DEVELOPMENT OF AN ALTERNATIVE METHOD FOR THE DESULFURIZATION OF FLUID CATALYTICALLY CRACKED GASOLINE

by

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Abstract

Canada recently developed new regulations for the amount of total sulfur in fuel, as of January 1st, 2005, thereby limiting the total sulfur to 30 ppmw. Current technology for the removal of sulfur involves hydrotreating, is an expensive process, which may reduce the value of fossil fuels when operated under deep desulfurization conditions. This thesis reports on experiments with a variety of solvents, metal salts, acids, and bases which were unsuccessful at removing sulfur-containing compounds from FCC gasoline. The thesis also reports on the success achieved through the use of Raney nickel. Simply by varying the reaction time and temperature, a maximum reduction of 99 % in the sulfur concentration was obtained using Raney nickel. Finally, experiments were performed that recovered the nickel as nickel oxide. This allows for further processing in order to convert the nickel oxide into nickel aluminum alloy.

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Nomenclature

AMU = Amine Processing Unit

Co(Ni)Mo = Cobalt/Nickel/Molybdenum imbedded into a zeolite catalyst

C^+ = Carbonium Ion

CEPA = Canadian Environmental Protection Act

FCC = Fluid Catalytically Cracked

FID = Flame Ionization Detector

GC = Gas Chromatography

LPG = Liquefied Petroleum Gas

Ni-Al = Nickel Aluminum Alloy

$Ni\text{-}H_{2\text{Raney}}$ = Raney Nickel

ppmw = Parts per Million by Weight

SCD = Sulfur Chemiluminescence Detector

SEM = Scanning Electron Microscope

UVF = Ultraviolet Fluorescence

Vol % = Volume Percent

Wt % = Weight Percent

XRF = X-ray Fluorescence

Acknowledgement

Firstly, I would like to thank my supervisor, Dr. Ron Thring, for his support throughout my graduate studies at UNBC. Also, I am grateful for the financial support he provided me from his Natural Sciences and Engineering Research Council of Canada (NSERC) Research Grant. I would also like to express my gratitude to the other members of my supervisory committee, namely, Dr. David Dick and Mr. Cory Sieben, whom, despite their hectic schedules, were both more than willing to meet with me whenever the need arose. I would like to acknowledge the Prince George Husky Refinery for their collaboration on this project, and especially the laboratory staff, namely, Mr. Ken Gallant, Mr. Brad Hensby and Ms. Katja Otting, for their technical assistance.

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Chapter 1: Introduction

1.1 Introduction

The environmental impacts of the oil and gas sector are becoming increasingly important. The reduction of sulfur requires new technology. As of January 1st, 2005 Canada's aim was to have the sulfur levels down to 30 parts per million by weight (ppmw) for gasoline compared to the old regulation of 150 ppmw (CEPA, 2004). In order to meet increasingly strict regulations there have been several methods developed for the removal of sulfur from fossil fuels. The following is a brief literature review of the environmental risks, the important current technologies used, analytical chemical methods and the approach this thesis investigates.

1.2 Environmental Hazards and Catalyst Poisoning Potential of Sulfur

There are several environmental hazards that sulfur in fossil fuels can create both in the environment and during processing. The combustion products of sulfur are known to cause much environmental damage and are also poisonous to processing catalysts and catalytic converters in vehicles (Ertl *et al.*, 1999). It is estimated that over 100 million tonnes of sulfur enter the atmosphere per year from human activities alone (Kennedy, 1992). Natural sources of sulfur include hydrogen sulfide (H_2S) from decaying organic matter and sulphate respiration (Kennedy, 1992). In addition, the burning of fossil fuels causes sulfur-containing compounds within the fossil fuels to become oxidized into sulfur dioxide, which is the leading cause of acid rain (Kennedy, 1992).

1.2.1 Acid Rain

The production of sulfur dioxide leads to the creation of acid rain, through two mechanisms: aqueous phase oxidation and gas phase oxidation (Schwedt, 2001). In gas phase oxidation sulfur dioxide is being oxidized to SO_3 then forming sulfurous acid in either a gas or liquid phase (Schwedt, 2001). In the aqueous phase sulfur dioxide can be oxidized by hydrogen peroxide. The hydrogen peroxide is minor part of the atmosphere, which is formed by the disproportionation of HO_2 radicals (Bunce, 1994). The aqueous phase oxidation involves sulfur dioxide being hydrolyzed into sulfurous acid, and then it is oxidized further to sulfuric acid (Schwedt, 2001). These two mechanisms have several steps and typically take place in cloud droplets, producing acid rain. The reactions for formation of acid rain through aqueous phase oxidation can be seen in the following reactions 1.1, 1.2, and 1.3, whereas the reactions for gas phase oxidation can be seen in reactions1.4 and 1.5 (Bunce, 1994):

$$2HO_2 \rightarrow H_2O_{2(aq)} + O_{2(g)} \qquad (1.1)$$

$$SO_{2(aq)} + H_2O_{2(aq)} \rightarrow H_2SO_{4(aq)} \qquad (1.2)$$

$$HSO^-_{3(aq)} + H_2O_{2(aq)} \xrightarrow{H^+} HSO^-_{4(aq)} + H_2O_{(l)} \qquad (1.3)$$

$$SO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2SO_{3(aq)} \qquad (1.4)$$

$$H_2SO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HSO^-_{3(aq)} \qquad (1.5)$$

The acid rain produced has several impacts on the forest and lake ecosystems. Plants are impacted especially when they adsorb sulfur trioxide as a gas (Kennedy, 1992). This causes mineral acids to form on the cytoplasm. Another major problem can occur if soils are exposed to continued acidification from acid rain. This continuous acidification can cause an imbalance in the natural buffering capacity of a soil causing serious pH declines in the soils (Kennedy, 1992). This pH decline can lead to weakened vegetation, which is more susceptible to pathogen and insect attack, crown thinning from leaf or needle loss, nutrient deficiencies, changes in branching habit, and decline in radial growth (Kennedy, 1992). The affects of pH decline eventually lead to tree death and forest decline (Kennedy, 1992).

The acidification of lakes affects the lake biota. It has been found that at a pH of 5.8, lake trout were eliminated in some cases (Kennedy, 1992). At a pH below 6 the populations of small animals (shrimp, etc) can decrease and several plant species are substituted for other, hardier species (Kennedy, 1992). Therefore, acidification of lakes causes a reduction in the diversity of both plant and animal species.

1.2.2 Health Risks

Besides acidification of forest soils and lakes, particulate matter and soil or water contamination with thiophenes can be a serious health risk. Also, sulfur dioxide is a gas, which can adsorb to fine particulates in the atmosphere and can irritate respiratory tracts (Schwedt, 2001). Sulfur dioxide is typically removed from flue gases directly after combustion. This is typically achieved through the addition of calcium hydroxide ($Ca(OH)_2$), calcium carbonate ($CaCO_3$) or activated charcoal as seen in reaction 1.6 (Schwedt, 2001). However, not all sulfur dioxide is removed in this process as the reaction is quite temperature sensitive (Schwedt, 2001).

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \quad (1.6)$$

There have been recent studies reported on the toxicities of thiophenes in the environment. These studies particularly have been looking into the toxicological effects of thiophenes in petroleum mixtures. The research is ongoing but it has been found that some of the higher molecular weight thiophenes have mutagenic and carcinogenic potential (Kropp and Fedorak, 1998). However, more research is needed on this topic to determine degradation potential of the thiophenes and the ability of biological organisms or the environment to degrade organic sulfur compounds. Also, more research is necessary to determine the specific health effects of these contaminants.

1.2.3 Catalyst Poisoning

Finally, the poisoning of catalysts in refineries and vehicles causes many problems. In refineries, the poisoning of refinery catalysts causes many processing problems. For example some sulfur compounds, such as hydrogen sulfide and sulfur dioxide, can be corrosive to equipment and damage or reduce activity of processing catalysts, which is similar to the affects seen in catalytic converters of vehicles (Krishnan and Sotirchos, 1994).

