after sieving	Gasifier ash catalyst
Element	(mg/kg)	Concentration (mg/kg)	(%)	(mg/kg)
Calcium	124946	167030	33.7	224021
Potassium	20077	18430	-8.2	17496
Magnesium	12308	15733	27.8	22993
Manganese	14852	15936	7.3	11844
Aluminium	6522	8463	29.8	20026
Iron	12339	12814	3.8	15574

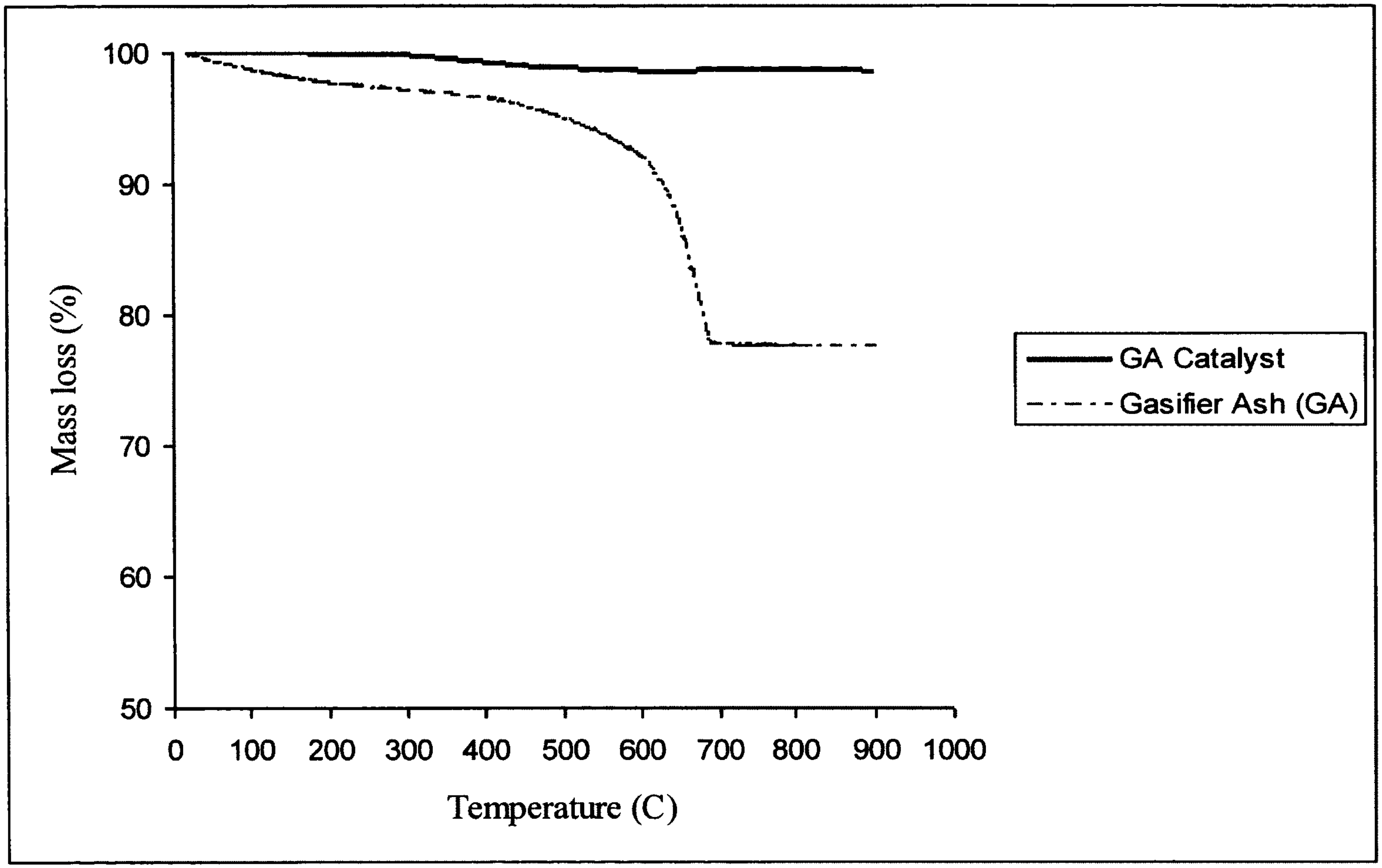


Figure 3.1. *TGA curves of catalyst and ash at heating rate of 10°C/ min.*

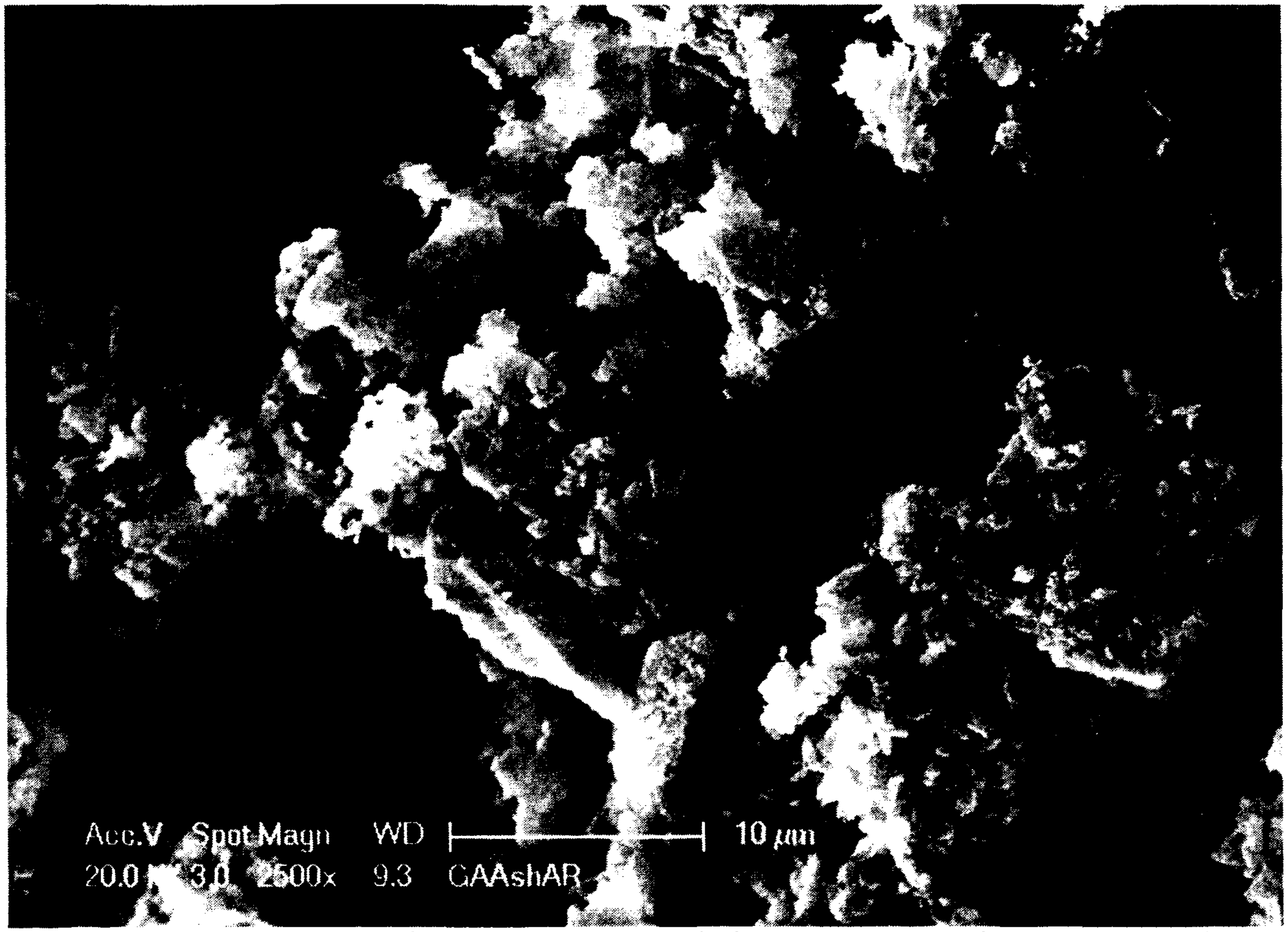


Figure 3.2 *:SEM image at 2500x magnification of gasifier ash as received after sieving to particle size <150µm. The acceleration voltage was 20 kV.*

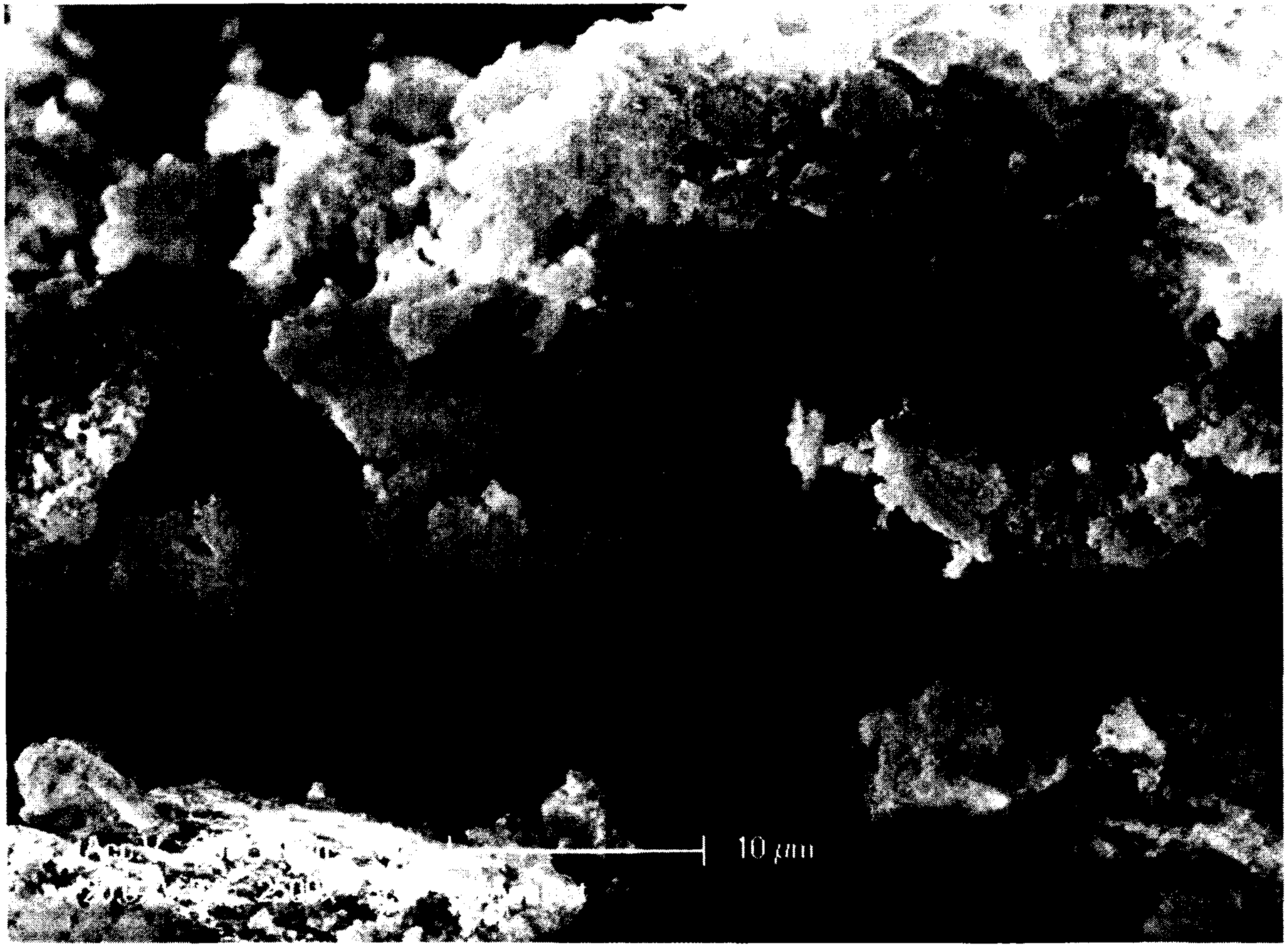


Figure 3.3: *SEM image at 2500x magnification of calcined ash used as catalyst. The accelerating voltage was 20kV.*

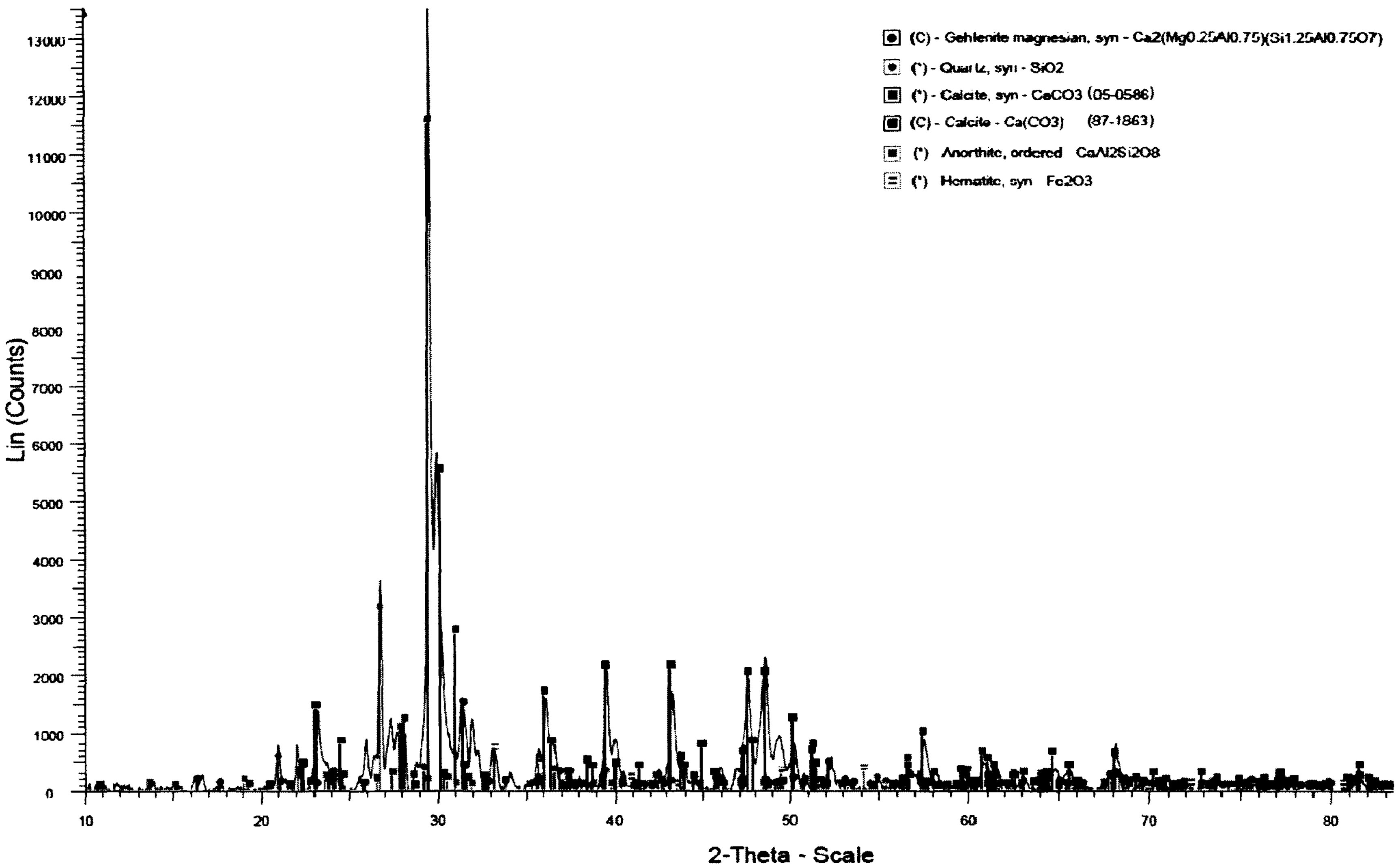


***Figure 3.4**: XRD of GA (<150 μm) before calcination for 2Θ 0^{0} to 80^{0}. The different peak patterns marked over the experimental pattern show the relation between experimental data and best fit patterns for the identified materials. The match was acquired using EVA software and ICDD powder diffraction database.*

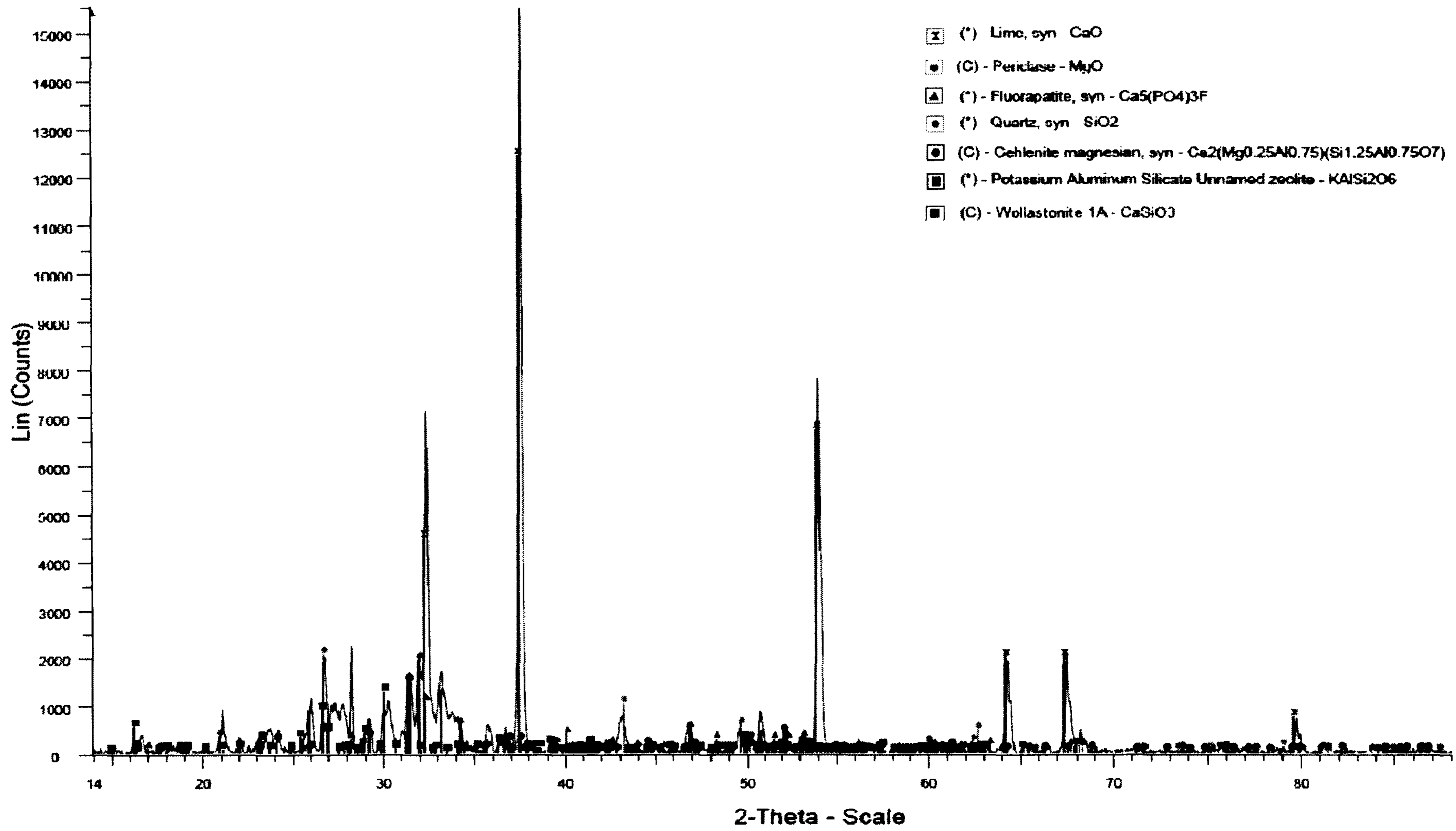


***Figure 3.5**: X-ray diffraction pattern of GA catalyst prepared after calcination, for 2Θ 0^0 to 85^0. The different peak patterns marked over the experimental pattern show the relation between experimental data and best fit patterns for the identified materials. The match was acquired using EVA software and ICDD powder diffraction database.*

Figure 3.2 and 3.3 show the SEM of GA and GA catalyst respectively. The first image shows a surface with no uniformity, which might be attributed to the presence of a variety of phases of carbonates and silicates. The second image shows material arranged in layers, in a somewhat orderly manner, indicative of the presence of a more uniform crystalline system in the ash after calcination.