The poisoning of catalysts in vehicles involves the ability of sulfur oxides to reduce the activity of wash coat oxides such as aluminum oxides and cesium oxides that surround the noble metal portion of the catalyst (Ertl *et al.*, 1999). Adsorption and/or chemisorption of sulfur oxides on to wash coat oxides can occur at low temperatures, deactivating the catalysts (Ertl *et al.*, 1999). Oxides of sulfur also have the ability to poison the noble metal portion of the catalyst in the catalytic converters (Dupain *et al.*, 2003). However, this reaction can usually be reversed once the catalyst is operating at a higher temperature.

Catalyst deactivation in vehicles can also occur from the precious metals being poisoned by sulfur oxides (Ertl *et al.*, 1999). The sulfur oxides come from the combustion of sulfur-containing compounds in the fuel. The result of the catalyst poisoning is a decrease in catalyst activity for the reactions, which destroy carbon monoxide and nitric oxides. The reactions involving the elimination of carbon monoxide and nitric oxides can be seen in reactions 1.7, 1.8, 1.9, and 1.10 (Ertl *et al.*, 1999). This will reduce a vehicle's pollution control efficiency and increase other, potentially more harmful, pollutants entering the atmosphere (Gokeler *et al.*, 2002).

$$CO+\frac{1}{2}O_2 \rightarrow CO_2 \qquad (1.7)$$

$$CO+H_2O \rightarrow CO_2+H_2 \qquad (1.8)$$

$$CO+NO \rightarrow \frac{1}{2}N_2+CO_2 \qquad (1.9)$$

$$H_2+NO \rightarrow \frac{1}{2}N_2+H_2O \qquad (1.10)$$

1.3 Canada's New Sulfur Regulations for Gasoline

With the variety of environmental and health concerns around sulfur, the regulation's of sulfur in gasoline fall under the Canadian Environmental Protection Act (CEPA). The CEPA was revised on April 30th 2004, to include new sulfur regulations (CEPA, 2004). The new regulations stated that as of January 1st 2005, sulfur levels in gasoline would need to be below 30 ppmw when calculated using a pool average (CEPA, 2004). The CEPA states that the pool average is the volume-weighted average concentration of sulfur in gasoline produced at that refinery. This means, for example, that if the fluid catalytically cracked (FCC) gasoline stream makes up 40% of the total gasoline produced at that refinery then it will contribute 40% of the sulfur concentration to the final product. Therefore, the FCC gasoline can have a sulfur concentration higher than 30 ppmw, as long as when it is added to the rest of the gasoline produced at the refinery the concentration is below 30 ppmw. The new Canadian regulations and regulations around the world result from the growing concern over sulfur in fossil fuels and are leading towards sulfur-free fuels in the future.

1.4 Fluid Catalytic Cracking Process

The idea of fluid catalytic cracking is to crack lower-value, higher molecular weight stocks to produce higher-value, lower molecular weight products (Matar and Hatch, 2001). These higher value products are typically gasoline, distillates and C_3/C_4 olefins (Meyers, 2004). The main feeds for catalytic cracking are heavier refinery streams and excess refinery gas oils which typically contain higher concentrations of basic and polar molecules and asphaltenes (Matar and Hatch, 2001). The crackability of any one of these feeds is a function of the proportions of paraffinic, naphthenic, and aromatic species (Meyers, 2004). Three basic process functions affect the product yield of FCC units: operating conditions, feedstock properties and catalyst characteristics (Sertic-Bionda *et al.*, 2000).

Due to the strict regulations surrounding sulfur, it is important to determine the most contaminated fuels. The gasoline from reforming or isomerization units is typically made from distillate feeds, which contain almost no sulfur (Leflaive *et al.*, 2002). However, the FCC feedstock is a combination of a variety of heavier feeds, which contain between 0.5 – 1.5 wt percent of sulfur (Leflaive *et al.,* 2002). The amount of sulfur in the feed is a result of the geographical origin of the crude oil (Meyers, 2004). However, Leflaive *et al* (2002) determined that in the presence of H_2S, olefins and diolefins the FCC catalyst could transform these compounds into thiophenic compounds. Also, long alkyl chain thiophenes can be cracked by FCC catalysts into thiophene and short alkyl chain thiophenes, which are then stable under FCC conditions (Leflaive *et al.*, 2002). Therefore, as FCC gasoline typically makes up between 30-40% of the gasoline pool, it is important to reduce its sulfur concentration as much as possible (Leflaive *et al.*, 2002).

1.4.1 FCC Catalysts

FCC units continually circulate a zeolite catalyst in a fluidized bed reactor, which rapidly reacts in the vapour phase with the feed (Meyers, 2004). The catalysts used in cracking have improved from synthetic amorphous silica/alumina to silica/alumina catalysts with incorporated zeolites (Matar and Hatch, 2001). These zeolite catalysts have both Lewis and Brønsted acid sites and the presence of holes in the crystal lattice which make them superior to amorphous silica-alumina catalysts (Matar and Hatch, 2001). An example of both the Brønsted acid (left side) and the Lewis acid (right side) form of silica-alumina can be seen in Figure 1.1.

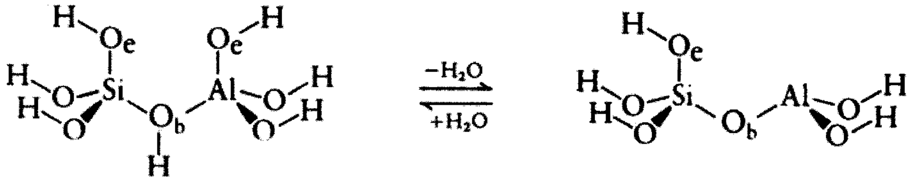
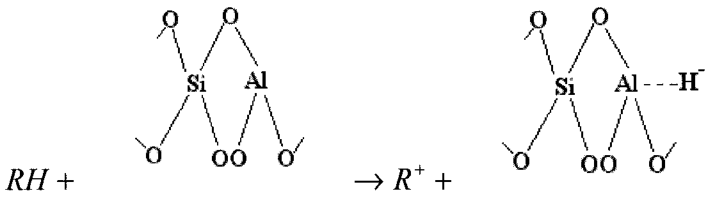


Figure 1.1: **Illustration of silica/alumina catalyst with both the Brønsted acid (left side) and Lewis acid (right side) sites (Campbell, 1988).**

The Lewis acid sites are a result of the bonding of the silica and alumina structure. The other potential site is a Brønsted acid site. The Brønsted acid site can be created through the interaction of a Lewis acid site with a hydroxide ion (Campbell, 1988). This creates a negative charge on the aluminum atom while the proton can bond with an oxygen atom forming a partial bond (Campbell, 1988). This partial bonding of the hydrogen atom allows it to be easily donated thus creating a Brønsted acid site (Campbell, 1988). The greater acid site density and higher adsorption power along with smaller pores creates higher activity and better selectivity (Matar and Hatch, 2001). Lewis acid and Brønsted acid sites are locations for the reactions in the FCC unit.

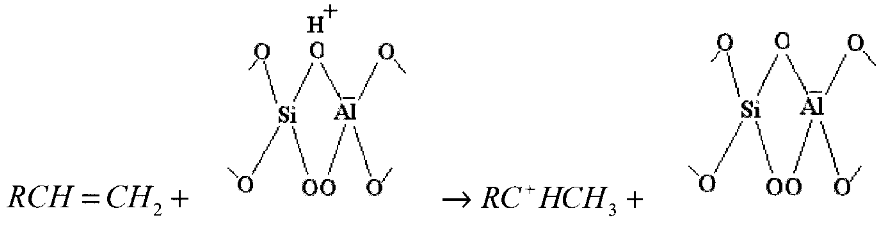
1.4.2 FCC Reactions

There have been several attempts to model the kinetic reactions occurring in FCC units; this has become important in order to optimize fuel processing in the FCC unit (Dupain *et al.*, 2003). This is especially important as it is not feasible to change the process conditions in a commercial FCC unit in order to test each scenario (Pareek *et al.*, 2003). There are three main reactions produced during catalytic cracking, which will produce carbonium ions. The carbonium ions are more selective towards specific bonds than free radicals, which are formed in thermal cracking and cause random bond breaking (Meyers, 2004). As shown below, the first reaction involves the abstraction of a hydride ion by a Lewis acid site (Matar and Hatch, 2001):



(1.11)

The second possible reaction is between a BrØnsted acid site and an olefin as seen in reaction 1.12 (Matar and Hatch, 2001):



(1.12)

Finally, in reaction 1.13, the reaction of a carbonium ion formed in either of the above equations with another abstraction of a hydride ion (Matar and Hatch, 2001):

$$R^{+}+RCH_2CH_3 \rightarrow RH+RC^{+}HCH_3 \quad (1.13)$$

Once these carbonium ions are formed they can react in four potential ways. The molecules containing the C^{+} ion can crack into smaller molecules, react with another molecule, isomerize into a different form or react with the catalyst to stop the reaction (Meyers, 2004). It is most important to note that the reactions proceed to form the most stable carbonium ion, so isomerization of secondary to tertiary carbonium ions occurs frequently (Meyers, 2004).