The XRD patterns shown in Figures 3.4 and 3.5 give an accurate picture of the mineralogy of the gasifier bottom ash and the catalyst respectively. The ash is found to be rich in Calcite, Gehlenite, Anorthite, Quartz, Fluorapatite and Haematite as can be seen in Figure 3.4. Studies on investigating the mineralogy of biomass ashes have reported the presence of Calcite (Vamvuka 2009; B.-M. Steenari and Karlfeldt Fedje 2010; Singh et al. 2011; Nordgren et al. 2013), Gehlinite (B.-M. Steenari and Lindqvist 1997; Vassilev, Braekman-Danheux, and Laurent 1999; Pettersson et al. 2008), Anorthite (Fryda et al. 2006; Llorente and García 2008; Koukouzas et al. 2009), Quartz (Olanders and Steenari 1995; Vamvuka, Troulinos, and Kastanaki 2006; Vamvuka and Kakaras 2011; Werkelin et al. 2011; Xiao et al. 2011; Andrea Jordan and Akay 2012; Boström et al. 2012), Haematite (Olanders and Steenari 1995; C. Wang et al. 2011; Werkelin et al. 2011; Boström et al. 2012) and Fluorapatite (Jenkins, Bakker, and Wei 1996; Deydier et al. 2005). Also, studies focused specifically on biomass gasification bottom ash have found these minerals to be present in abundance (B.-M. Steenari and Lindqvist 1997; Andrea Jordan and Akay 2012; Rocca et al. 2012). Calcite was first known to be a major component of fused wood ash stones (Milton and Axelrod, 1947). Aluminosilicates are also documented components of ash originating from woody biomass (Steenari and Lindqvist 1997; Vassilev, Braekman-Danheux, and Laurent 1999; Osán et al. 2002;

Pettersson et al. 2008; Fryda et al. 2010). Periclase is present in ash residue produced by operations utilizing combustion of biomass to generate energy (Olanders and Steenari 1995; Steenari and Lindqvist 1997; Vassilev, Braekman-Danheux, and Laurent 1999; Pettersson et al. 2008; Koukouzas et al. 2009; Steenari and Karlfeldt Fedje 2010; Vamvuka and Kakaras 2011; Boström et al. 2012). On calcination, the dominant phase in the catalyst is lime (CaO), accounting for 70% of the mineral present in sample (Figure 3.5). Other phases identified include periclase (MgO) and calcium silicate. The XRD data corroborates with the TGA mass losses associated with decomposition of carbonates to release carbon dioxide. The relative semi-quantitative data of the identified materials is presented in Table 3.2.

Table 3.2: *Semi-quantitative composition of GA and GA catalyst as determined by XRD*

Gasifier ash (<150 µm)		Gasifier ash catalyst	
Mineral	%	Mineral	%
Calcite, syn	44.2	Lime, syn	70.9
Calcite	20.9	Wollastonite	7.9
Anorthite, ordered	21.4	Fluorapatite, syn	7.4
Hematite, syn	2.1	Potassium Aluminium Silicate	5
		Gehlenite magnesian, syn	3.4
		Quartz, syn	3.4
		Periclase	1.9

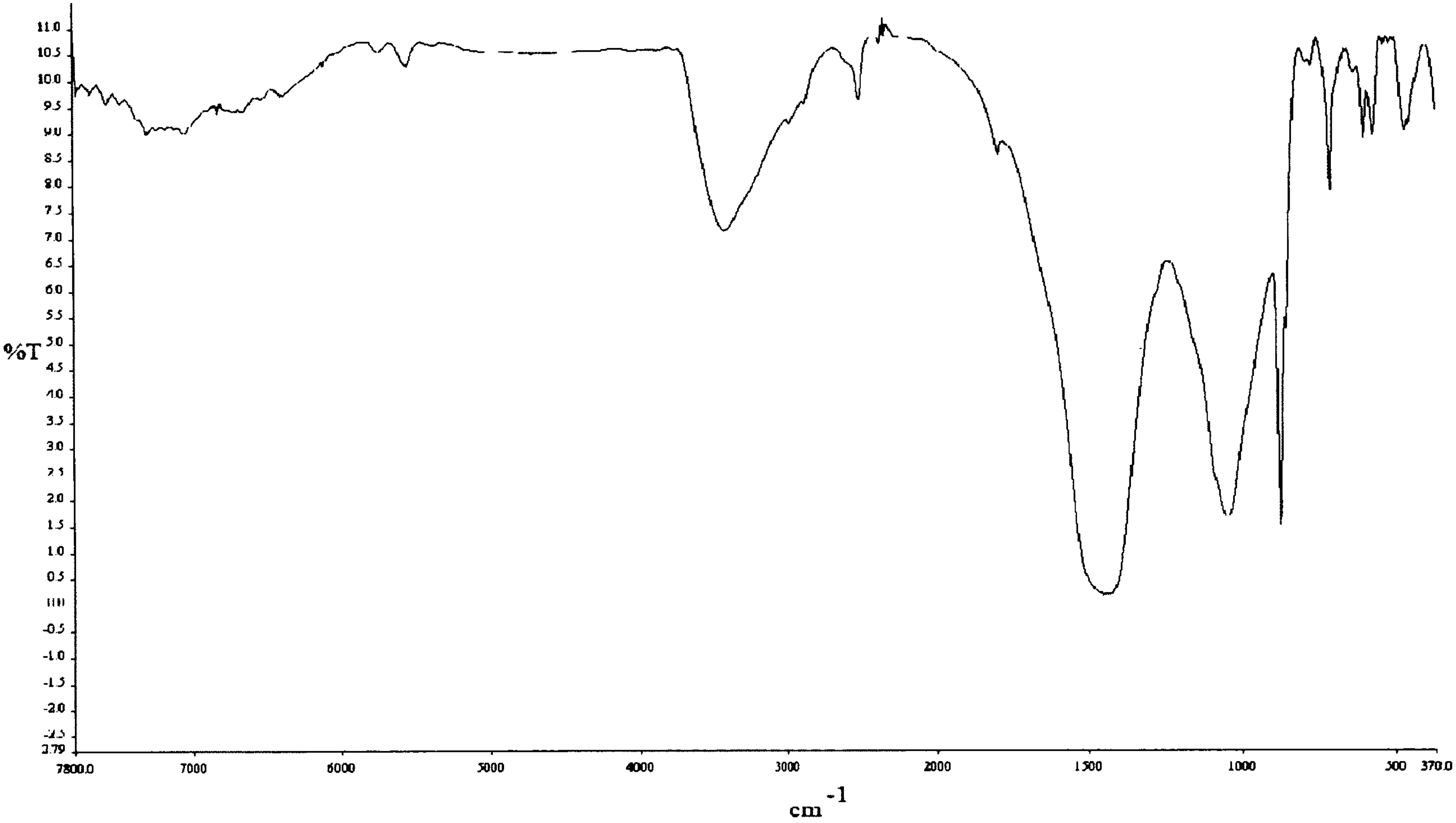


Figure 3.6: FT-IR spectrum of gasifier ash <150 μm.

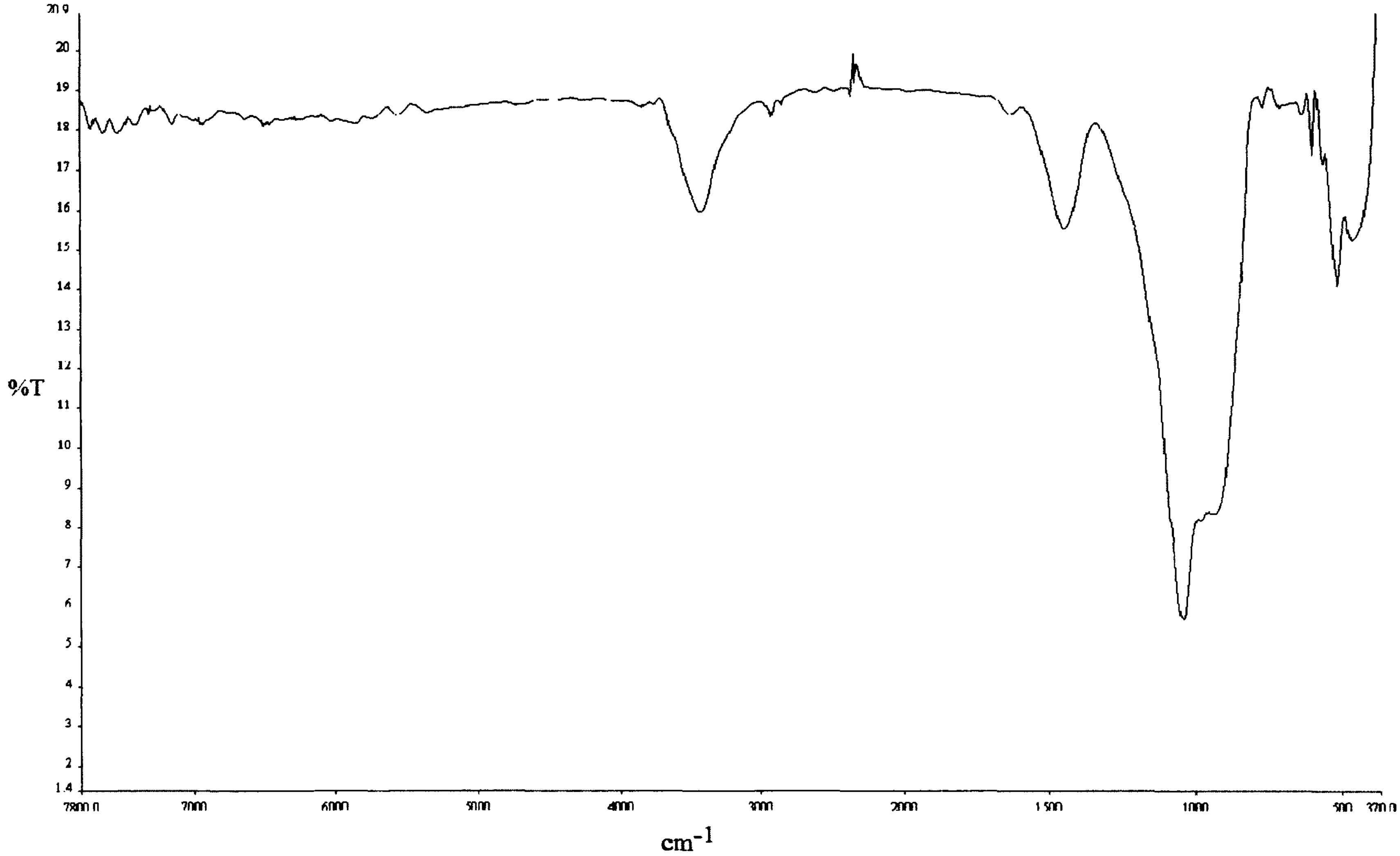


Figure 3.7. *FT-IR spectrum of catalyst prepared upon calcination of the ash.*

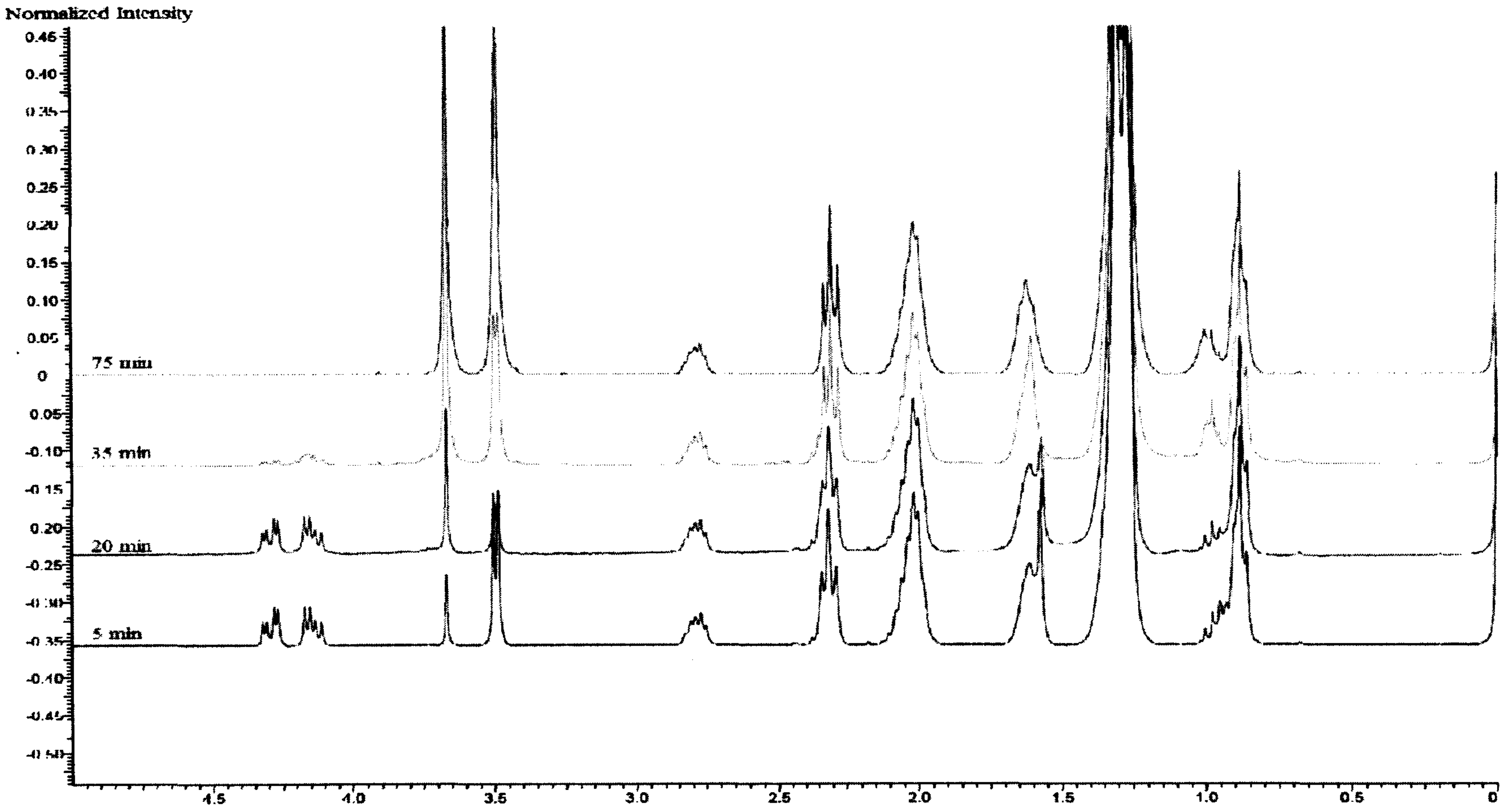
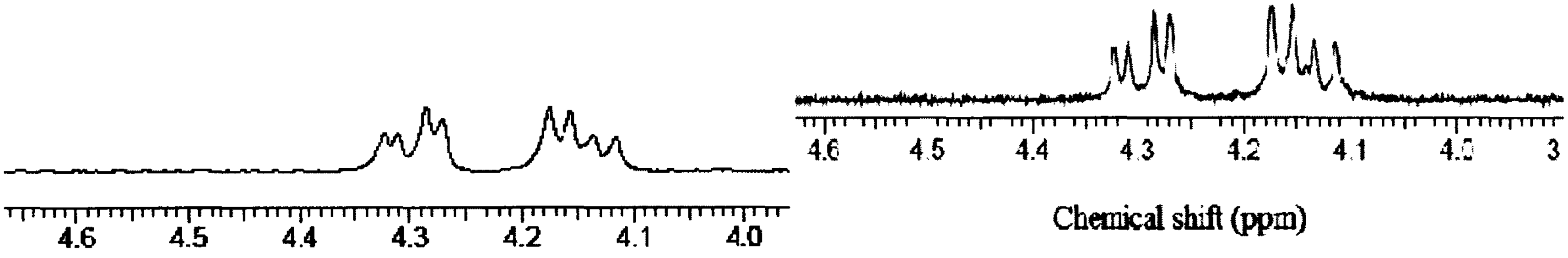


Figure 3.8. *^{1}H-NMR spectra overlap of samples at different times, for the reaction at 120^{0}C, 12:1 Methanol to oil molar ratio and 5 wt% catalyst.*



(a)

(b)

Figure 3.9: *^{1}H-NMR region from 4 – 4.5 ppm chemical shift showing Triacylglycerol (TAG) as a doublet of doublets with no overlap or interference by reaction intermediates for (a) 90 minutes at 65° C and (b) 20 minutes at 120 °C.*

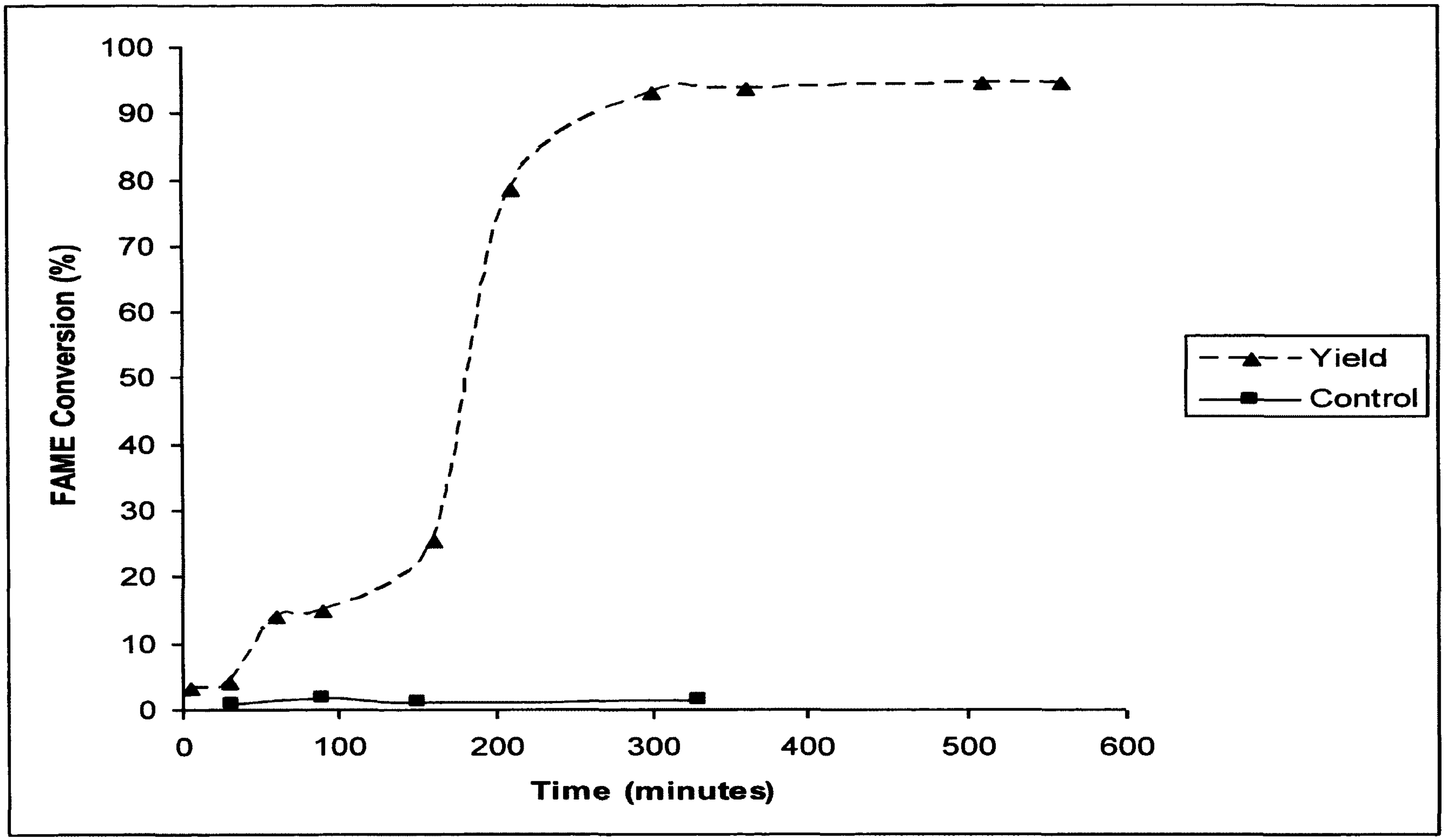


Figure 3.10: *The conversion of oil to methyl ester using GA catalyst and the control reaction using untreated ash. The reaction conditions were 5 (wt %) catalyst, 65^0 C and a 12:1 molar ratio of methanol to oil. The higher yields (≈93 %) were obtained after 300 minutes of reaction. The ramp up time for the reaction was 25 minutes.*

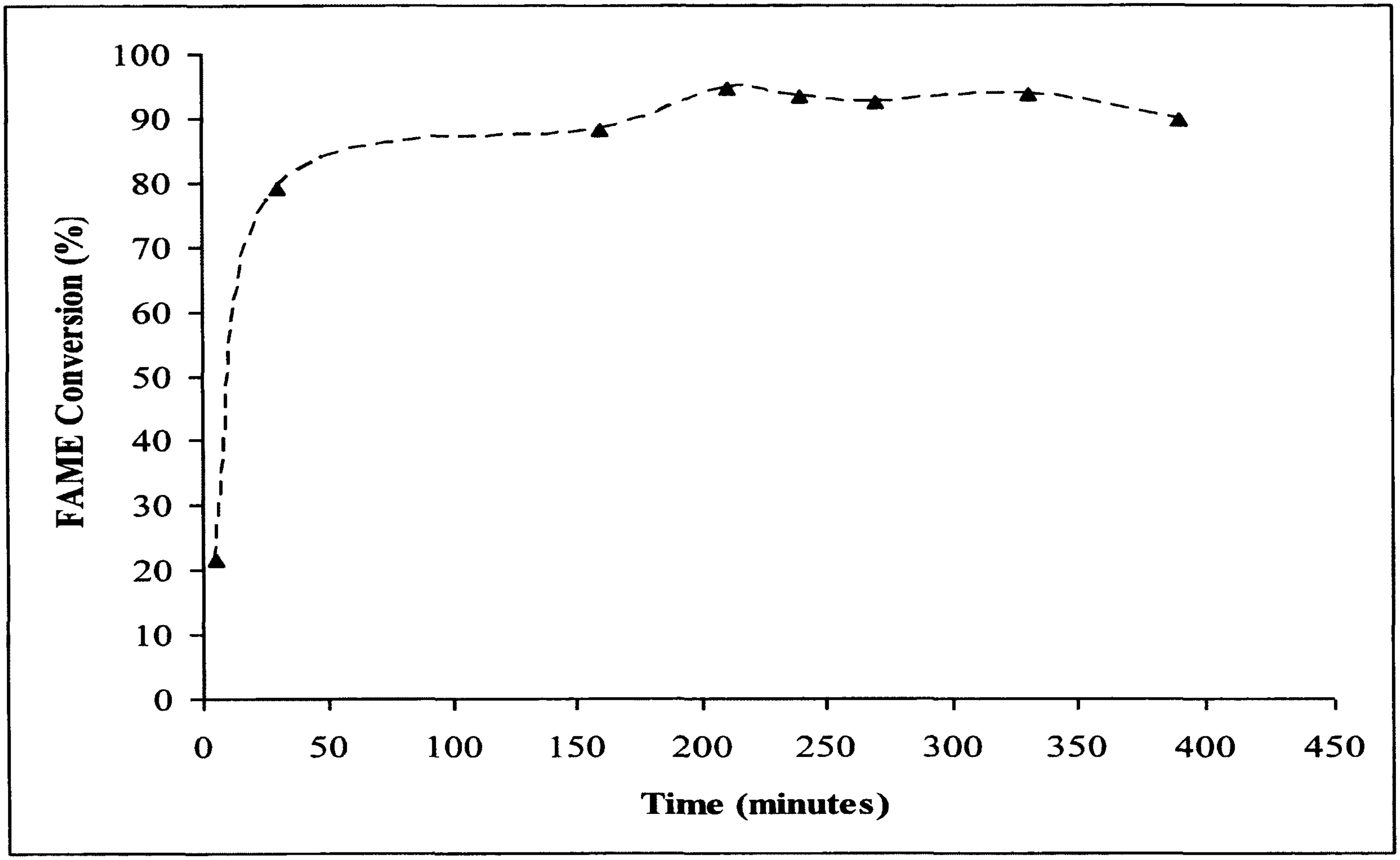


Figure 3.11: *The conversion of oil to methyl ester using GA catalyst. The reaction conditions were 5 (wt %) catalyst, 80^0 C and a 12:1 molar ratio of methanol to o7il. The higher yields (≈92 %). were obtained after 160 minutes of reaction. The ramp up time for the reaction was 25 minutes.*

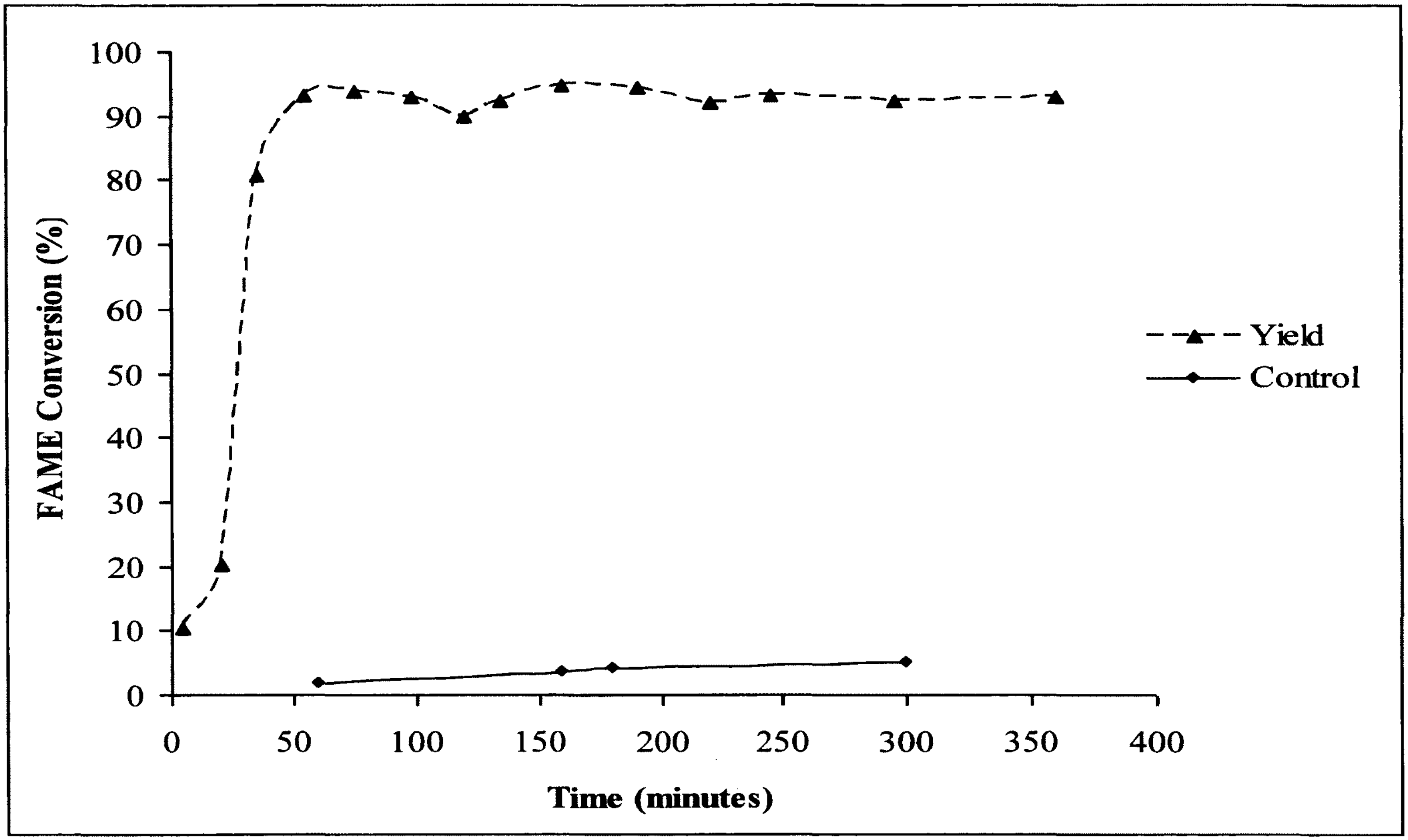


Figure 3.12: *The conversion of oil to methyl ester using GA catalyst and control reaction using untreated ash. The reaction conditions were 5 (wt %) catalyst, 120^0 C and a 12:1 molar ratio of methanol to oil. The higher yields (≈93 %). were obtained after 75 minutes of reaction. The ramp up time for the reaction was 25 minutes.*

The presence of calcite, calcium oxide and fluorapatite identified by XRD are also confirmed by FT-IR spectra of gasifier ash and catalyst. The ash spectrum observed in Figure 3.6 shows peaks at wavenumbers 712 cm^{-1}, 874 cm^{-1}, 1051 cm^{-1} and 1456 cm^{-1}. These peaks confirm the presence of calcium carbonate, which displays characteristic peaks at 715 cm^{-1}, 880 cm^{-1} and 1400-1500 cm^{-1} (Pouchert 1997; Kleiner et al. 2002; Rodriguez-Blanco, Shaw, and Benning 2011). The FT-IR spectrum shown in Figure 3.7 does not contain the peaks specific to calcium carbonate confirming the release of carbon dioxide from the ash. It has sharp peaks at 519 cm^{-1}, 604 cm^{-1}, 1043 cm^{-1} and a broad peak in the region closer to 500 cm^{-1}. The broad peak up to 500 cm^{-1} is characteristic of CaO (Granados et al. 2007), and also the peaks between 1419 cm^{-1} – 1479 cm^{-1} are attributed to the presence of CaO surface exposed to air (Witoon 2011). Some remaining peaks are attributed to fluorapatite which is in agreement with XRD analysis as well. Fluorapatite displays characteristic peaks at 520 cm^{-1}, 605 cm^{-1} and 1050 cm^{-1} (Bhatnagar 1967). The FT-IR and XRD analysis have identified similar compositions for both ash and catalyst. The agreement of these two analysis shows that the dominant phases were correctly identified.

3.3.2 Reaction yield and catalyst performance

The monitoring of the reaction yield was done by ^{1}H-NMR procedure described earlier. The integrated intensity of the methoxy and oil signal may be used in the expression given by Morgenstern et al. (2006) to establish FAME yield as the reaction progresses over time.

As previously discussed, the relative intensity of the methoxy peak appearing at 3.70 ppm and the triacylglycerol (TAG) peak appearing between 4.25 – 4.35 ppm was used to calculate the yield at any given point. The TAG signal decreases in intensity as the reaction progresses. This may be seen from the time based spectral overlap shown in Figure 3.8 for the reaction at 120 °C. The decrease in signal strength of the reactant peak, TAG and increase in signal strength of the methoxy peak at ~3.70 ppm is evidence of FAME production in the sample. The TAG signal observed from 4.27 – 4.33 ppm is a doublet of doublets. This may be observed in Figure 3.9 which shows the region of interest for two samples. Figure 3.9(a) displays the spectrum for 90 minutes at 65 °C and 3.9(b) for 20 minutes at 120 °C. The overlap from di and mono-glycerol is of particular concern as it may induce error in the integrations of the TAG peaks. The multiplet of 1,2-diacylglycerol (1,2-DAG) or the doublet of doublets of 1-monoacylglycerol (1-MAG) were not observed in the spectra shown in Figure 3.8 and 3.9. As established by Anderson et al. (2012) the multiplet for 1,2-DAG appears between 4.17 – 4.29 ppm and the doublet of doublets of 1-MAG appears at 4.15 – 4.25 ppm. These reaction intermediates produce interference and distort the results for integration of TAG peaks from the ^{1}H-NMR spectra. The reaction yields at various temperatures using gasifier ash as a catalyst are shown in Figure 3.10 to 3.12. The reaction is slowest at the lowest temperature, and the yield for the reaction at 65 °C shown in Figure 3.10 required extended time periods to achieve high conversion. The highest yield of ~93 % occurred after 300 minutes of reaction time. A lower process temperature has advantages such as reduced heating cost, and requires minimal pressure to keep volatile reactants such as methanol in a homogeneous phase. The reaction at 80 °C, seen in Figure 3.11 proceeded relatively faster and the yield of ~92 % was obtained after 100 minutes of reaction. The fastest reaction was observed to be at 120 °C and 75 minutes of reaction in Figure 3.12. The reactions achieve a stable conversion and may be seen from the plateau of the yield curves. These are also observed in Figure 3.8 as the complete utilization of the TAG signal in the ^{1}H-NMR spectra and the TAG region flattens out and decreases in intensity over time. The control reaction curves in Figure 3.10 and 3.12 demonstrate that sieved ash without calcination does not show similar catalytic activity for this particular reaction. The small quantity of oxides such as haematite and silicates such as anorthite might influence the reaction yield but as is evident from the control curves, it is not significant even after 5 hours or more of reaction time.

3.3.3 Catalyst Re-Use

The re-use of the catalyst was done by first washing the used catalyst with methanol and then preparing it under similar conditions as the original procedure. The catalyst was dried at 105 °C for four hours, heated to 500 °C at a fixed heating rate, and then maintained at 500 °C for four hours. The catalytic activity and reaction yield decreased as expected, probably due to poisoning or loss of active sites (Figure 3.13). The re-use of the catalyst gave 60 % yield after 300 minutes of reaction time at 120 °C.

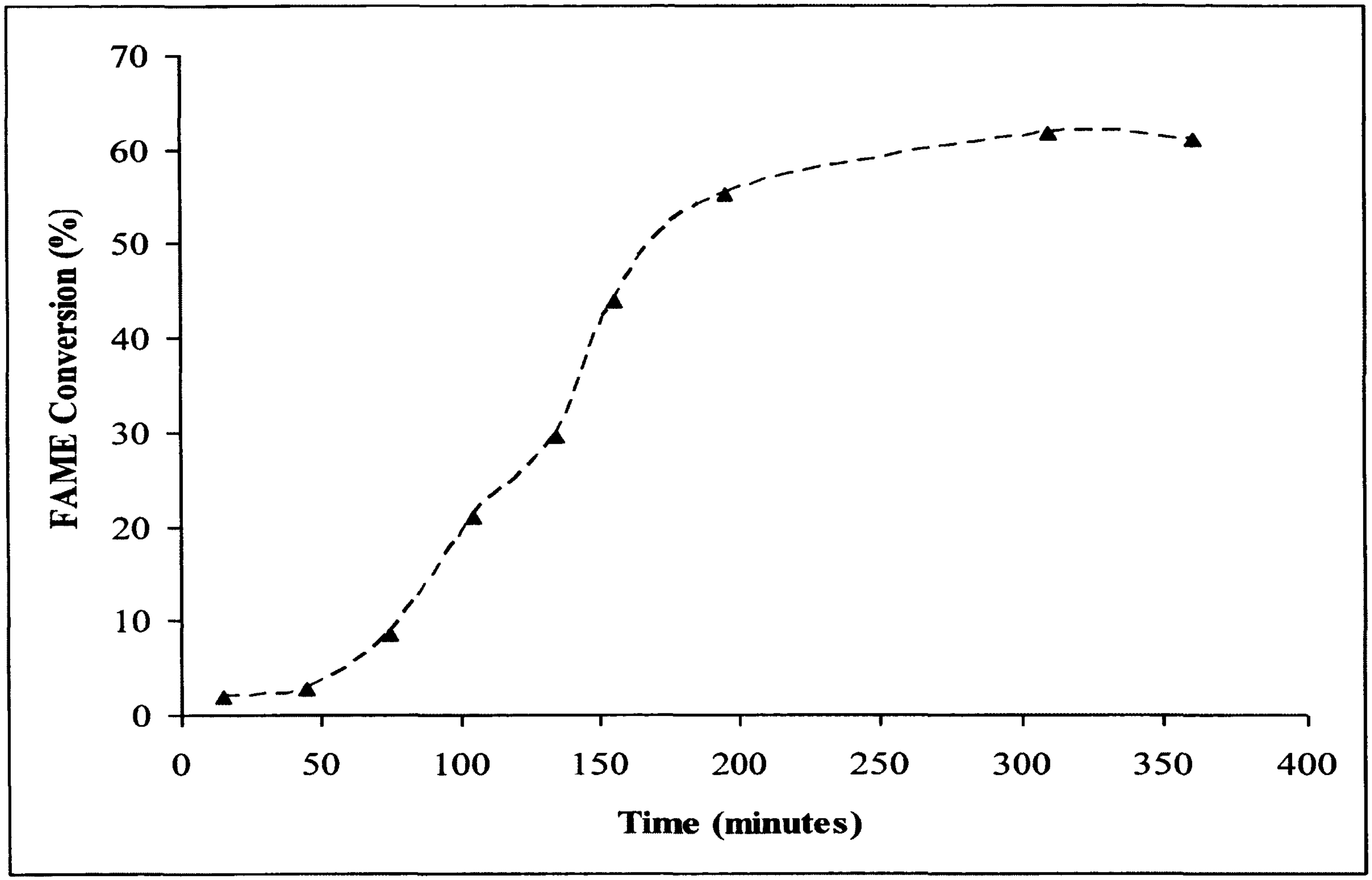


Figure 3.13: *The conversion of oil to methyl ester using recycled ash as catalyst. The reaction conditions were 5 (wt %) catalyst, 120^0 C and a 12:1 molar ratio of methanol to oil. The higher yields (≈60 %). were obtained after 300 minutes of reaction. The ramp up time for the reaction was 25 minutes.*

3.4 Summary and Conclusions

Biodiesel has been extensively studied as a green substitute to conventional fuel, and its blending with diesel and gasoline has been mandated in regions such as the EU and North America. The process of manufacturing biodiesel uses homogeneous catalysts that have a high yield. The product must go through the energy intensive processes of neutralization and washing to remove these homogeneous catalysts. This increases the cost of final product and in some cases may also reduce product quality by the formation of gel and emulsions. The use of heterogeneous catalysts is a well-established alternative due to the elimination of cost and energy intensive processes. In the last decade, bioenergy operations that utilize combustion and gasification of woody biomass have increased across the globe especially in countries aiming to reduce their greenhouse gas emissions. Locally produced waste wood residues may be gasified under an oxygen deficit environment to produce syngas, which is then burnt to retrieve energy. The utilization of biomass to create bioenergy has been widely used by pulp mill and other such wood based industries. The production of bottom ash is expected to increase in the near future as more resources are dedicated to a cleaner and more efficient energy source. The bottom ash produced from gasification operations is rich in inorganic content in the form of metal oxides, carbonates and silicates. The GA contained 12 wt.% Calcium, and this concentration was increased to 16 wt.% by sieving the sample to particle size <150 μm. The sieving was done to increase the concentration of inorganics, and also to obtain finer particles of uniform sizes for use as catalyst. The XRD provided evidence for the presence of inorganic content in the form of Calcite, Haematite, Anorthite and Gehlenite, which have been related to ash from woody biomass. Calcination further concentrated the calcium content to about 22 wt%. The XRD spectra of catalyst identified useful metal oxides which justified the application of the ash as a catalyst. Calcium oxide was found to be approximately 71%, followed by Fluorapatite and Calcium Silicate estimated at 7.5% each. Using gasifier ash as catalyst, the maximum yield of FAME was 95 % using 12:1 methanol to oil molar ratio, 120 °C, 5 wt% catalyst and 160 minutes of reaction. The issue of waste products and their useful utilization is vital to creating new efficient processes. The wastes also have costs related to disposal, handling, landfilling etc. The ash is a waste produced as a residue in biomass to bioenergy operations, and its alternate utilization is the focus of many scientific studies. This study demonstrated the use of the two waste products of low value to be processed and converted to a valuable product such as FAME. The ash was characterized, prepared and used as an effective and cheap heterogeneous catalyst to give a high conversion of waste cooking oil to FAME.