These reactions occur when the feedstock contacts the hot regenerated catalyst (Meyers, 2004). The feedstock becomes vaporized and is converted by the catalyst through the above reactions to lower boiling fractions, such as gasoline, light cycle oil and dry gas (Meyers, 2004). As sulfur is the focus of this thesis it is important to note that sulfur compounds do not affect the crackability of a feed, however the cracked sulfur compounds show up in the liquid products. Sulfur also exits the FCC units as H_2S and sulfur oxides causing air pollution problems if not captured (Meyers, 2004).

1.4.3 FCC Reactor Types

These reactions typically occur in one of two main types of reactors: fluidized bed or moving bed. The fluidized bed is more common and involves the catalyst typically being a porous powder with an average particle size of 60 μm (Matar and Hatch, 2001). In this process the feed is preheated and held at a temperature of about 450 – 520 ^{0}C. A concurrent upward flow of heated feed and hot regenerated catalyst occurs in the riser with an approximate pressure of 10 – 20 psig (Matar and Hatch, 2001). The vapours are then separated from the catalyst using cyclones, which are passed into a fractionator for separation of different product streams (Matar and Hatch, 2001). The separated catalysts are regenerated due to coke deposits forming on the catalysts surface during FCC thus making it less active (Meyers, 2004). Typically, the catalysts are combusted with air to strip the coke from the catalyst surface (Meyers, 2004). This regenerated catalyst is then returned to the riser to go through the process again. In the moving bed process, the catalyst is in the form of beads rather than a powder. These beads descend through the feed by gravity action to the regeneration zone (Matar and Hatch, 2001). A general schematic of a straight – riser unit can be seen in Figure 1.2.

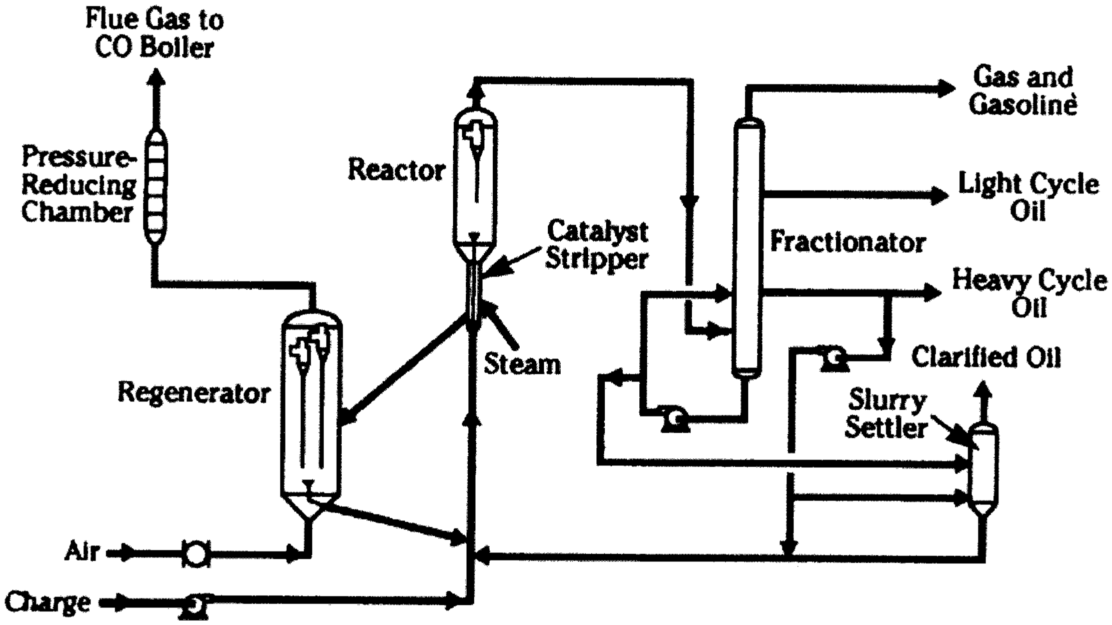


Figure 1.2: **UOP straight-riser FCC unit flow chart (Meyers, 2004).**

1.5 Current Sulfur Processing Techniques

There are currently several commercial processes to remove sulfur from refinery feeds either before they reach the FCC unit or after they have been treated in the FCC unit. Most of these processes are designed for the recovery of H_2S and mercaptans. There are very few processes that remove the heavier sulfur compounds such as thiophenes. The many processes for H_2S and mercaptan recovery include amine-processing units, wet sulfur scrubbers, Claus process, Merox process and limestone beds. One of the only processes in operation at refineries for the removal of other sulfur species is hydrotreating. While hydrotreating has the ability to reduce sulfur concentrations to the new regulation levels, the problem is that with deep desulfurization, the production of light hydrocarbons can increase the amount of hydrogen consumed and decrease the yield of liquid fuel (Kemsley, 2003). Also, the olefins, which are responsible for the high octane number, can be destroyed decreasing the octane value of the gasoline causing more additives to be needed (Kemsley, 2003). A brief overview of these methods follows.

1.5.1 Amine Processing Units

The amine processing units (AMU) remove H_2S from the recycled gas streams and fuel gas/liquefied petroleum gas (LPG), which is produced during processing of crude oil (Meyers, 2004). The amines selected for these processes are typically monoethanolamine (MEA), diethanolamine (DEA), or methyldiethanolamine (MDEA). Typically, DEA is used in a 25 to 33 wt % solution in water (Meyers, 2004).

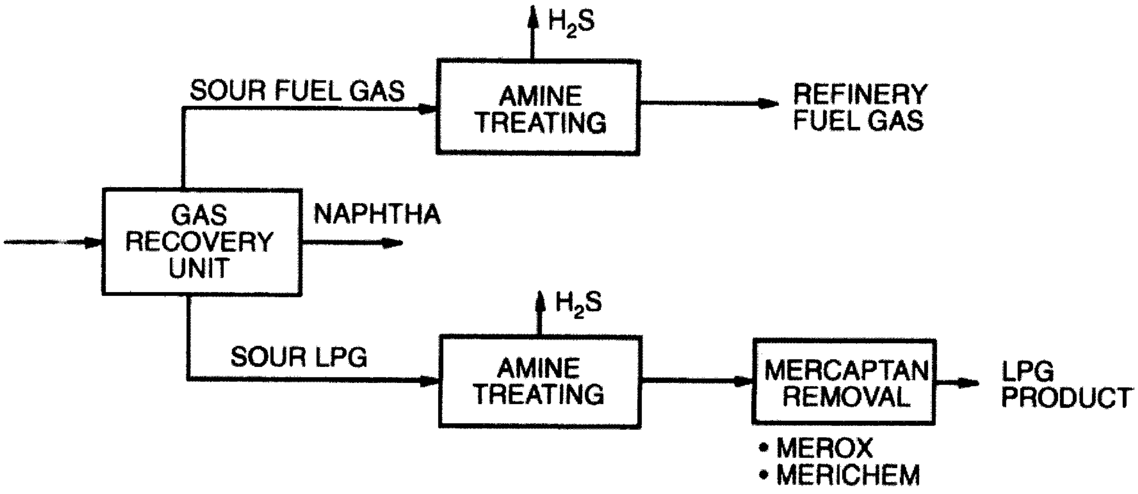


Figure 1.3: **Schematic of fuel gas amine treating (Meyers, 2004).**

The process for amine treating involves multiple amine absorbers with a common amine regeneration unit (Meyers, 2004). A circulating amine stream removes the H_2S from the recycled gas stream and the off-gases from the LPG recovery units as seen above in Figure 1.3 (Meyers, 2004). The contaminated amine then flows to the regenerator where steam strips the H_2S from the amine as seen in Figure 1.4. The amine is then cooled before being returned to the absorbers (Meyers, 2004). This stripping procedure produces sour water, which is further treated with steam to vaporize the H_2S, this vaporized H_2S flows to the sulfur plant where the Claus process concentrates and oxidizes it into elemental sulfur (Meyers, 2004). The clean water is then cooled in order to be reused in the refinery.

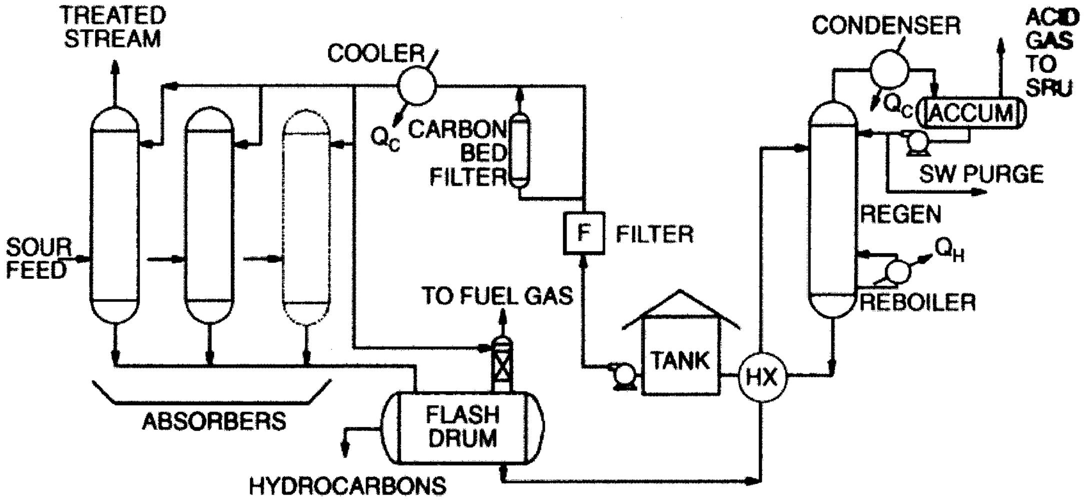


Figure 1.4: **Amine Regeneration Unit (Meyers, 2004).**

1.5.2 Wet Sulfur Scrubbers

Sulfur scrubbers are used to remove SO_x from the air emissions (Meyers, 2004). The SO_x emissions come from the sulfur being attached to the coke on FCC catalysts, which is then oxidized and emitted with the flue gas. The wet sulfur scrubbers use a caustic soda (NaOH) to react with SO_2, which is then removed as a soluble salt, while SO_3 forms a sulfuric acid mist in the presence of NaOH. The soluble salts and acid mist are then filtered into a spray tower where condensation occurs, collecting the soluble salts and acid mist (Meyers, 2004). Finally, the flue gas is sent through a droplet separator, which causes the gases to spiral down a tower with the centrifugal force causing any remaining water droplets to run down the sides of the tower. This process has been shown to be 92 % efficient at removing harmful sulfur oxide containing particles and can be seen in Figure 1.5 (Meyers, 2004).

However, this thesis is more concerned with the sulfur in the gasoline products rather than in the air emissions.

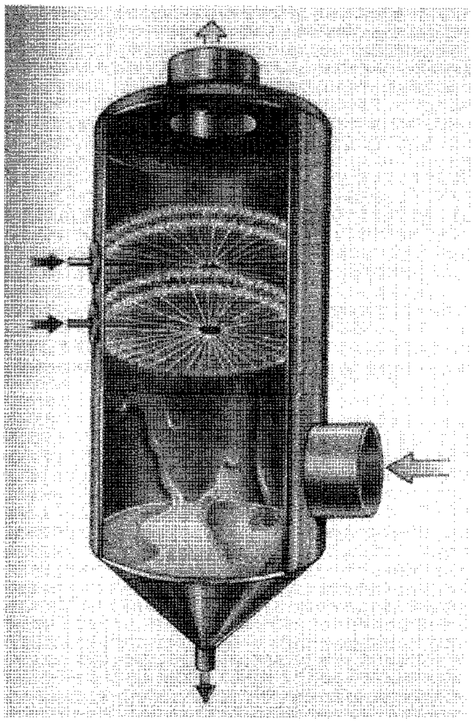


Figure 1.5: **Wet Scrubber absorber vessel/spray tower (Meyers, 2004).**

1.5.3 The Merox Process

The Merox process uses a catalytic procedure to remove mercaptans or convert them to lesser disulfides as the schematic in Figure 1.6 shows (Meyers, 2004). A caustic solution is used for mercaptan removal from LPG, treating gases, and light-gasoline fractions. Once the mercaptans are dissolved in the caustic solution, air is injected into the stream. The air converts the mercaptans to disulfides, which are then separated from the caustic stream (Meyers, 2004). The disulfides are then sent to a processing unit for conversion to elemental sulfur.

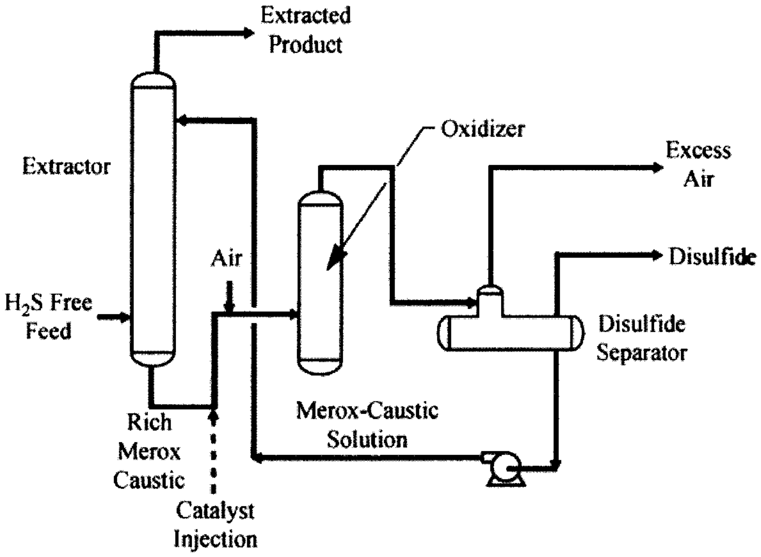


Figure 1.6: **Merox mercaptan-extraction unit (Meyers, 2004).**

1.5.4 The Claus Process

The Claus process partially oxidizes H_2S to create sulfur (Matar and Hatch, 2001). This process is present at almost every refinery and uses the hydrogen sulfide feeds from the above-mentioned methods to produce sulfur. There are two parts to the Claus process, a burning section that oxidizes sulfur, and a reactor which causes a reaction between H_2S and a bauxite catalyst as seen in Figure 1.7 (Matar and Hatch, 2001).

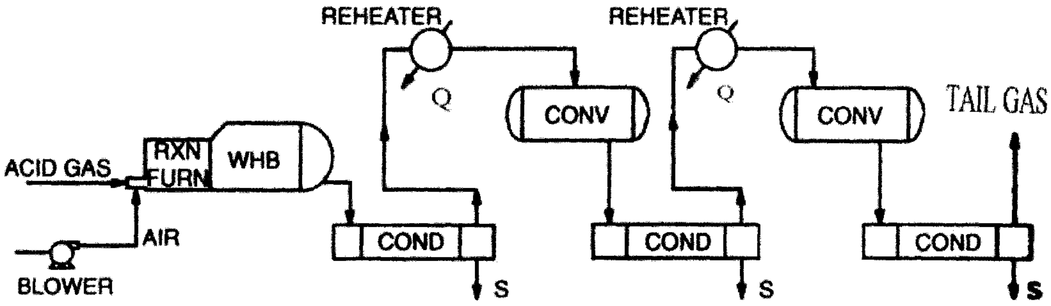


Figure 1.7: **Two-stage Claus unit (Meyers, 2004).**

The burner section involves the oxidation of hydrogen sulfide into sulfur dioxide and the partial oxidation of hydrogen sulfide into sulfur (Matar and Hatch, 2001). In the reactor the unchanged H_2S reacts with a bauxite catalyst in the presence of oxygen to produce sulfur. The sulfur in the reactor is then removed through condensation (Matar and Hatch, 2001). This process produces approximately 90 – 95 % of the world's sulfur, which is then sold and used in many industries, such as fertilizer production (Matar and Hatch, 2001).