CHAPTER 4: Comparative analysis of two heterogeneous catalysts

4.1 Introduction

In the previous chapters, two different catalysts were prepared from residues left after harnessing biomass for energy. The primary metal oxide dominating both catalysts was calcium oxide as determined by phase identification techniques such as XRD, FT-IR. The presence of Calcium was also confirmed by ICP-MS. This chapter presents a summary of the comparisons between the heterogeneous catalysts, their performance and the properties of the source biomass ashes. In order to present a detailed account of these key findings, we must first establish the difference in source biomass ashes.

4.2 Inorganic content

Tables 2.1 and 3.1 display a detailed metal profile for the biomass ashes used in the two studies. Both ashes have a high concentration of Calcium, Potassium and Magnesium. The difference in feedstock and energy harnessing processes produces ashes varying in physical and chemical properties.

The ash produced by the gasification of biomass (GA) has a lower concentration of metals such as calcium, potassium and magnesium than the ash produced on burning pellets (PBA). The GA has a higher concentration of Iron, Sodium and Barium than the PBA as may be observed from Table 2.1 and 3.1. Upon sieving a notable improvement in the concentration of metals in both the ashes may be observed. The relative increase in metal concentration upon sieving is higher for GA. The absolute increase in Calcium concentration in GA is close to 40,000 mg/kg, and for PBA this is only 21,000 mg/kg as seen from Table 3.1 and 2.1 respectively. The GA ash has a more stratified inorganic content, as the metals are in a much higher concentration in the finer fraction. The PBA ash has a more uniform distribution of metals and a lesser variation across the two fractions is seen. The XRD patterns for the two ashes also displayed different phases. The PBA ash predominantly consisted of metal carbonates and oxides. Potassium and calcium carbonates in the form of fairchildite and calcite were identified. Also present were magnesium oxide and calcium oxide, which may be seen from Figure 2.3. The GA ash was not a product of complete combustion, so it contained some fused silica alumina metal oxides such as gehlenite, anorthite and potassium aluminium silicate as shown in the XRD in Figure 3.4. The other phases such as quartz, calcite and haematite were also identified. Quartz in the residue is most probably from soil and dirt associated with unprepared wood waste such as hog fuel. The GA and PBA bottom ashes were also analysed by BET for the adsorption surface area prior to treatment. The PBA bottom ash had a surface area 5.24 m^2/g and while for the GA ash it was 25.20 m^2/g. The GA ash had a better porosity and more surface area than PBA ash. There are two major factors contributing to these differences in the two ashes and they are the preparation of the fuel and method of combustion. The pellet burner uses wood pellets that are a densified form of wood. These pellets are produced in order to increase burning efficiency and energy content per kilogram of fuel. The gasifier uses hog fuel which is waste residue left from sawmill operations. The hog fuel is not prepared in a special process to increase the energy density, or the density of biomass to ease transportation and handling. The process of the pellet burner and gasification are also different. The pellet burner burns the biomass in an oxygen rich environment to maximize the energy yielded by the combustion of the pellets. The gasifier is an oxygen deficient operation, which produces syn gas from the biomass. The syn gas is then burnt in a boiler to produce energy. The mixture of combustible gases produced in gasification operations are easy for energy transport and offer cleaner combustion parameters such as particulate emissions, SOx and NOx emissions among others. There are various advantages of both processes, and energy generation at the University of Northern British Columbia is achieved with a combination of both these processes.

4.3 Catalyst Performance

Due to the differences in inorganic content and mineralogy of the parent ashes as discussed earlier, the two ash catalysts (PBA and GA) behave slightly differently in the reaction process. The dominating phase is calcium oxide in both the catalysts; it comprises approximately 71% of the GA catalyst and 45% of the PBA catalyst. Some of the calcium in the PBA catalyst is present as calcium silicate $Ca_2(SiO_4)$, accounting for about 15% of the identified phases. The surface area of the PBA catalyst determined by BET method was 2.74 m^2/g and for GA catalyst this was 7.1 m^2/g. Due to similar active phase of calcium oxide, both catalysts provide the function of heterogeneous catalysis of the transesterification reaction. The heterogeneous function of calcium oxide is primarily due to its low solubility in methanol, and formation of methoxide phases. The high concentration of alkaline earth metals is clearly observed in the catalysts. The alkoxides of alkaline earth metals are highly insoluble in organic solvents. This results in a more heterogeneous function in catalysis (Bradley, Mehrotra, and Gaur 1978). Calcium methoxide may form on the surface of calcium oxide exposed to methanol. The formation of calcium methoxide is the real catalyst of methanolysis of triglycerides (Tanabe 1970). Alkaline-earth metal alkoxides, which are stable in a non-aqueous medium, are strong bases and nucleophilic reagents (Gryglewicz 2000). The strong base and nucleophilic properties are evident from the high activity displayed by both catalysts for a transesterification reaction. The higher activity of GA catalyst than the PBA catalyst may be attributed to the fact that the former has a higher Calcium concentration, and a higher percentage of CaO (Lime) content. The slightly soluble state of alkoxides also justifies the deactivation of catalysts upon the first use, as some of the formed alkoxides may have leached out and been lost upon the first reaction.

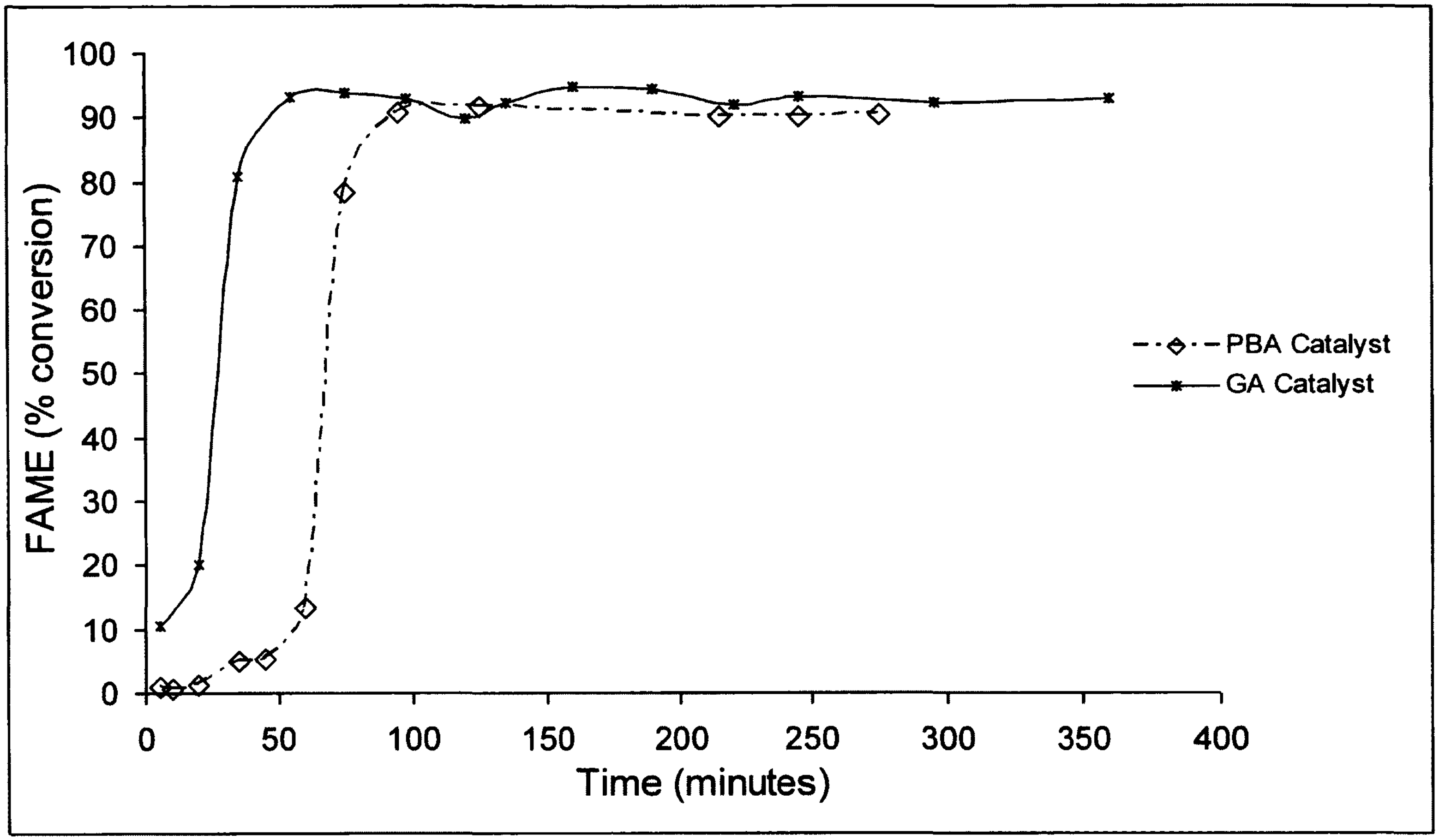


Figure 4.1: *Conversion of oil to methyl ester using PBA and GA catalysts. The reaction conditions for both reactions were 5 (wt %) catalyst, 120^0 C and a 12:1 molar ratio of methanol to oil. The ramp up time for the reactions was 25 minutes.*

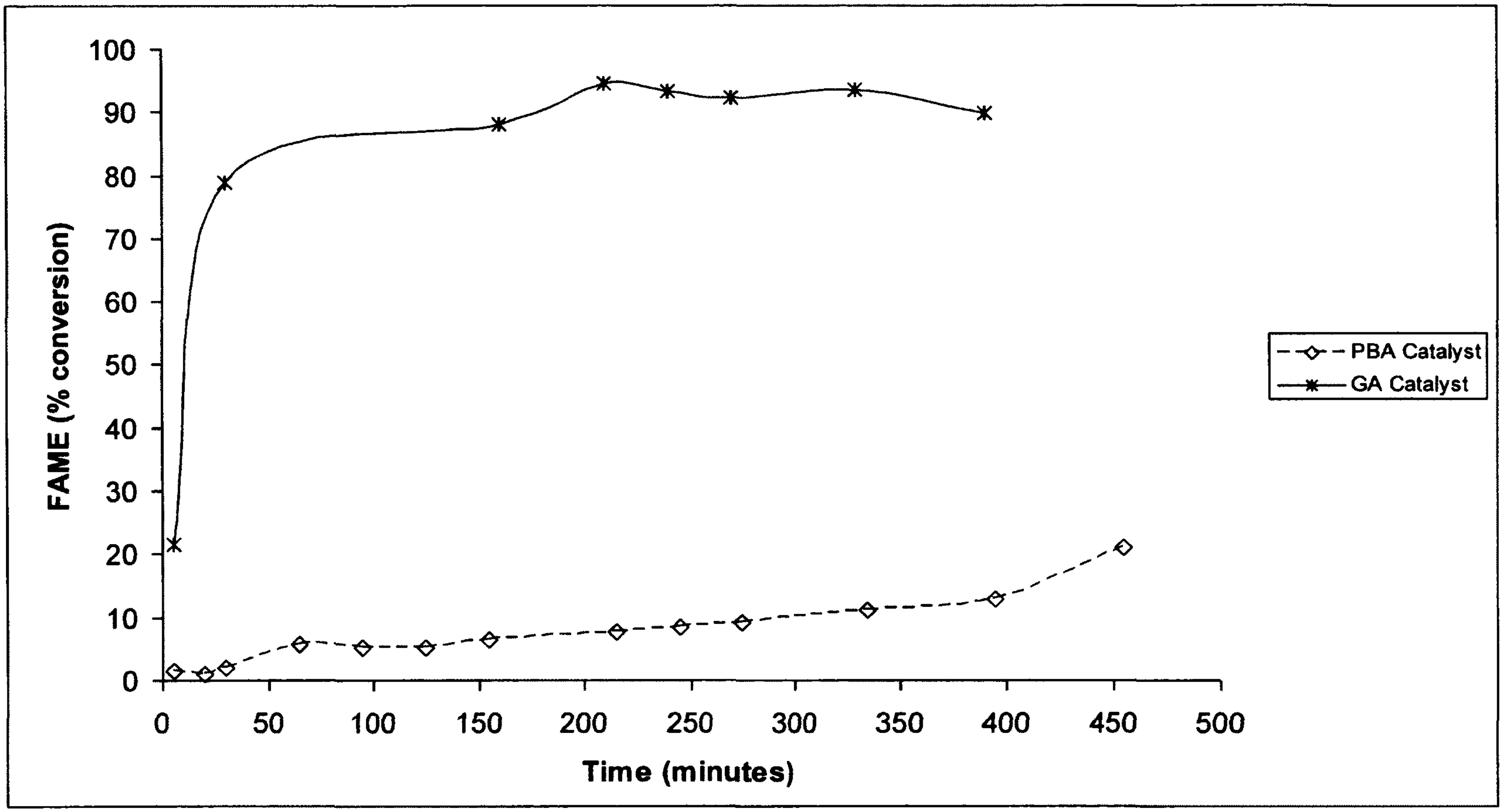


Figure 4.2: *Conversion of oil to methyl ester using PBA and GA catalysts. The reaction conditions for both reactions were 5 (wt %) catalyst, 80^0 C and a 12:1 molar ratio of methanol to oil. The ramp up time for the reaction was 25 minutes.*

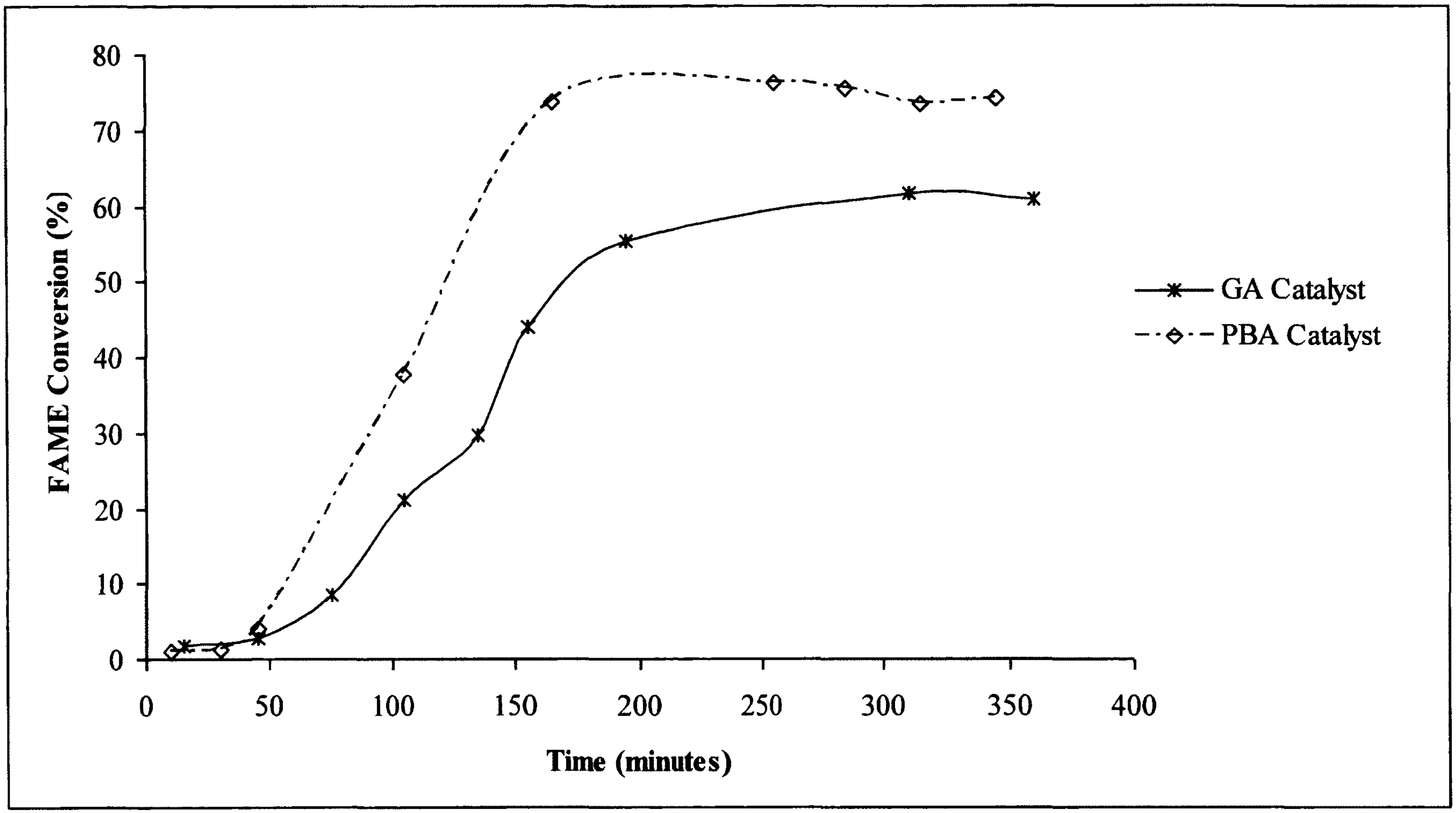


Figure 4.3: *Conversion of oil to methyl ester using recycled PBA and GA catalysts. The reaction conditions for both reactions were 5 (wt %) recycled catalyst, 120^0 C and a 12:1 molar ratio of methanol to oil. The ramp up time for the reaction was 25 minutes.*

The GA catalyst gave higher yields at both 120 °C and 80 °C as may be seen from Figures 4.1 and 4.2. The PBA catalyst was ineffective at 80 °C and only gave ~20% yield after 450 minutes of reaction (Figure 4.2). The GA catalyst on the other hand performed quite well at this temperature and resulted in ~90% yield after 175 minutes of reaction. The GA catalyst has approximately 22.4 wt% of calcium and the PBA had 28.8 wt% from Table 3.1 and 2.1 respectively. Although these concentrations of Calcium determined by ICP-MS were comparable, but GA catalyst contained 70.9% CaO (Lime) while PBA catalyst only had about 45% as found by semi-quantitative XRD. This meant that the GA was lower in Calcium in the ash, but its preparation gave a higher CaO (lime) content in the catalyst. Apart from having a higher content of the basic oxide, the GA catalyst also had a higher BET surface area than the PBA catalyst. Hence, high content of active metal oxide and large adsorption area for catalytic action are most probably the primary reasons why the GA catalyst performed better than PBA catalyst.

The recycle of the two catalysts was done in a similar procedure to evaluate the reuse capability. The PBA catalyst gave a better yield upon reuse than the GA catalyst as may be seen from Figure 4.3. The reaction condition of the initial catalysts were the same, at 120 °C, 5 wt% catalyst loading and 12:1 molar ratio of methanol to oil. After the reaction, these catalysts were washed with methanol, dried and heated to 500 °C to burn organic content. Their reuse performance was tested by using them in the abovementioned reaction conditions again. The GA catalyst gave only ~60% yield in the reaction while the PBA catalyst fared marginally better and gave ~75% yield in 300 minutes of reaction. The reduced action of the catalyst may be attributed to deactivation due to reduced surface area and residual organics, loss of active sites due to heating and leaching. The presence of higher CaO content which is affected by deactivation may decrease the yield of the catalyst significantly. Other compounds in PBA catalyst such as periclase (MgO) (Kouzu et al. 2008) also provide catalytic activity similar to that of lime (CaO) for the transesterification reaction. The lack of these oxides in the GA catalyst may also contribute to a decreased yield in case of partial deactivation or leaching of CaO content. The other identified phases in the GA catalyst such as minor quantities of phosphates and silica-aluminates are not active catalysts for the transesterification reaction.

A comparison of the properties of two different biomass ashes and an insight into the methods that generated the residue is vital to understanding the applications of biomass ashes to transesterification. The ash must be of high calcium content with preferably a large amount of oxides. In case the carbonates are the dominant phase, they must be calcinated to prepare oxides for good yield. Sieving the ash particles to finer sizes also increases the useful metal concentration by a significant amount. Ash from a pellet burner had lower surface area and lesser activity in the reaction. The gasifier ash or ash from oxygen deficient thermochemical degradation of biomass has a very large surface area and significant inorganic concentration. The GA catalyst prepared with higher CaO content, has an excellent yield in the first run, but loses activity in subsequent runs probably due to leaching and deactivation. The PBA catalyst has a smaller surface area and the extent of deactivation is lesser which is observed by the better performance of the catalyst upon re-use. Ash from complete combustion had better recycle properties, and ash from gasification had an excellent initial yield.

CHAPTER 5: Conclusions and recommendations for future work

In this study, waste products generated in the vicinity of University of Northern British Columbia, Canada were used to prepare valuable products. A process for the manufacture of biodiesel from waste cooking oil, using ash residue from bioenergy operations as a catalyst was demonstrated. In separate operations, two prepared catalysts were tested for the conversion of waste cooking oil to fatty acid methyl esters over a range of different temperatures. The two catalysts gave an excellent yield of ~95% over varying time periods. The gasifier ash (GA) catalyst performed better than pellet burner ash (PBA) catalyst. The current study employed and investigated a batch process for upgrading these wastes into useful products. For further research, the performance and product properties upon using a flow reactor and the ash catalyst on a fixed bed should be explored.

The two catalysts were characterized by a variety of techniques, and major variations were seen in BET surface area, calcium metal concentration and amount of CaO in catalyst samples. These differences were the prime factors that appeared to have governed the observable performance variations of each catalyst. The GA catalyst had higher calcium, CaO content and surface area. It gave higher yield in the first run, but lost its catalytic activity probably due to deactivation and leaching. The PBA catalyst had a lesser surface area and marginally lower calcium content. Besides CaO, it also had MgO present accounting for about 25% of the sample. It fared better than the GA catalyst in the recycle run. This is probably because there was lower leaching or deactivation in the PBA catalyst due to a smaller surface area. For more clarity, the leaching properties of species from both catalysts in methanol, and other organic solvents should be studied.

Both wastes used in the process are of environmental significance, with a long list of applications that continue to grow. Recent years have seen waste cooking oil to be the source of a large number of chemical products, including but not limited to biofuel and biolubricants. Ash from bioenergy processes has been validated as a soil amendment, forest fertilizer and additive in construction materials. The ash is a cheap residue that exists in large quantities in communities that utilize biomass for energy. The present day heterogeneous catalysts need to be prepared from abundant materials that are cheap and renewable. A study into the economics of catalyst preparation and value of products is also of relevance.

The catalysts prepared from ash residue enhance the list of alternate applications that biomass ashes may be employed for. The presence of a plethora of chemically active compounds such as carbonates, oxides, zeolites, quartz, aluminosilicates is a boost to the process significance of ash. It is imperative to develop new processes that provide competitive efficiency, reduced environmental cost and greater value. The process design and development may only be successful if we actively pursue unconventional sources of chemical and mineral compounds and test their utility against current processes. It is certain that the large number of inorganic phases in the ash will have an ever increasing range of applications. A temporal study into the cost-benefit facets of utilizing these alternate materials on a large scale would also be highly advantageous.

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APPENDIX I

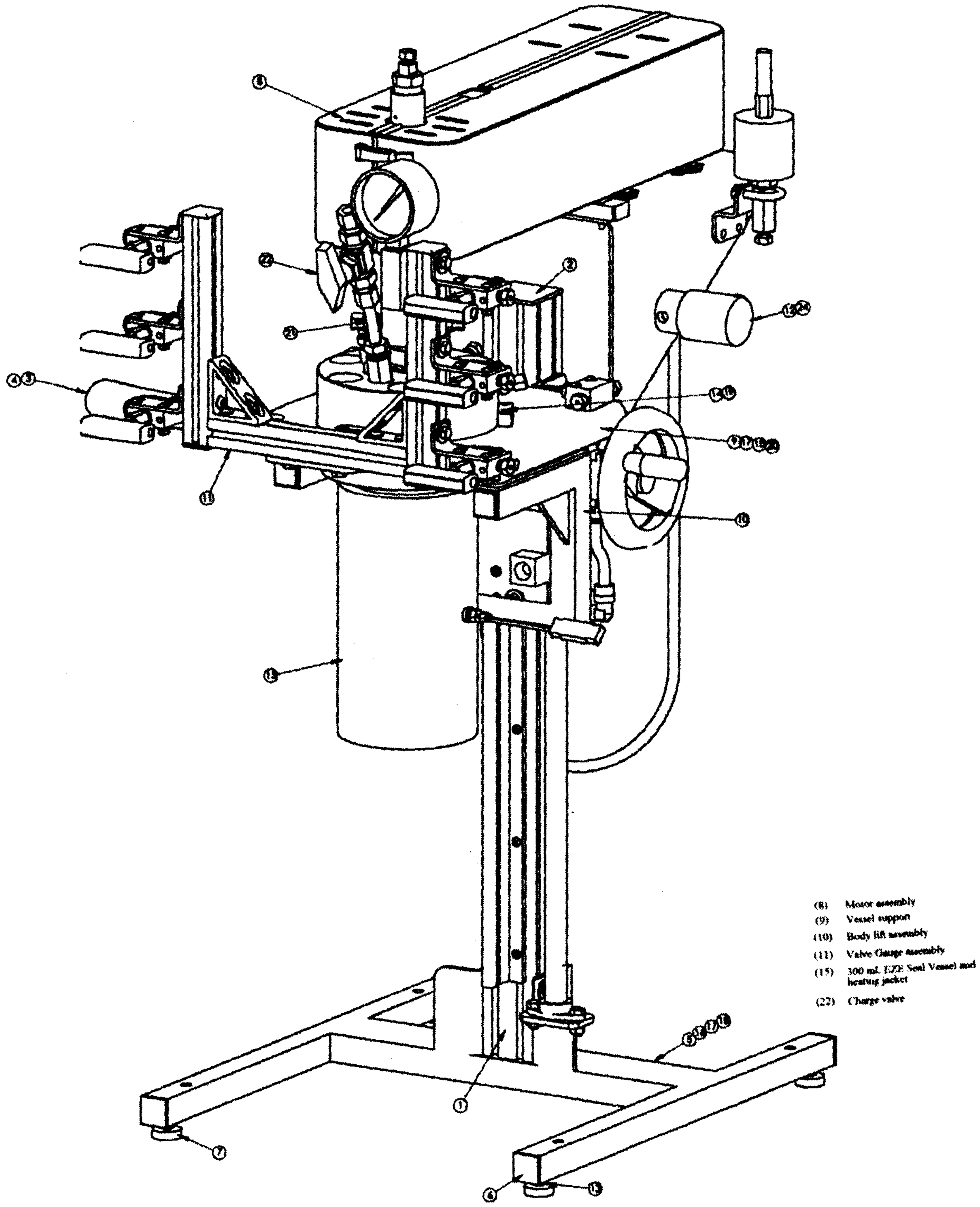

Figure A1: Diagram of 300 mL Autoclave Engineers EZE-Seal reactor used in the study.

APPENDIX II

The sample calculations for plotting the yields in one of the graphs have been shown. The section relates to Figure 3.12 as a reference and attempts to explain the methods and calculations involved therein. Every other graph in chapters 2 and 3 for the yield calculations follows a similar format, and has 11 or 12 distinct ^{1}H-NMR to arrive at the reaction conversion. Each ^{1}H-NMR included in this section depicts an individual sample at a specific time for the reaction using gasifier ash catalyst at 120 °C (GA-120). The ^{1}H-NMR analysis of the control reactions (GAC-120) has also been included. The other reaction conditions were 12:1 molar ratio of methanol to oil and 5 wt% catalyst.

Density of waste cooking oil

Density of waste cooking oil was measured by 5 repetitions. The density used was the average.

(0.912 + 0.908 + 0.915 + 0.912 + 0.913)/ 5 = 0.91165, ~ 0.912 gm/mL

Amount of catalyst added

Catalyst added was 5% by weight of WCO. In each reaction, 100 mL of WCO was used. Using density calculated above, mass of WCO used was 91.2 grams. The catalyst to be added was approximately 4.56 grams. In the GA-120 reaction, the amount of catalyst added was 4.4629 grams.

Amount of methanol added

The molar mass of oil was taken as 856 gm/mol. Molar mass of methanol was 32.04 gm/mol. Based on mass of oil added, its corresponding moles were calculated. Then the molar ratio of 12:1 was used to determine moles of methanol to be added. The moles of methanol were translated to grams of methanol by multiplication with 32.04. The weight of methanol was converted to volume by using the density of methanol at room temperature, 0.791 gm/mL. In the GA-120 experiment,

91.2 grams of oil was used, representing (91.2/856) = 0.0107 moles of oil.
The methanol to be added was (12*0.0107) = 1.279 moles of methanol.
The mass of methanol to be added was (1.279*32.04) =40.96 grams
The volume of methanol to be added was (40.96/ 0.791) = 51.78 mL.
The methanol added in the reactor was 52 mL.

Table B1: Table showing summary of ^{1}H-NMR values, and conversion calculations for gasifier ash catalyst (GA-120) and gasifier ash control (GAC-120) reactions.

GA-120	I_{ME}	I_{OIL}	$C_{ME} = \frac{2I_{ME}}{2I_{ME} + 9I_{OIL}}$	Conversion% (100 x C_{ME})
5 min	1	1.8903	0.105	10.52
20 min	1	0.888	0.201	20.12
35 min	1	0.0527	0.808	80.83
55 min	1	0.0163	0.932	93.17
75 min	1	0.0149	0.937	93.72
98 min	1	0.0168	0.930	92.97
120 min	1	0.0253	0.898	89.78
135 min	1	0.0189	0.922	92.16
160 min	1	0.0127	0.946	94.59
190 min	1	0.0132	0.944	94.39
220 min	1	0.0193	0.920	92.01
245 min	1	0.0163	0.932	93.17
295 min	1	0.0183	0.924	92.39
GAC-120				
60 min	1	11.94	0.018	1.83
160 min	1	6.03	0.036	3.55
180 min	1	4.97	0.043	4.28
300 min	1	4.08	0.052	5.17