1.5.5 Hydrotreating

Hydrotreating can be used to pretreat feeds before entering the FCC unit or can be used to treat the gasoline fraction after the FCC process (Dupain *et al.*, 2003). This is one of the only methods commercially available to remove heavier sulfur compounds such as thiophenes. Hydrotreating reactions typically occur in the liquid phase with Figure 1.8 showing a schematic of the process (Meyers, 2004). The feed is saturated with hydrogen gas, which then flows through the catalyst pores and adsorbs to the catalysts surface. The reaction then occurs on the catalyst surface where sulfur-containing molecules are cracked into smaller molecules (Meyers, 2004). The reactions are very exothermic and, in the case of sulfur, involve breaking the two sulfur-carbon bonds and adding four hydrogen atoms. The removed sulfur then forms H_2S, which can diffuse out of the catalyst pores and be removed from the hydrotreater (Meyers, 2004).

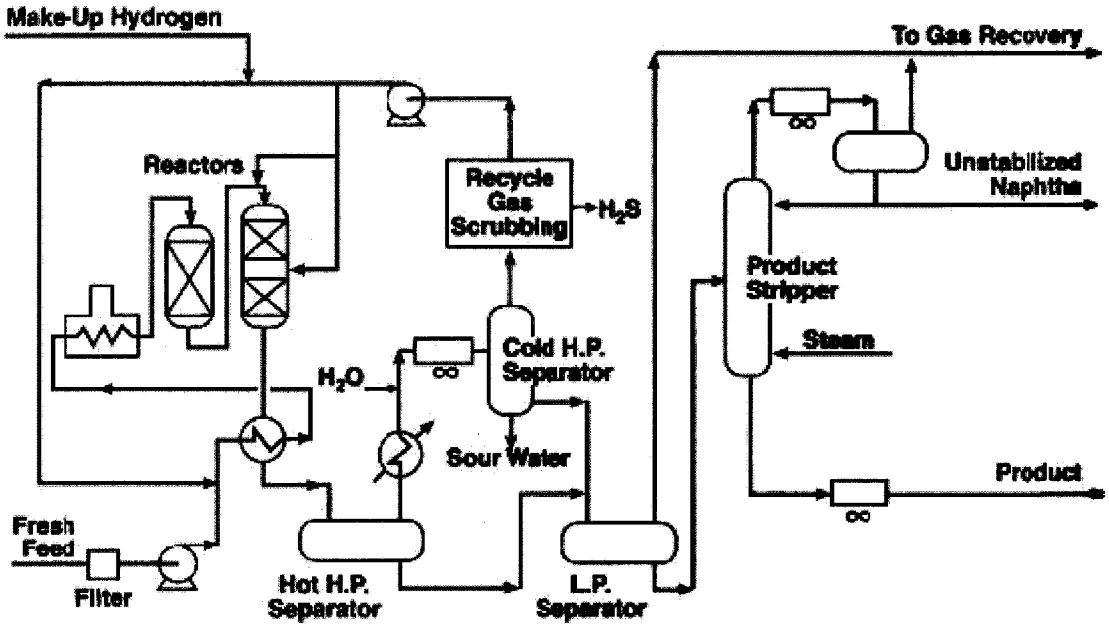


Figure 1.8: **Hydrotreating flow scheme (Meyers, 2004).**

Perfecting hydrotreating catalysts has been extensively researched to increase its ability to remove contaminants and give the catalyst a long life, which are both accomplished by decreasing the poisoning of catalysts. The hydrotreating catalysts are typically Co(Ni)Mo or NiW supported by aluminum oxide (Coulier *et al.*, 2002). There has been some research on the addition of chelating agents to improve the effectiveness of the catalyst preparation. The addition of nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) stabilizes Ni and Co until a temperature is reached where Mo or W have reacted with sulfur to form sulfides (Kishan *et al.*, 2001). Medici and Prins (1996) also showed that by adding chelating agents during the impregnation step and leaving out the calcination step for SiO_2-supported hydrotreating catalysts, the activity is just as strong as γ-Al_2O_3-supported hydrotreating catalysts.

The development of new hydrotreating catalysts other than the typical Co(Ni)Mo catalysts is fast growing. Oyama *et al,* (2002) have developed a new type of catalyst from the transition metal phosphides group, such as Ni_2P and Fe_2P. The catalyst, Ni_2P, has shown promise as 98 % of the sulfur was removed compared to only 78 % with NiMo (Oyama *et al.*, 2002). These metal phosphide catalysts are also promising due the lack of a layered structure, allowing the entire surface area to be exposed and due to the moderate preparation temperatures and inexpensive precursors (Oyama *et al.*, 2002).

In terms of catalyst poisoning, both H_2S and NH_3 are present in fossil fuels, which can inhibit the hydrotreating catalysts by competitive adsorption with unsaturated hydrocarbons (Blanchin *et al.*, 2001). The most important property about Co(Ni)Mo hydrotreating catalysts is the ability to perform the conversion of sulfur-containing compounds into hydrocarbons even in the presence of H_2S and NH_3 (Hensen *et al.*, 2003). The inhibiting effect of H_2S is much more significant at high rather than low partial pressures (Blanchin *et al.*, 2001).

Much of the research into poisoning of catalysts involves the effects of the support on the sulfidation of the metals. Coulier *et al,* (2002) determined that the presence of tungsten prevented cobalt and nickel from interacting with the support. This allowed a higher degree of sulfidation starting at lower temperatures and more catalyst poisoning (Coulier *et al.*, 2002). So a strong interaction with the support is necessary to reduce catalyst poisoning. Also, Hensen *et al,* (2003) showed that the poisoning effect of H_2S could be reduced by supporting the Co(Ni)Mo catalysts on materials with high Brønsted acidity and a strong metal-support interaction. These materials include carbon or aluminum oxide supports.

Carbon has been shown to be a much better support than aluminum oxides as there is a 30 % increase in the catalytic activity (Glasson *et al.*, 2002).

1.5.6 Limestone Fluidized Beds

Limestone has been used for many years to remove H_2S from coal through reaction 1.14 (Fenouil and Lynn, 1995):

$$CaCO_{3(s)} + H_2S_{(g)} \rightleftharpoons CaS_{(s)} + H_2O_{(g)} + CO_{2(g)} \qquad (1.14)$$

This reaction takes place in the gasifier during coal processing at high temperatures and pressures and is carried out by simply adding limestone or its precalcined form (Fenouil and Lynn, 1995). The particles must react directly with H_2S to cause desulfurization (Krishnan and Sotirchos, 1994). Fenouil and Lynn (1995) discovered that a large excess of limestone is needed compared to theoretical values in order to remove H_2S. Therefore, Fenouil and Lynn (1995) used sorption into a moving bed of limestone particles.

The kinetic study of the moving bed of limestone found that at temperatures below 670 ^{0}C the reaction between $CaCO_3$ and H_2S is the rate-limiting step for sulfidation (Fenouil and Lynn, 1995). However, at temperatures above 670 ^{0}C the CaS product forms a layer around the limestone grains and prevents CO_2 and H_2O from diffusing out (Fenouil and Lynn, 1995). Therefore, this is the rate-limiting step at higher temperatures, not the $CaCO_3$ and H_2S reaction shown in reaction 1.14. Fenouil and Lynn (1995) also found in another study that the calcination of limestone at high temperatures could compete with the $CaCO_3$ and H_2S reaction.

The competition reaction is as follows in reaction 1.15 (Fenouil and Lynn, 1995):

$$CaCO_3 \rightleftharpoons CaO + CO_2 \quad (1.15)$$

This reaction forms lime, which can then react with H_2S. The difference between precalcined limestone and regular limestone is the pore structure present within the precalcined limestone (Krishnan and Sotirchos, 1994). This pore structure allows diffusion to occur so reactions can continue at the interface between CaS and the coal gas within the pores (Krishnan and Sotirchos, 1994). This reaction may occur continuously on precalcined limestone but the reaction with regular limestone only occurs at the surface of the reacting particles (Krishnan and Sotirchos, 1994). However, as with the initial study, the reaction was ultimately controlled by the diffusion through the CaS layer (Fenouil and Lynn, 1995).

Fenouil and Lynn (1995), and Nakazato *et al.* (2003), both used fluidized bed reactors. Nakazato *et al.* (2003) found that the H_2S removal in a fluidized bed reactor was dependent upon the limestone particle diameter. As the particle diameter decreased the efficiency increased (Nakazato *et al.*, 2003). Also, it was determined that the H_2S removal efficiency increased with temperature until approximately 1073 K, where the efficiency then decreased with increasing temperature (Nakazato *et al.*, 2003). Therefore, the limestone appeared to be good at removing H_2S under certain reaction conditions. However, it does not appear to remove any other types of sulfur-containing compounds. With each of these sulfur removal methods, it is important to have a reliable way to measure the sulfur contained in fossil fuels.

1.6 Analytical Methods

There have been many methods developed in order to analyze for sulfur in petroleum products. Sulfur is one of the major sources of concern for heteroatoms in petroleum products next to nitrogen (Hsu, 2003). The methods developed for analyzing sulfur include gas chromatography with a variety of detectors, ultraviolet fluorescence, energy-dispersive X-ray fluorescence spectrometry, and inductively coupled plasma spectroscopy. Each of these methods has its advantages and disadvantages, which will briefly be described below.

1.6.1 Gas Chromatography

Refineries and analytical laboratories have used gas chromatography to analyze for sulfur extensively. There are several different types of detectors that can be used. These include: flame photometric detector (FPD), electrolytic conductivity (Hall) detector, atomic emission detector (AED), electron capture sulfur detector (ECD) and a universal sulfur chemiluminescence detector (SCD) (Hsu, 2003). Each detector has associated pros and cons for sulfur analysis.

The FPD is used frequently but the response is adversely affected by co-eluting water and hydrocarbons (Hsu, 2003). Flame photometric detectors are typically problematic when large concentrations of hydrocarbons mask certain sulfur species present at lower concentrations (Hsu, 2003). The AED is also useful for identifying and quantifying sulfur. However it is quite costly and requires time-consuming calibrations (Hsu, 2003). The ECD and electrolytic conductivity detectors are rarely used for sulfur analysis.

The SCD is currently one of the best detectors for sulfur. It is superior to the FPD as there is no interference from hydrocarbons or water vapour, and is very sensitive to lower sulfur concentrations (Hsu, 2003). The SCD operates under the following reactions (Hsu, 2003):

$$RSR' + O_2 \rightarrow SO + \text{Other products} \quad (1.16)$$

$$SO + O_3 \rightarrow SO_2^* + O_2 \quad (1.17)$$

$$SO_2^* \rightarrow SO_2 + hv \quad (1.18)$$

When the sulfur compounds pass through the GC column and the FID SO is produced, it emits a blue chemiluminescence of SO_2 when it reacts with ozone (Hsu, 2003). The light is emitted between 260 to 480 nm (Hsu, 2003). The FID is not capable of determining individual sulfur compound concentrations so an SCD can be used. There has also been an ASTM method developed for the use of SCD to measure sulfur concentrations. The ASTM method D5623 is the standard test method for sulfur compounds in light petroleum liquids by gas chromatography and sulfur selective detection (Annual book of ASTM standards, 2003). This method gives the reproducibility and repeatability of the standard test under the selected operating conditions (Annual book of ASTM standards, 2003).

A method published by Yin and Xia (2004) uses both GC/FPD and GC/MS to identify sulfides and thiophenes. In order to separate the thiophenes, the sample is washed with silver nitrate and then passed through a GC/FPD (Yin and Xia, 2004). The sulfides are extracted using a solvent, which causes a separation of the sulfides into the aqueous phase from the oil phase. The aqueous phase is diluted with water and then extracted with petroleum ether (Yin and Xia, 2004). This produces the crude sulfur compounds, which are further purified using vacuum distillation. This phase is then diluted with water and extracted with hexane to produce purified sulfur compounds (Yin and Xia, 2004). These purified sulfur compounds are then analyzed using GC/MS and GC/FPD.

Recently, a two-dimensional GC x GC has been combined with a SCD to separate the different sulfur groups and identify sulfur compounds (Hua *et al.*, 2003). The two-dimensional GC x GC analysis uses the retention time on the x-axis and the polarity-based retention time on the y-axis (Hua *et al.*, 2003). This reduces the necessity of a highly efficient column and highly stable retention times in the GC (Hua *et al.*, 2003). So far this has been applied mostly to diesel fuels, as diesel fuels typically have more thiophenes and dibenzothiophenes than gasoline.

1.6.2 Ultraviolet Fluorescence

In the method involving ultraviolet fluorescence, a hydrocarbon sample is injected into the instrument where a temperature of over 1000 ^{0}C causes the sample to combust (Annual book of ASTM standards, 2003). The sulfur is oxidized into sulfur dioxide, which is then exposed to an ultraviolet light. The sulfur dioxide becomes excited and fluoresces. The photomultiplier tube then detects this fluorescence and the signal is a measure of the sulfur concentration in the sample.

For this method, as the sulfur concentration varies from 1 mg/kg S to 400 mg/kg S, the repeatability increases from 0.2 mg/kg S to 16.0 mg/kg S. Using equation e.1.1, the repeatability can be calculated for sulfur concentrations less than 400 mg/kg S (Annual book of ASTM standards, 2003):

$$r = 0.1788(X)^{0.75} \qquad \text{(e.1.1)}$$

Where: X = the sulfur concentration in mg/kg. Similarly, the reproducibility increases from 0.6 mg/kg S to 51.9 mg/kg S. However, the reproducibility for less than 400 mg/kg S can be calculated using equation e.1.2 (Annual book of ASTM standards, 2003):

$$R = 0.5797(X)^{0.75} \qquad \text{(e.1.2)}$$

This method is considered acceptable for samples whose boiling range is from 25 ^{0}C to 400 ^{0}C (Annual book of ASTM standards, 2003). Therefore, gasoline has acceptable precision under this method with samples containing 1.0 to 8000 mg/kg of total sulfur. This method is also the one accepted by the Canadian Environmental Protection Act (2004).

1.6.3 Energy Dispersive X-Ray Fluorescence Spectrometry

The energy-dispersive X-ray fluorescence spectrometry method places the hydrocarbon sample in a beam emitted from an X-ray source (Annual book of ASTM standards, 2003). The radiation emitted from sulfur is then measured and a count is made that is then compared with the counts from the calibration standards (Annual book of ASTM standards, 2003). This comparison gives the sulfur concentration in mass percent.

This method is applicable for non-leaded gasoline and gasoline-oxygenated blends and for samples with a sulfur range of 48 to 1000 ppmw (Annual book of ASTM standards, 2003). The repeatability can be determined by equation e.1.3:

$$r = 12.30(X+10)^{0.1} \quad \text{(e.1.3)}$$

Where: X is the sulfur concentration in mass percent (Annual book of ASTM standards, 2003). The reproducibility of this method is determined by equation e.1.4:

$$R = 36.26(X+10)^{0.1} \quad \text{(e.1.4)}$$

However, it has been found that X-ray fluorescence methods are not suitable for low-level sulfur concentrations and are therefore not commonly used in industry; instead UV fluorescence, chemiluminescence detectors or FIDs are typically employed (Gokeler *et al.*, 2002).