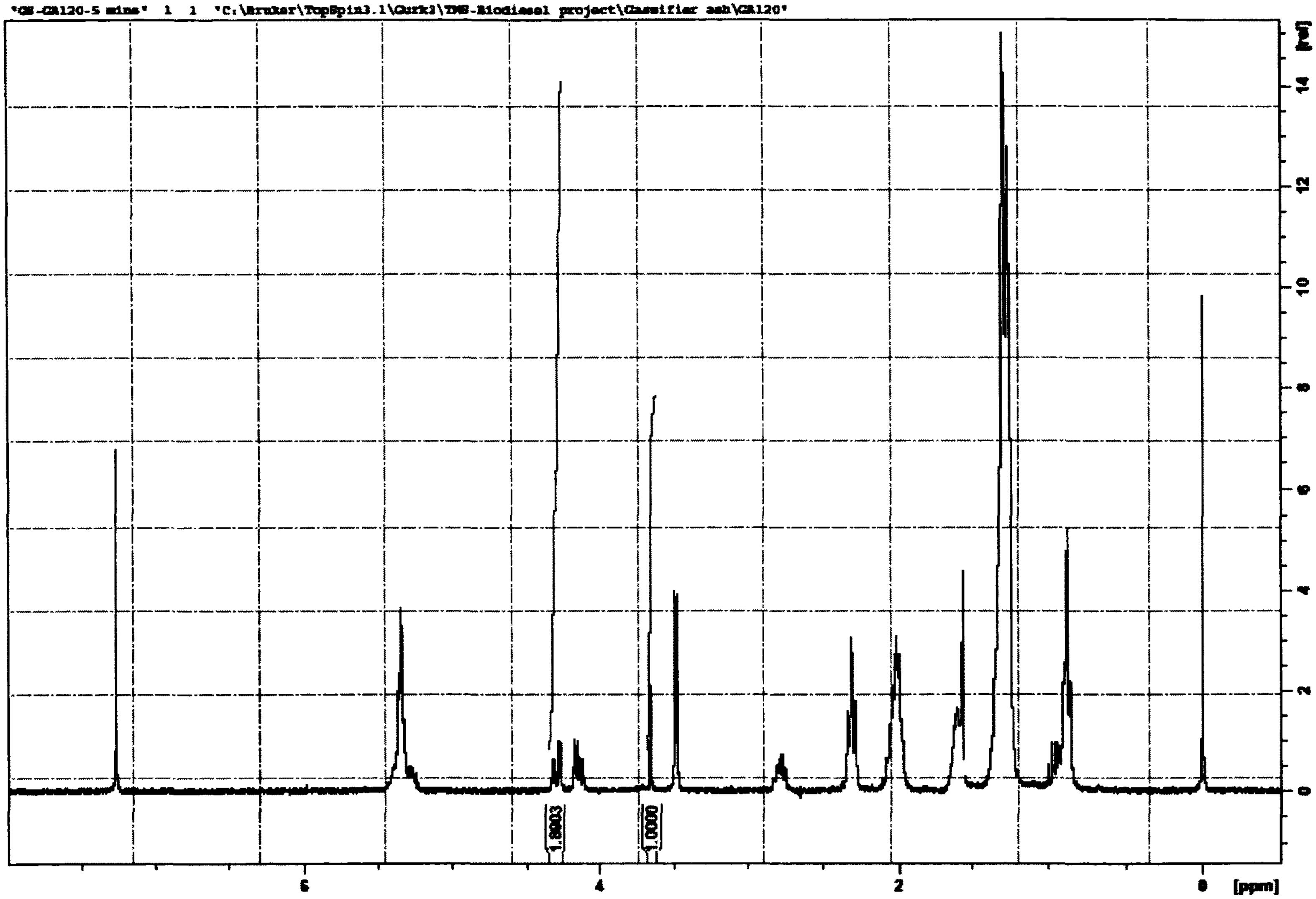

Figure B1. ^{1}H-NMR of GA-120 at 5 mins

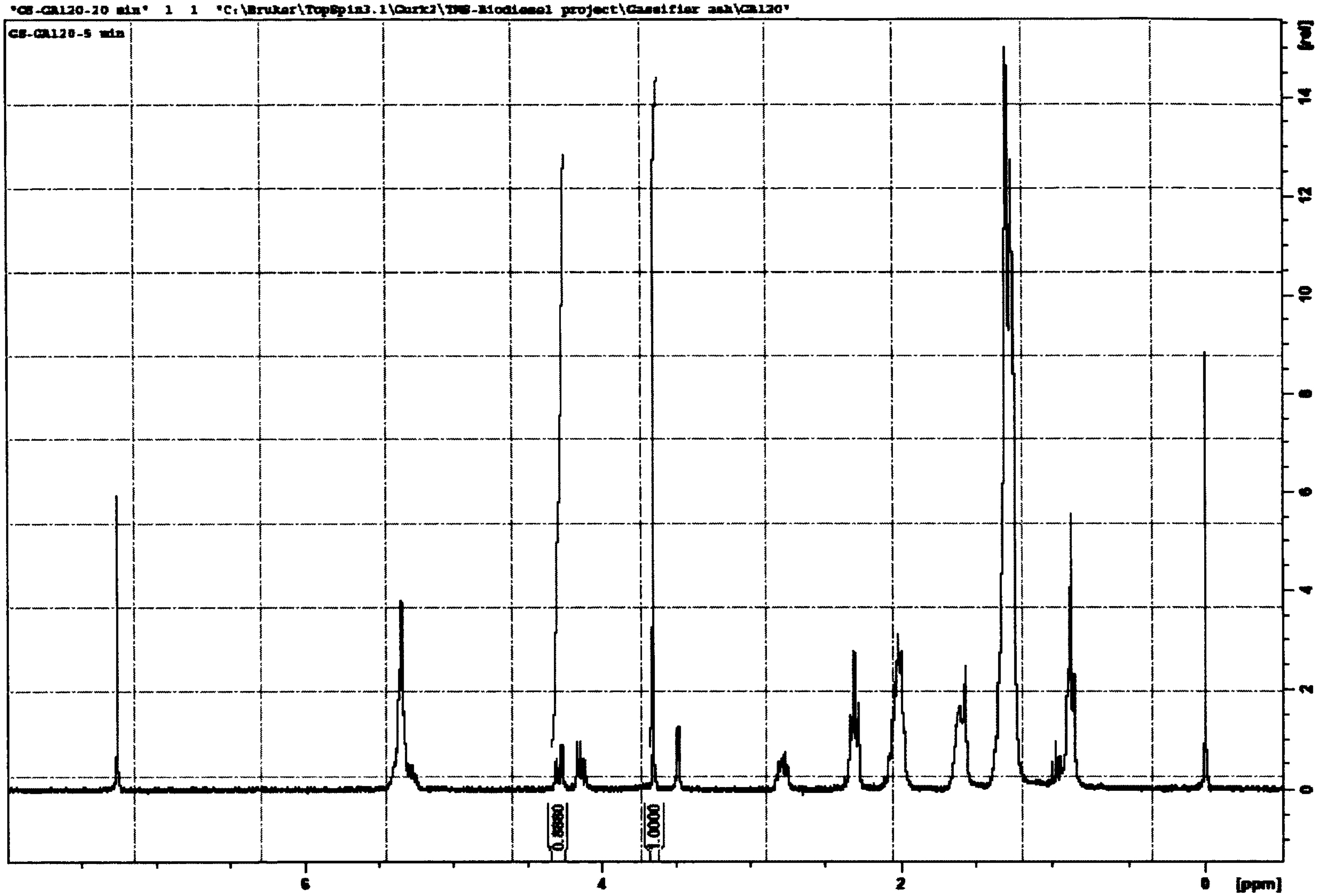

Figure B2. ^{1}H-NMR of GA-120 at 20 mins

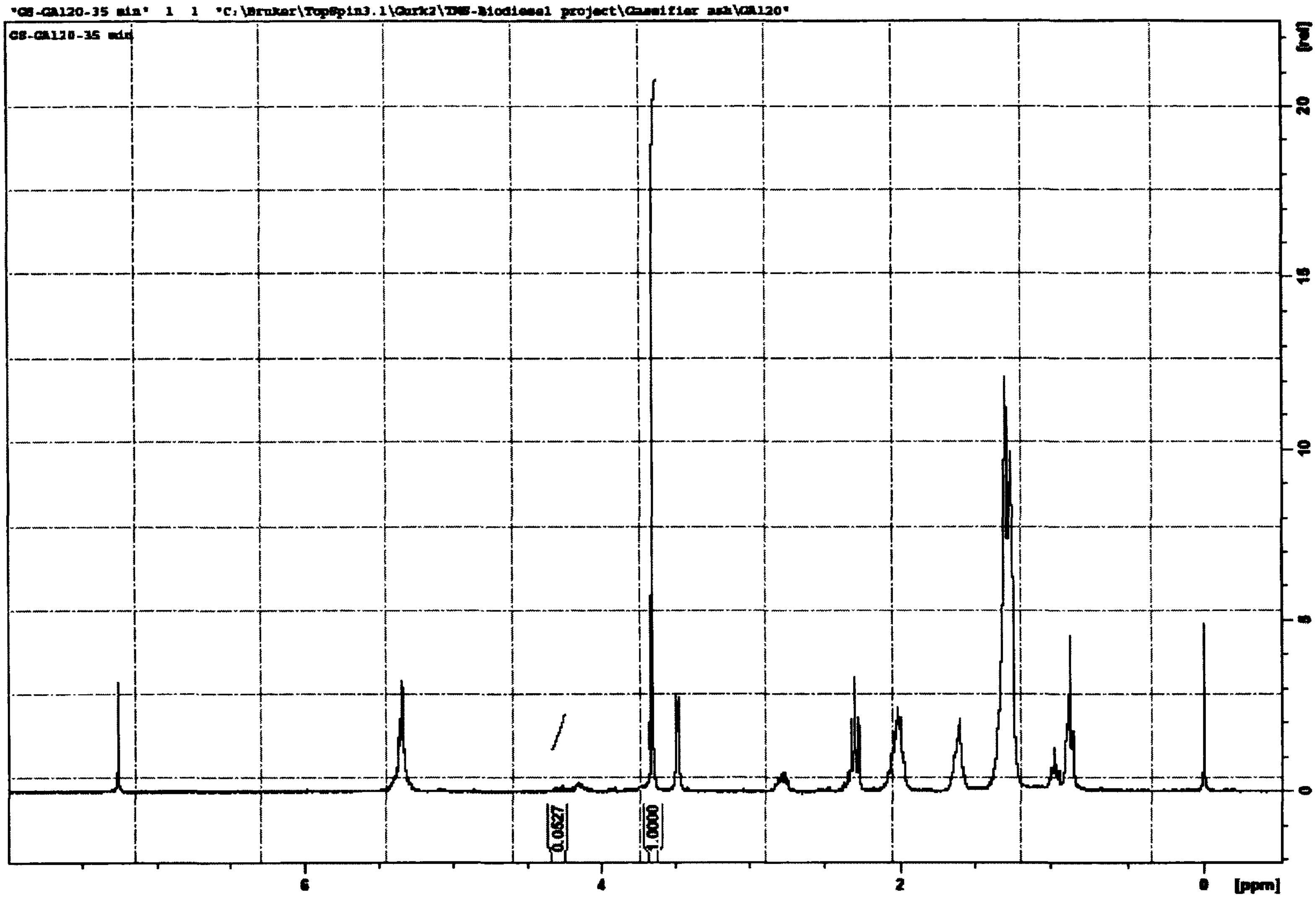

Figure B3. ^{1}H-NMR of GA-120 at 35 mins

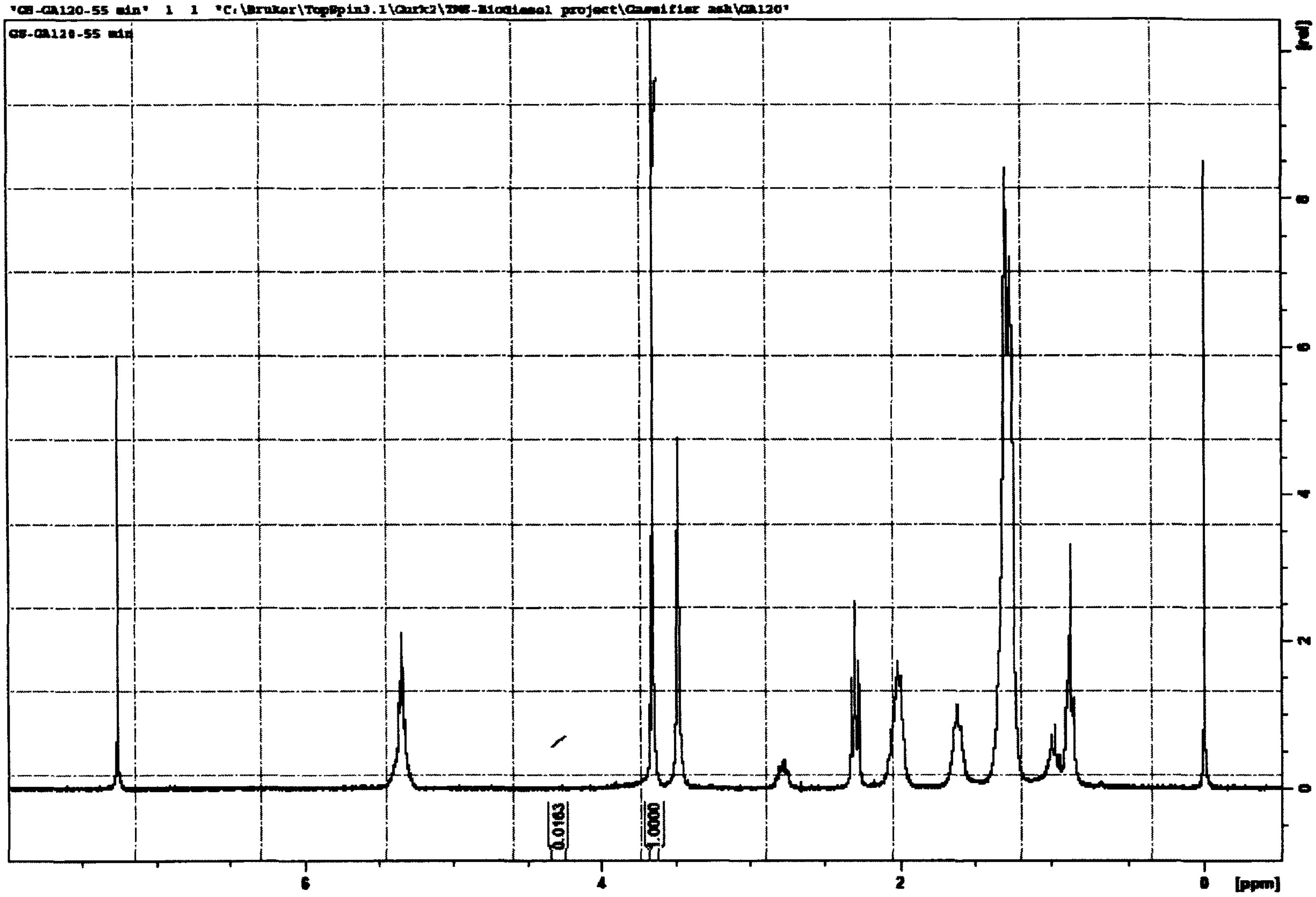

Figure B4. ^{1}H-NMR of GA-120 at 55 mins

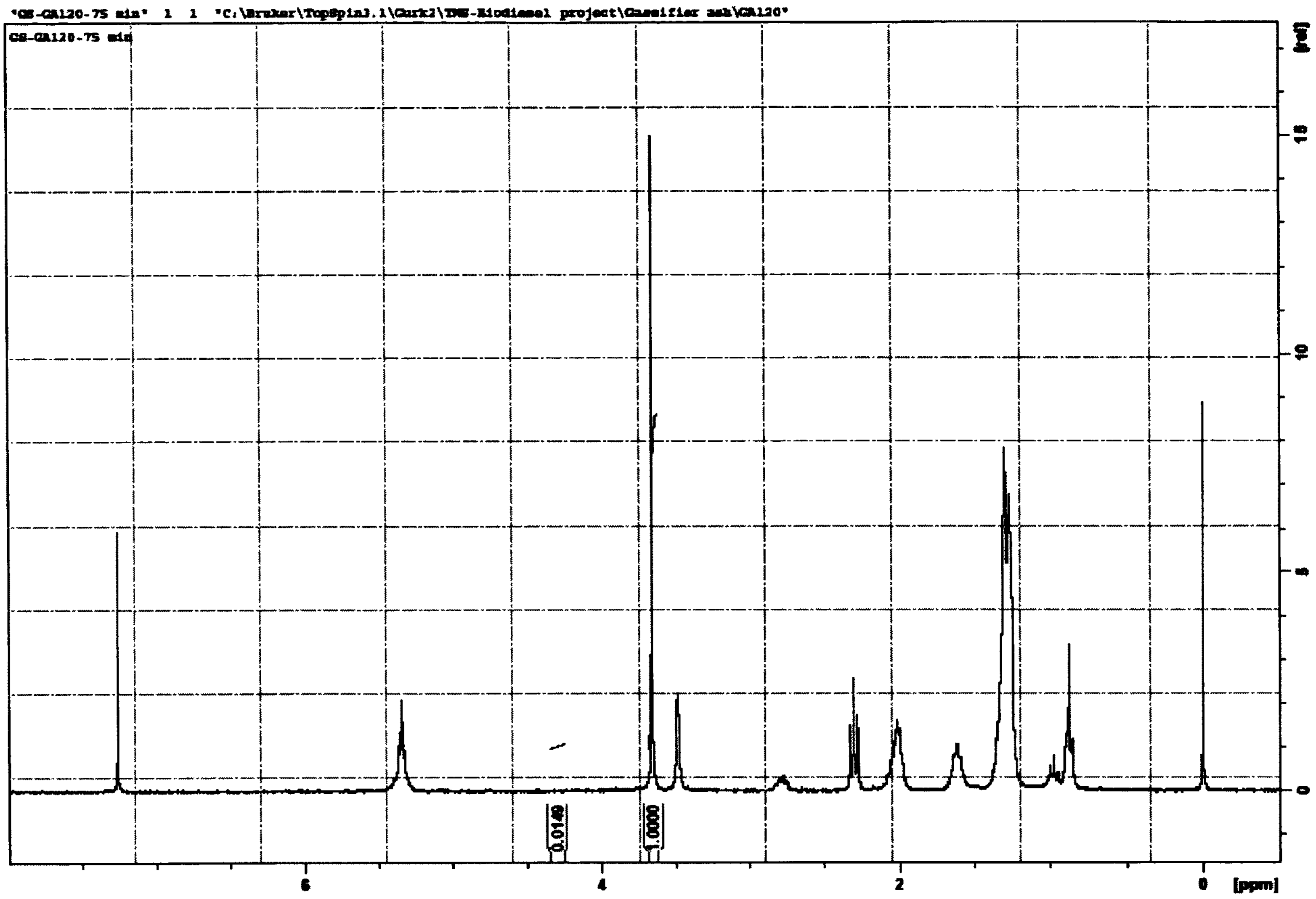

Figure B5. ^{1}H-NMR of GA-120 at 75 mins

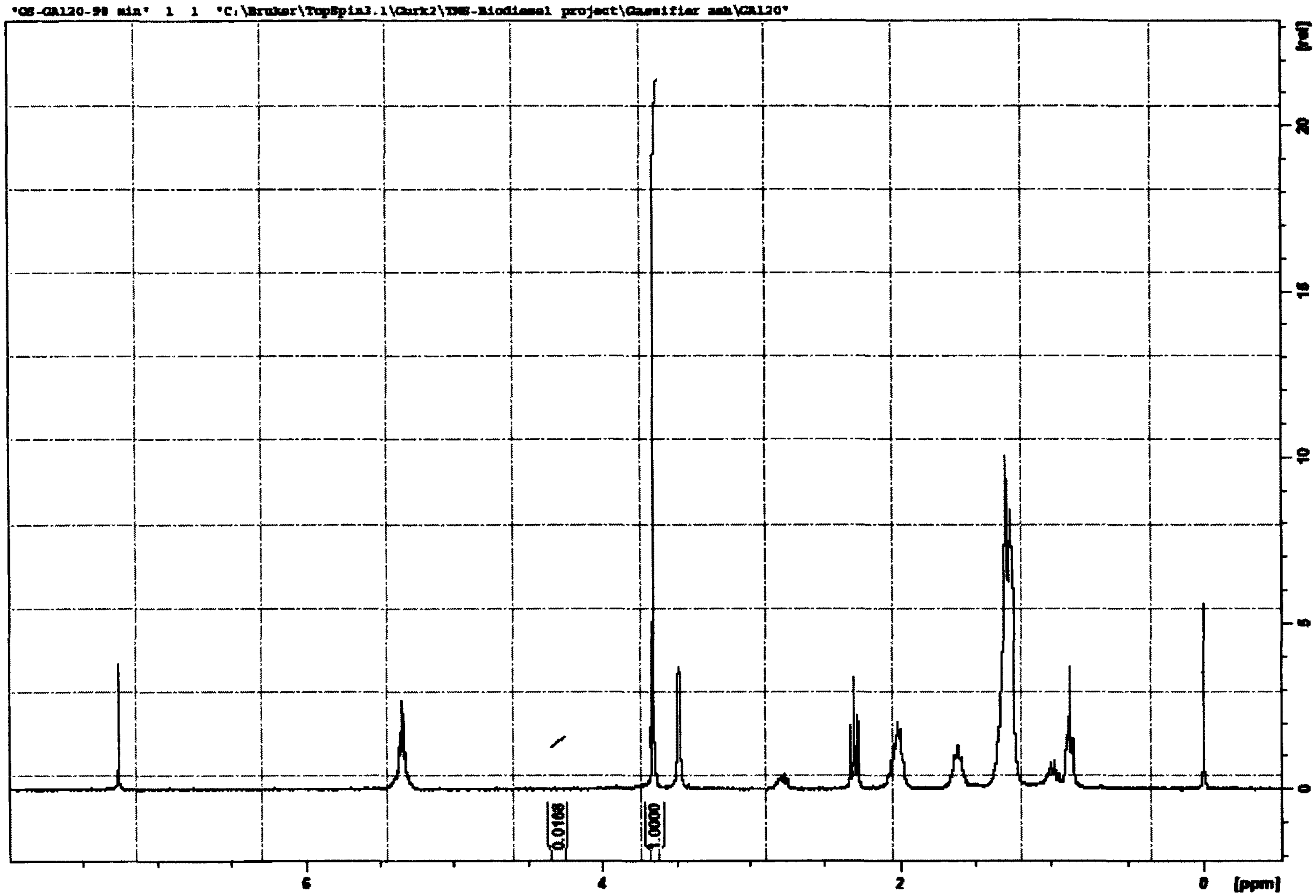

Figure B6. ^{1}H-NMR of GA-120 at 98 mins