1.6.4 Inductively Coupled Plasma

Inductively coupled plasma (ICP) methods have been developed for fossil fuels and other petroleum products. Also, there are other methods, which have been developed for ICP spectrometers coupled with other types of instrumentation. These coupled instruments include ICP-IDMS (isotope dilution mass spectrometry) and DIHEN-ICP-IDMS (direct injection high-efficiency nebulizer).

The ICP method typically uses a microwave digestion and has been used for sulfur determination in coal. Laban and Atkin (2000) developed a microwave digestion method. Hydrochloric acid was used to digest the sulfate sulfur, nitric acid for the digestion of pyritic sulfur and a combination of nitric, hydrochloric, hydrofluoric, and boric acid for the digestion of organic sulfur (Laban and Atkin, 2000). The solutions produced are analyzed using ICP-AES at a wavelength of 182.037 nm. The method proved to be good for coal when determining total sulfur, as the reproducibility is good with coefficients of variation less than 5 % in all cases. The method was determined to be optimal for a total sulfur range of 300 to 5000 ppmw (Laban and Atkin, 2000).

Similarly, a method for sulfur in gasoline and other fuel samples was developed by Heilmann *et al* (2004) using a microwave digestion followed by analysis with an ICP-IDMS or a DIHEN-ICP-IDMS. The microwave digestion involved using concentrated nitric acid (Heilmann *et al.*, 2004). The sample and nitric acid were placed in a quartz vessel, which was then placed inside the Teflon vessel. Distilled water and hydrogen peroxide were then added to the Teflon vessel to prevent venting of the quartz vessel and therefore, preventing sample loss (Heilmann *et al.*, 2004). The digested samples were then analyzed using both ICP-IDMS and DIHEN-ICP-IDMS. The ICP-IDMS method has good precision and accuracy. However, due to the long analysis time, it may not be suitable for routine analysis (Heilmann *et al.*, 2004). The DIHEN-ICP-IDMS method is fast and accurate. However, close attention needs to be paid to the preparation of the transparent micro-emulsion and optimization of ICP-MS measurement conditions (Heilmann *et al.*, 2004). The DIHEN-ICP-IDMS method has a detection limit of 20 μg/g while the detection limit of the ICP-IDMS is 10 μg/g (Heilmann *et al.*, 2004). Therefore, either method would be suitable under the new Canadian regulatory limits.

1.7 Solvent Extraction and Solubility Parameters

Solvents have been used for years to extract components from mixtures. There are several conventional solvent extraction processes such as mixer-settler arrangements or continuous countercurrent contacting equipment (Alonso *et* al., 2001). In order to be able to efficiently extract a substance, the solvent requires similar properties to the solute being extracted (Reichardt, 1988). There are several properties, which can be used to assess the extractability of different solvents. These properties include partition coefficients and solubility parameters (Reichardt, 1988). In particular, solvents used in hydrocarbon processing, for example, methyldiethanolamine (MDEA), are very selective for the removal of H_2S (Jou *et al.*, 1997).

1.7.1 Solvent Extraction Methods

Mixer-settler arrangements are the most common solvent extraction techniques. A mixer-settler apparatus typically contains both the solvent and the solution containing the solute. The two solutions are mixed for some period of time then allowed to settle so that the more dense liquid settles to the bottom and can be decanted. However, there are several properties that need to be addressed with mixer-settler arrangements. When using a mixer-settler arrangement the solvent must be dispersed throughout the mixture, there must be a density difference between the fluids and emulsifications should be avoided (Alonso *et al.*, 2001). Non-dispersive solvent extraction can overcome many of these disadvantages. In non-dispersive solvent extraction, the two liquids flow on opposite sides of a porous interface so that mixing of the two liquids does not occur (Alonso *et al.*, 2001). However, non-dispersive solvent extraction involves much more complex equipment, whereas mixer-settlers can be as simple as shake flask or sonication methods (Fitzpatrick and Dean, 2002). There are several ways to predict which solvents may work for the particular solute that is being extracted.

1.7.2 Solubility Parameter and Solvent Relationship

Fitzpatrick and Dean (2002) determined that solvents with similar solubility properties could form mixtures; therefore being capable of predicting which solvents can be used for analyte recovery. The greater the difference in chemical properties between any two solvents the less soluble they will be in one another (Reichardt, 1988). In order for a solvent to be effective at extracting a solute there must be a high degree of separation, high selectivity, no tendency to emulsion formation and rapid separation (Reichardt, 1988). The degree of separation can be determined by either the density difference of the two solvents or through the ratio of the partitioning coefficients (Reichardt, 1988). Also, the rapid separation of the phases requires a large density difference and a low viscosity. The lower the viscosity the more rapid the separation will occur between the phases (Reichardt, 1988). However, in order to match the chemical properties, solubility parameters can be used to narrow the list of solvents to be selected for a particular solute.

There are several different solubility parameters, for example Hoy's cohesion parameter, Hansen's parameter, and Hildebrand's solubility parameter. Each of these measures of solubility is slightly different. For example, Hildebrand solubility parameter (δ_t), total solubility, is a measure of the internal energy of cohesion (Fitzpatrick and Dean, 2002). Therefore, solvents with similar solubility parameters form mixtures and therefore a solvent and solute with similar solubility parameters should also form a mixture (Fitzpatrick and Dean, 2002). Hansen took the total solubility and based it on three separate components. The three components are hydrogen-bonding ability (δ_h), dispersion coefficient (δ_d), and polarity coefficient (δ_p) (Fitzpatrick and Dean, 2002). Hansen determined that these three components could be used to determine the total solubility of a solvent through equation e.1.5 (Barton, 1991):

$$\delta_t^2 = \delta_h^2 + \delta_p^2 + \delta_d^2 \qquad \text{(e.1.5)}$$

Hoy determined these individual components of solubility through a variety of methodologies. For example, Hoy calculated the total solubility by measuring the change in vapour pressure at a number of temperatures (Fitzpatrick and Dean, 2002). These solubility parameters have been determined for a variety of different solvents and can be found in the CRC Handbook of Solubility Parameters and Other Cohesion Parameters (1991). Fitzpatrick and Dean (2002) determined that by using the Hildebrand solubility parameter and the individual components an appropriate extraction solvent can be chosen. It should be mentioned, however, that solvents could have retarding effects on hydrodesulfurization catalysts (Ishihara and Kabe, 1993). Therefore, care should be taken to remove all solvents from the feed before further processing. Also, solvent extractions typically are based on hydrogen bonds or van der Waals interactions, whereas a stronger molecular interaction may be required to remove the desired solute.

1.8 Sorbent Extraction

There are other extraction processes besides solvents, such as sorbent extractions. Almost all adsorption processes in the industrial world are based on van der Waals interactions between two solids (Takahashi *et al.*, 2002). However, chemical complexation bonds are stronger and therefore more selective that van der Waals interactions (Takahashi *et al.*, 2002). For this reason there has been much work done in identifying sorbents that have chemical complexation bonds rather than simply van der Waals interactions.

Takahashi *et al.* (2002) have identified copper and silver zeolites, which can be used to remove thiophenes at temperatures near that of room temperature. Similarly, Ma *et al.* (2002) developed a deep desulfurization method using selective adsorption onto a transition metal supported on silica gel. This method placed the adsorbent into a column, where the fuel was then allowed to flow down through the adsorbent. The method showed good removal of the sulfur compounds; however the study was only in the preliminary stages. Other examples, of sorbents being used are limestone, which has shown good results for H_2S removal in coal processing (Nakazato *et al.*, 2003). However, in order to remove some solutes even strong chemical interactions are necessary, some forms of catalysis also use adsorption to remove contaminants.

1.9 Raney Nickel

Raney nickel is one of the most common metal catalysts and was discovered by Murray Raney in 1927 (Augustine, 1996). Raney nickel is prepared by the addition of sodium hydroxide to a powdered nickel-aluminum alloy. This reaction causes the nickel to form a porous structure, which gives it the name of spongy nickel (Freel *et al.*, 1969). The porous structure creates a high surface area, which increases the reaction surface (Augustine, 1996). Raney nickel can be used to effectively remove sulfur and has been used in analytical methods or purification methods for years.