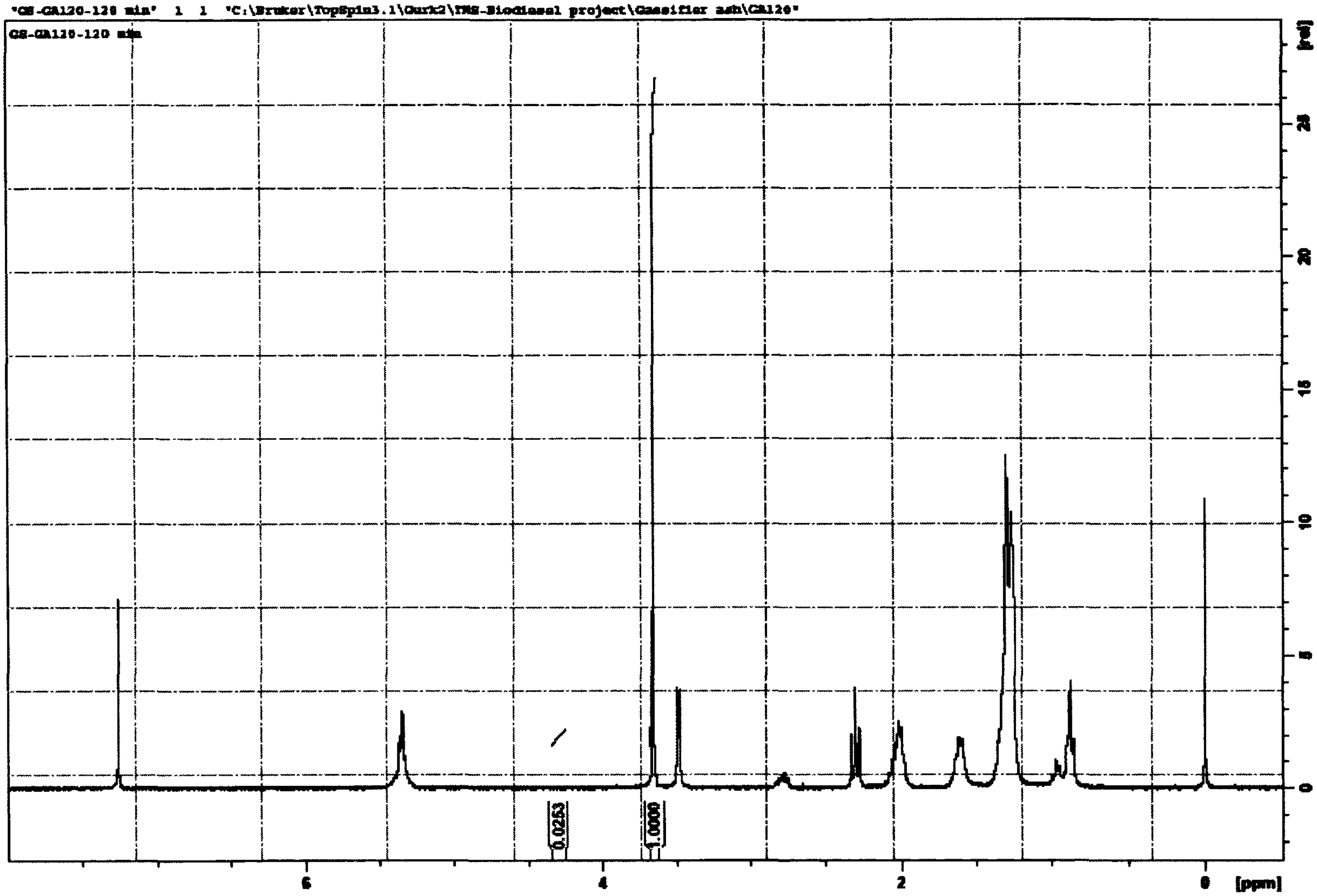

Figure B7. ^{1}H-NMR of GA-120 at 120 mins

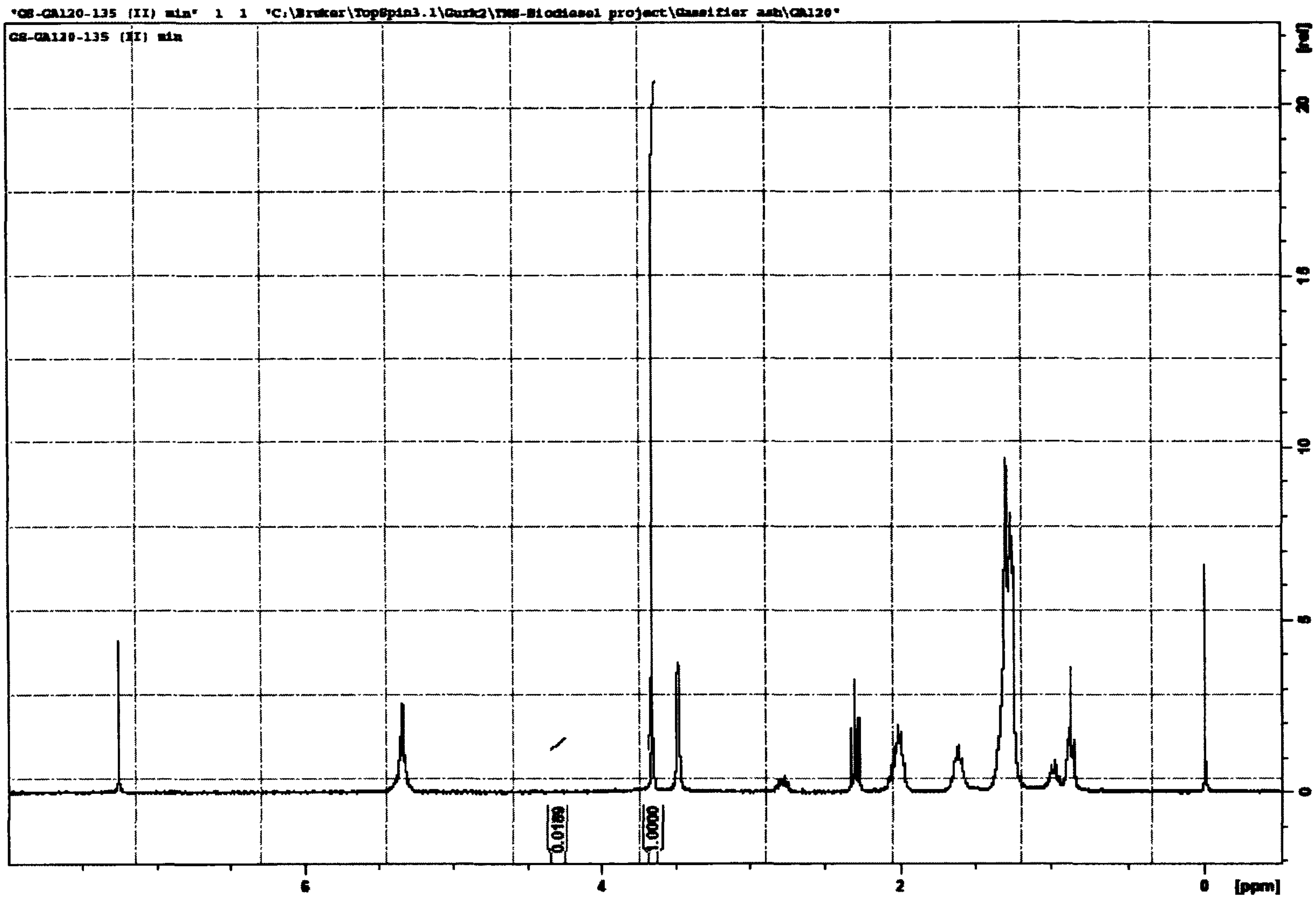

Figure B8. ^{1}H-NMR of GA-120 at 135 mins

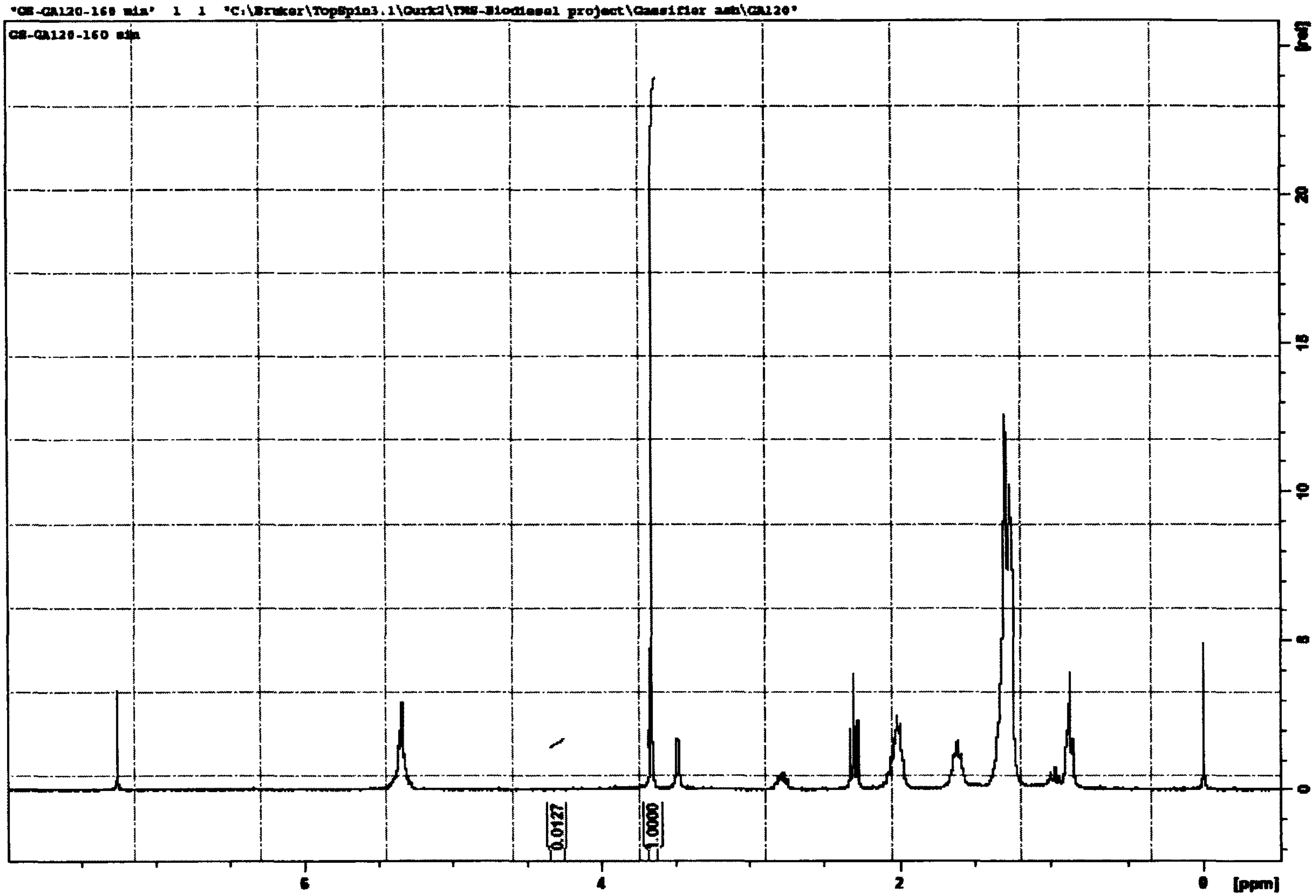

Figure B9. ^{1}H-NMR of GA-120 at 160 minutes

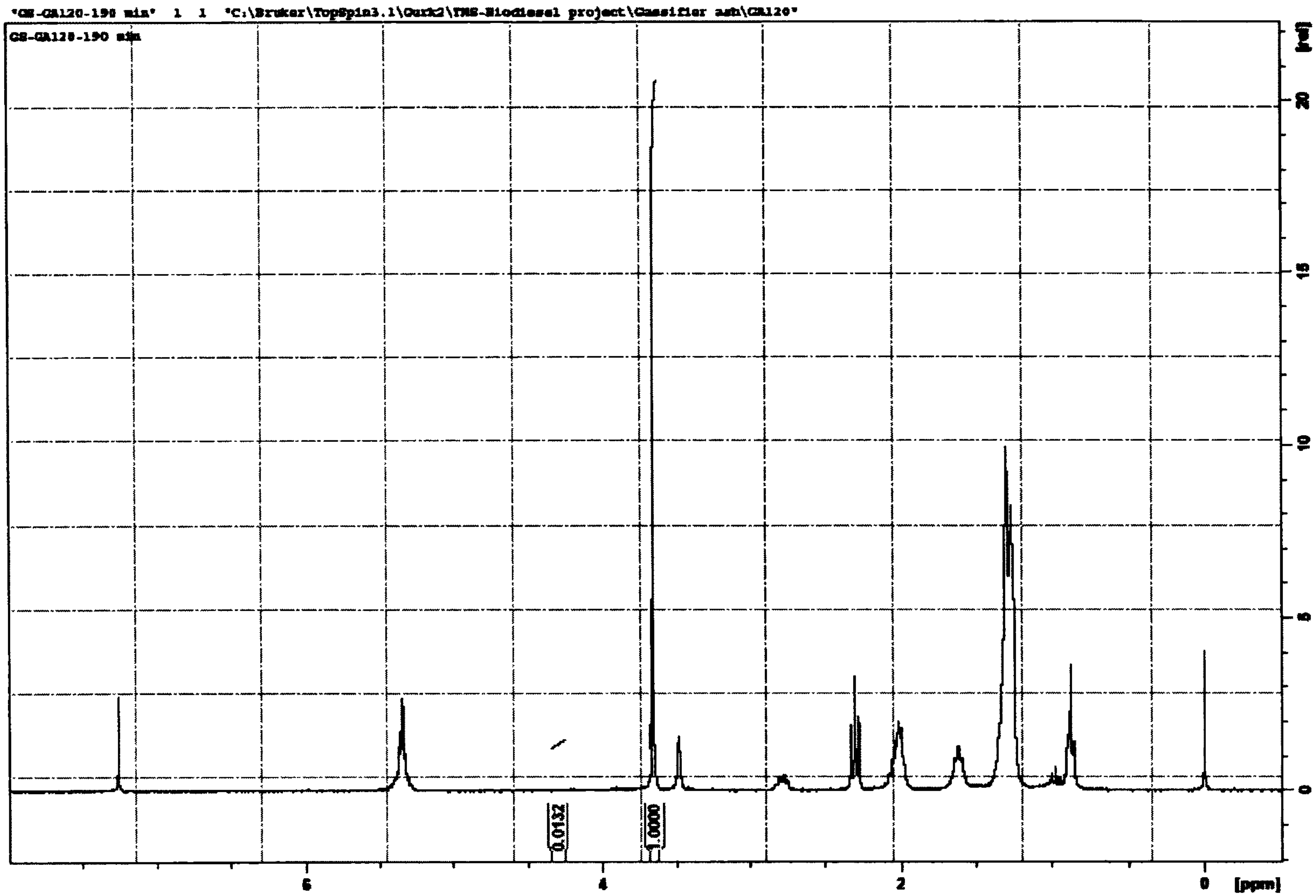

Figure B10. ^{1}H-NMR of GA-120 at 190 minutes

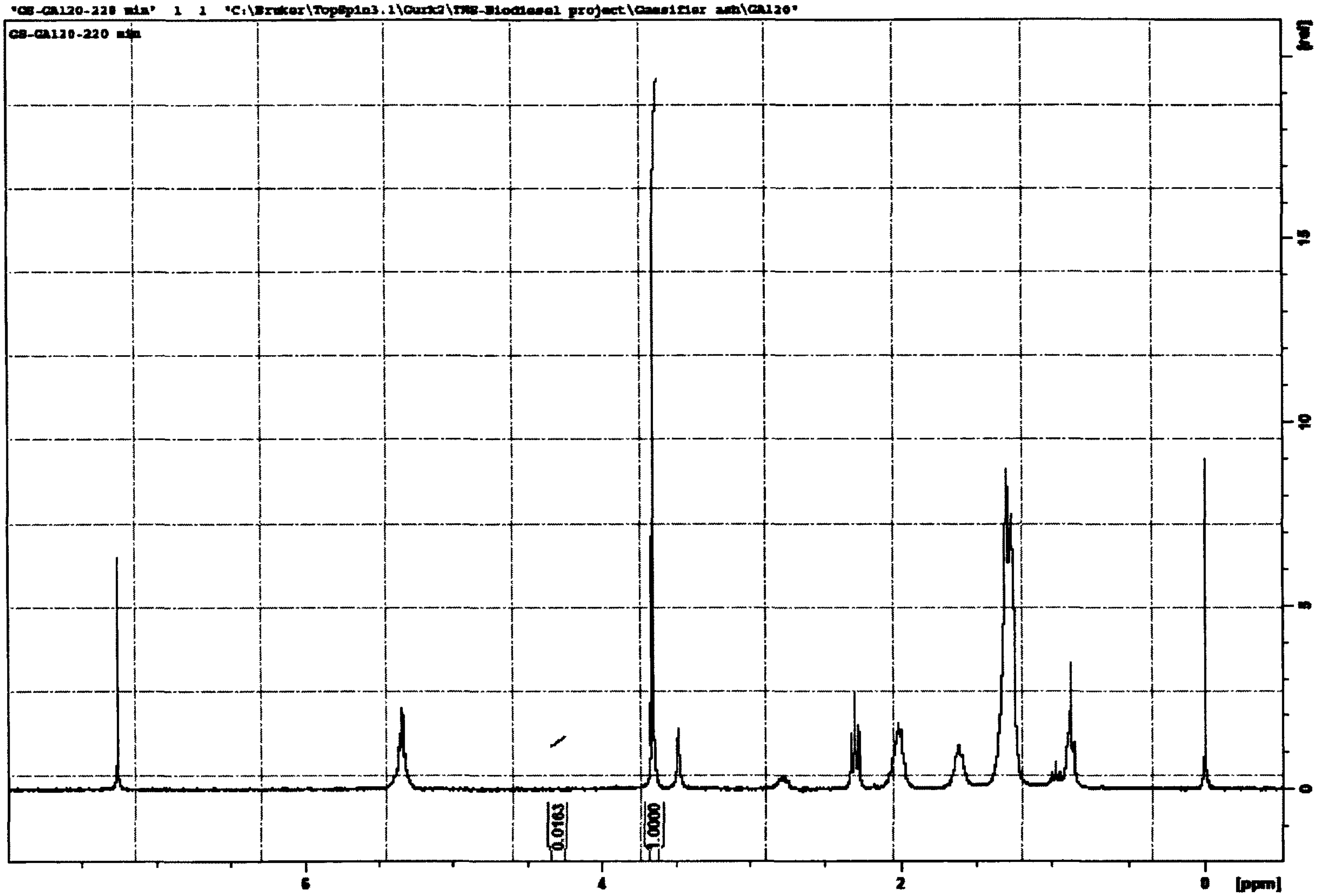

Figure B11. ^{1}H-NMR of GA-120 at 220 minutes

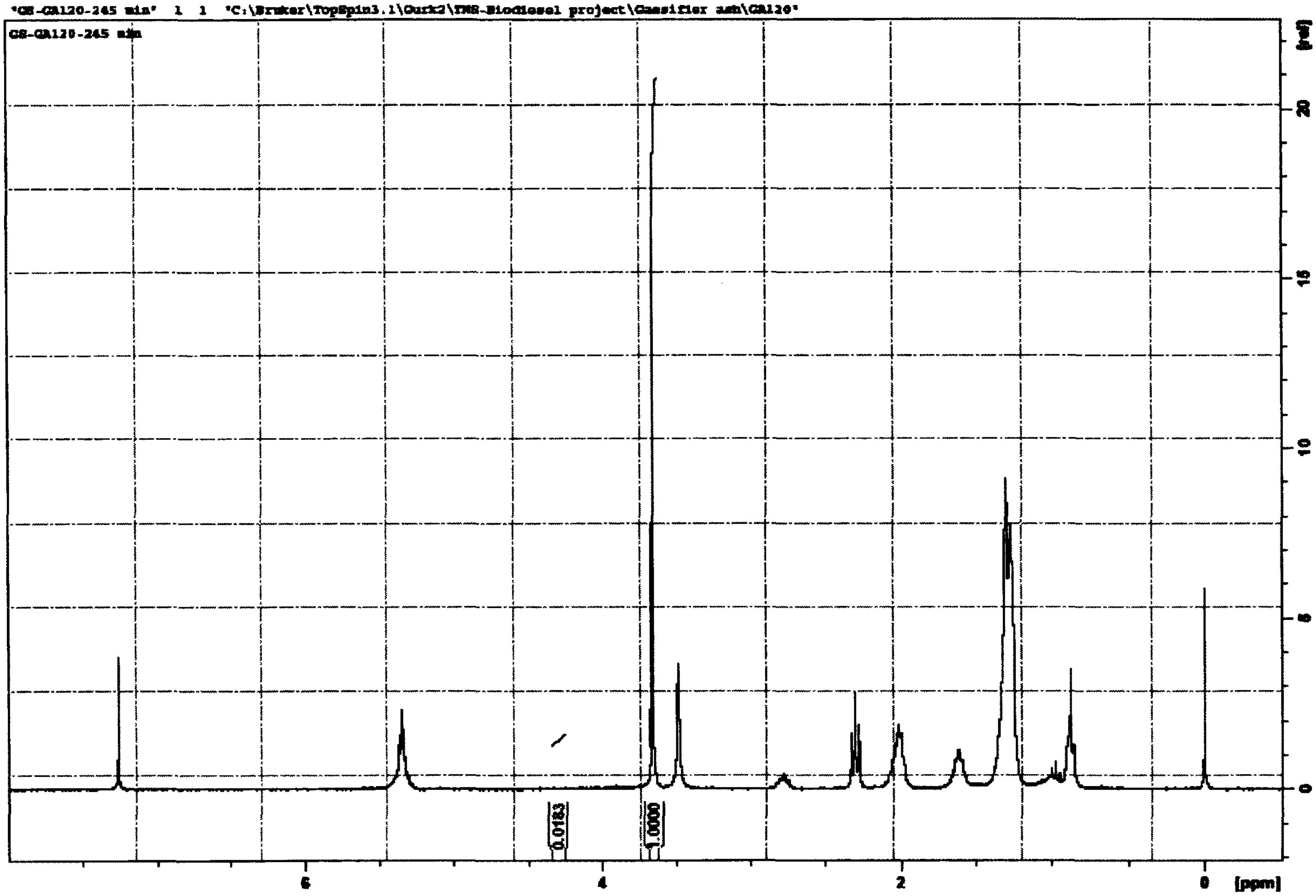

Figure B12. ^{1}H-NMR of GA-120 at 245 minutes

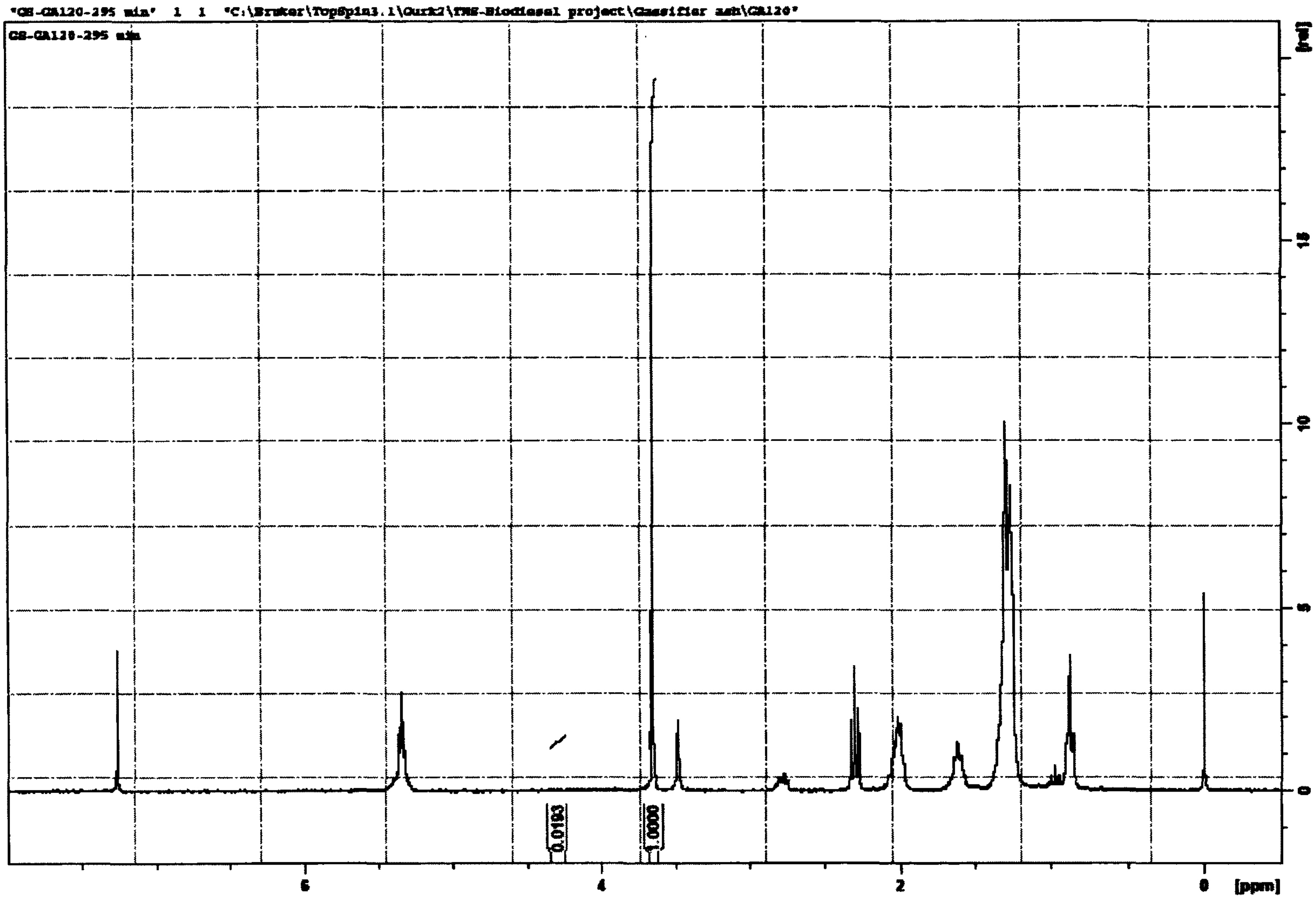

Figure B13. ^{1}H-NMR of GA-120 at 295 minutes

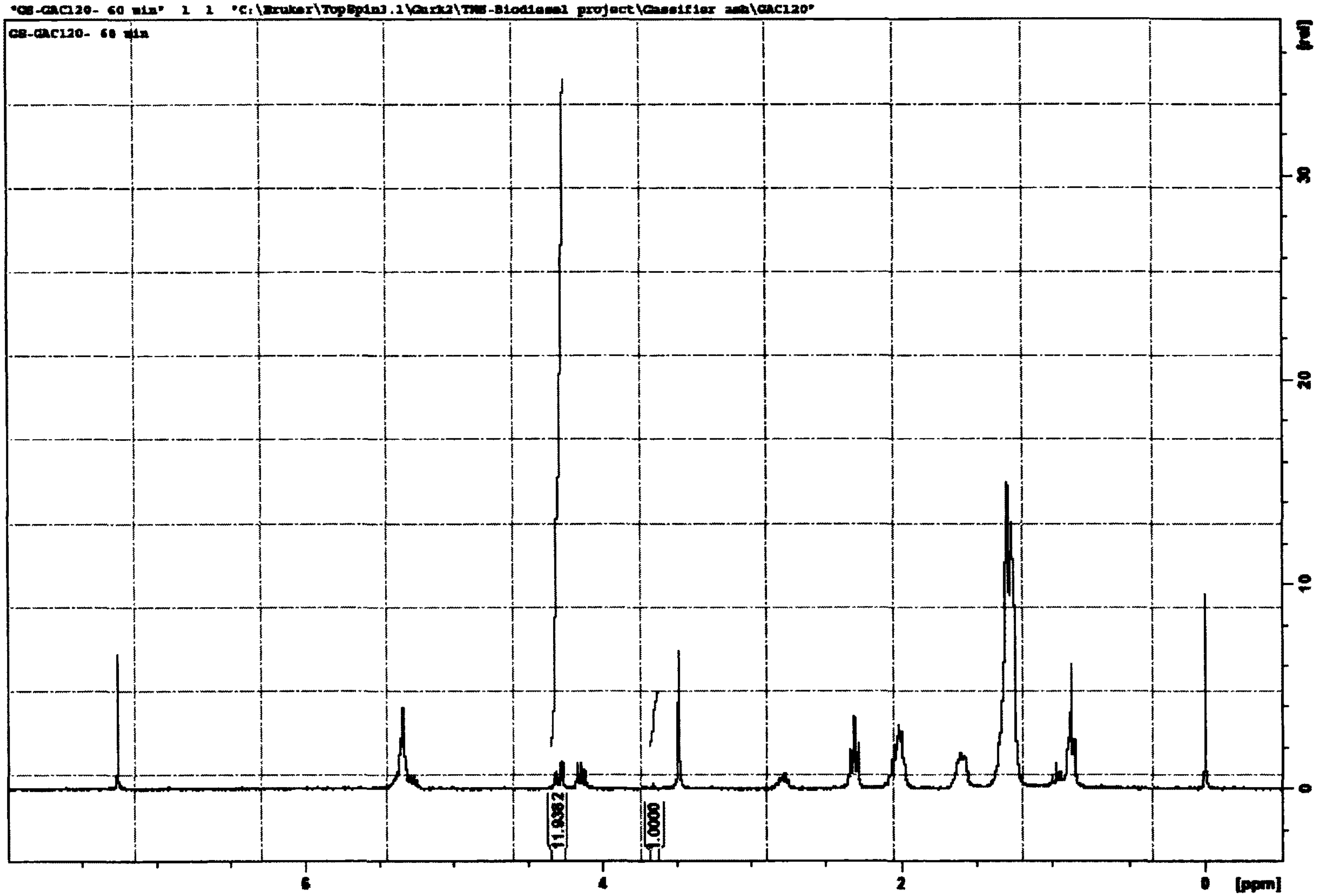

Figure B14. ^{1}H-NMR of GAC-120 at 60 minutes

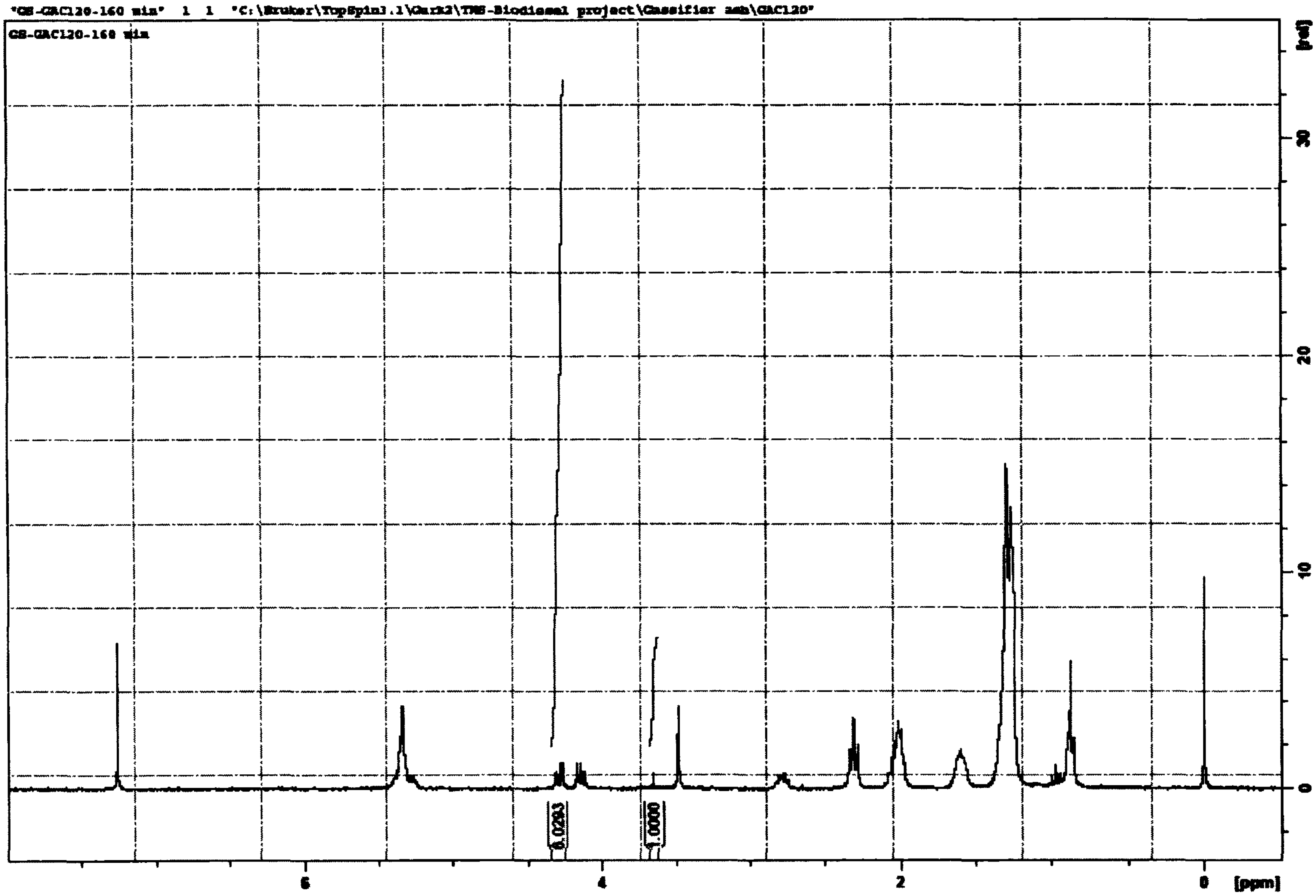

Figure B15. ^{1}H-NMR of GAC-120 at 160 minutes

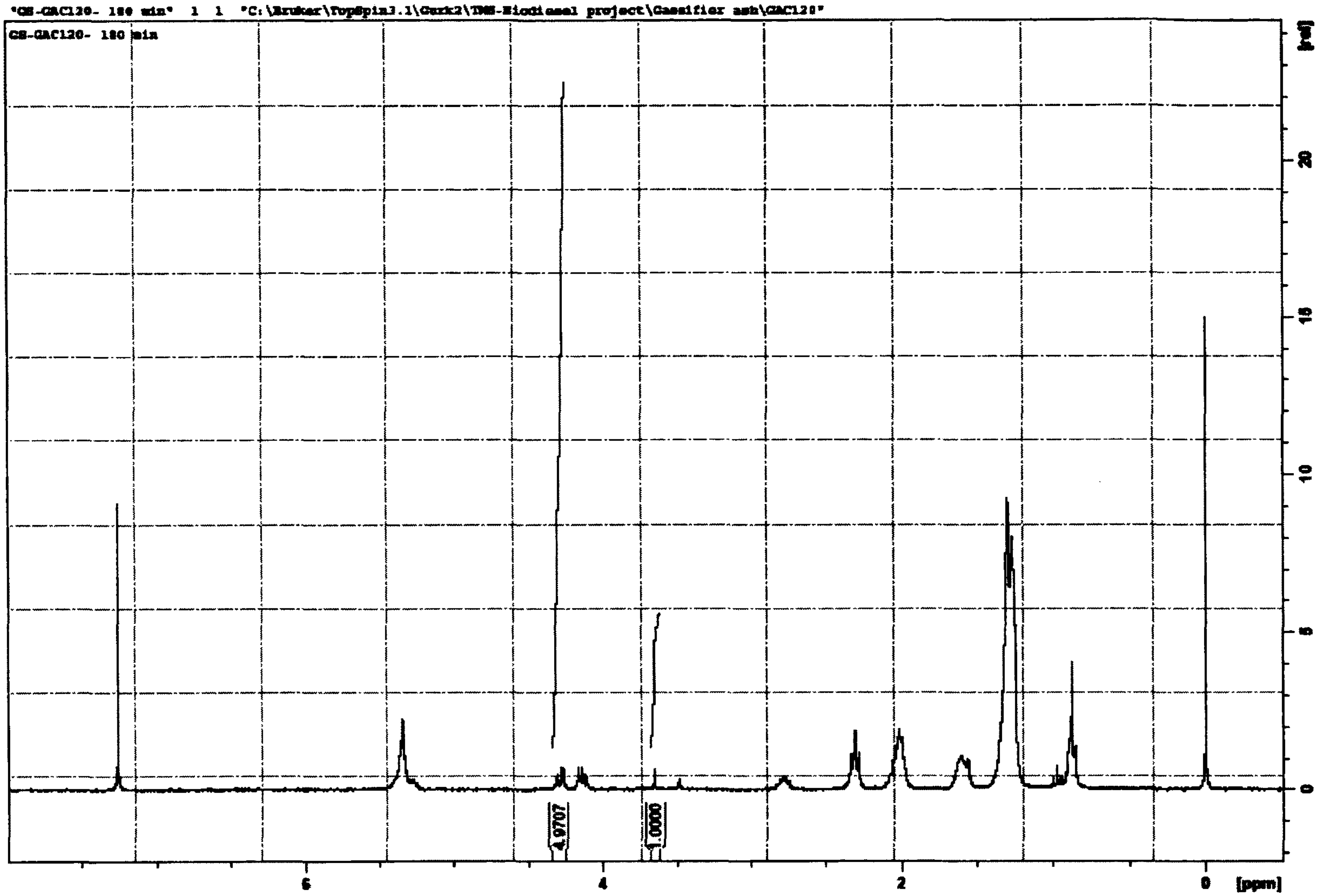

Figure B16. ^{1}H-NMR of GAC-120 at 180 minutes

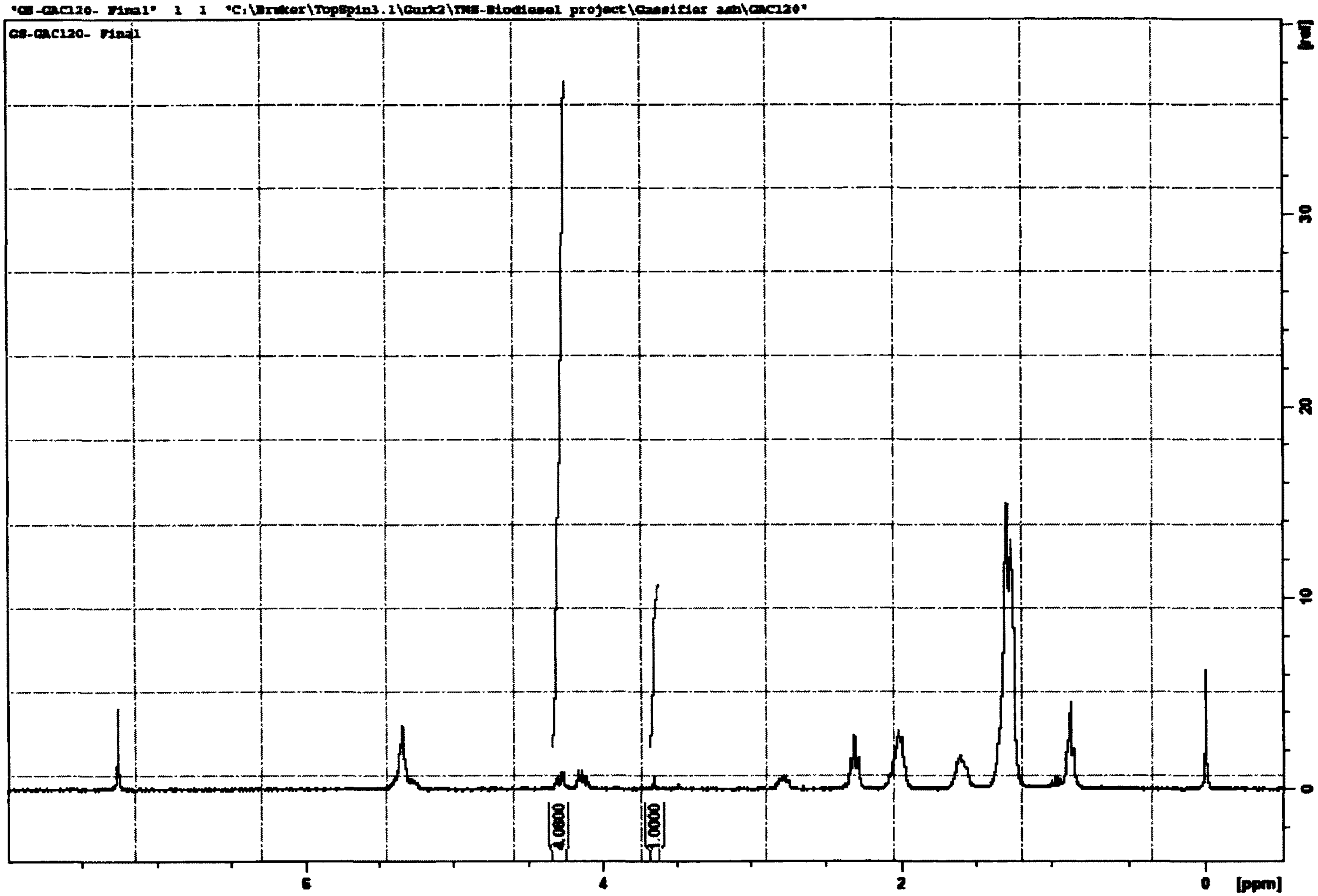

Figure B17. ^{1}H-NMR of GAC-120 at 300 minutes