1.9.1 Activation of Raney Nickel

The activation of Raney nickel with sodium hydroxide has been extensively studied with a variety of activation procedures identified. The nickel-aluminum alloy typically contains 50 % nickel and 50 % aluminum (Augustine, 1996). In the case of Raney nickel, the activation process is the process in which sodium hydroxide is added to the alloy to remove the aluminum and produce hydrogen (Augustine, 1996). This causes the nickel-aluminum alloy to become active Raney nickel. The hydrogen adsorbs to the nickel surface; however, there is not a one to one relationship as not all the Raney nickel surface is metallic and accessible (Fouilloux, 1983). This reaction can be seen in reaction 1.19 (Devred *et al.*, 2003):

$$2(Ni-Al)_{(s)}+2OH^{-}+6H_2O_{(l)}\rightarrow 2Ni-H_{2Raney}+2Al(OH)^{-}_{4(aq)}+H_{2(g)} \quad (1.19)$$

The amount and temperature of the sodium hydroxide determines the type of Raney nickel and are designated as W1-W8 Raney nickel (Augustine, 1996). The preparation procedures for these types of Raney nickel are summarized in Table 1.1, which was developed by Augustine (1996).

Table 1.1: W1-W8 Raney nickel preparation methods (Augustine, 1996).

Type	Addition Temp.	NaOH: Alloy Ratio	Digestion Temp. and Time	Washing Process	Relative Activity
W1	0^0C	1: 1	$115^0 - 120^0$C 4 hours	Neutralize with H_2O Ethanol wash	Least Active Approx. = W8
W2	25^0C	4: 3	Steam bath 8-12 hours	H_2O wash to neutral Ethanol wash	<W4: >W1 Most common
W3	-20^0C	4: 3	50^0C 50 minutes	H_2O wash several times Continuous wash with H_2O Ethanol wash without contact with air	Quite Active >W2: <W7
W4	50^0C	4: 3	50^0C 50 minutes	Same as W3	Same as W3
W5	50^0C	4: 3	50^0C 50 minutes	Same as W3	Same as W3
W6	50^0C	4: 3	50^0C 50 minutes	Continuous H_2O wash under H_2 atmosphere Ethanol wash without contact with air	Most active
W7	50^0C	4: 3	50^0C 50 minutes	Three decantations with H_2O Ethanol wash without contact with air	Very active <W6: >W4
W8	0^0C	1: 1	$100^0 - 105^0$C 4 hours	Continuous H_2O was Dioxane wash Distil dioxane portion from catalyst	Least active Approx. = W1

However, not all types of Raney nickel are classified in this manner. Further research done with Raney nickel has developed other methods for the activation of Raney nickel. For example, Granatelli (1959) used a 20: 1 ratio of sodium hydroxide to the alloy and allowed the reaction to occur at room temperature and overnight. Beigi *et al* (1999) used a ratio that ranged from 3 to 12: 1 of sodium hydroxide to the alloy and allowed the reaction to occur overnight at room temperature. Srivastava *et al* (1985) used a 30: 1 ratio and the digestion was gradually heated to 100 ^{0}C. Finally, Bartok *et al* (1987) used a 20: 1 ratio and the digestion occurred at 80 ^{0}C for 45 minutes. It should also be mentioned that each of these procedures has a slightly different washing process, but all involve washing with H_2O and then further rinsing with ethanol or isopropanol. The activation process can have remarkable affects on the structure of Raney nickel.

1.9.2 Structure

The structure of Raney nickel incorporates a large surface area, however, it is difficult to reproduce the surface area even if the same alloy and activation procedure is employed (Fouilloux, 1983). The preparation temperature has an impact on the porous structure and therefore, the surface area (Fouilloux, 1983). At low preparation temperatures the pores have a narrower diameter, whereas at higher preparation temperatures the pores are more cylindrical and create a higher pore volume (Fouilloux, 1983). Fouilloux (1983) determined that the more intense the alkali reaction the larger the pore diameter and the greater the pore volume. In general, Raney nickel is a sponge-like particle that is approximately 100 Å in diameter with a smaller microporous structure. The microstructure has pore diameters between 20 and 80 Å (Fouilloux, 1983). It is this porous structure that makes Raney nickel a good catalyst or reactant for the removal of sulfur.

1.9.3 Desulfurization with Raney nickel

There are two reaction mechanisms by which Raney nickel can be used to remove sulfur. The two mechanisms are as follows (Lieber and Morritz, 1953):

$$3RSR' + 3Ni - H_{2\,Raney} \rightarrow RR' + RR + R'R' + 3NiS + 3H_2 \qquad (1.20)$$

$$RSR' + Ni - H_{2_{Raney}} \rightarrow RH + R'H + NiS \qquad (1.21)$$

Typically, there is also a sulfur-to-sulfur cleavage for disulfides (e.g. R-S-S-R') removing both the sulfur atoms and introducing hydrogen. This was discovered since both ethane and methane are formed after the reaction with Raney nickel (Lieber and Morritz, 1953). With the thiols, Raney nickel causes a cleavage of the carbon-sulfur bond and the formation of a carbon-hydrogen bond (Pettit and Tamelen, 1962). A similar cleavage is seen with thiophenes during a hydrogenolysis reaction where the sulfur is removed and replaced with hydrogen (Pettit and Tamelen, 1962). It has been noted that the simple hydrogenolysis reaction does not always go to completion, so it is therefore necessary to treat the solution twice (Papa *et al.*, 1949). Thus, from the above cited literature, the effectiveness of Raney nickel for removing sulfur makes it a promising option for desulfurization of FCC gasoline. However, no such study has yet been reported to date.

1.10 Objectives of Research

This thesis was designed to determine if an alternative method could be developed for removing sulfur-containing compounds from FCC gasoline, the gasoline fraction produced from fluid catalytic cracking. In order to meet this purpose there are four objectives.

1. The first objective is to find a solvent or catalyst that will specifically target sulfur compounds. This will take an experimental approach for a variety of solvents, metals salts and Raney-type nickel.
2. The second objective is to reduce sulfur concentrations as much as possible with a goal of 30 ppmw or lower.

3. The third objective is to reduce the sulfur concentrations without making any major changes to the composition of the FCC gasoline.

4. The fourth objective is to determine if the reactants can be recycled.

1.11 Conclusion

We hope this research will contribute towards finding a solution to one of the major environmental issues concerning the burning of fossil fuels. The literature review performed here has given many insights into the processing of petroleum products and the options currently available for sulfur removal. The problem with sulfur in the environment is that it not only causes a risk to humans, it is also a risk to the plants and animals. FCC gasoline is the largest contributor to sulfur in gasoline and therefore needs to be the focus of sulfur removal efforts. Currently, hydrotreating is the most common method used to remove sulfur from FCC gasoline but there are several problems associated with using hydrotreating for deep desulfurization. Also, there are several methods available for analyzing for sulfur. However, a more appropriate one for FCC gasoline will need to be determined. As catalysts seem to be the current method as well as the most studied approach for removing sulfur from fuels, perhaps more research needs to be carried out into solvents or sorbents for sulfur removal. Finally, there has already been some research accomplished using Raney nickel for sulfur removal. However, most of this work has been for analytical or purification purposes only. Thus, there is potential for Raney nickel to be used in FCC gasoline sulfur removal. This approach, if successful, could be potentially used as an alternative to the expensive hydrotreater.

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Chapter 2: Chemical Methods Studied for the Desulfurization of FCC Gasoline

2.1 Introduction

Sulfur in fuels has been an environmental concern, particularly the transformation sulfur undergoes during combustion (Zannikos *et al.*, 1995). Current Canadian legislation allows 30 ppmw as the pool average for gasoline (CEPA, 2004). There are several different methods used to desulfurize fuels. However, chemical methods are preferred (Karaca and Yildiz, 2005). The most acceptable method for sulfur removal currently is hydrotreating (Zannikos *et al.*, 1995).

Hydrotreating removes sulfur from gasoline by transforming it into hydrogen sulfide (Meyers, 2004). The problem with hydrotreating is that in order to meet current legislation, deep desulfurization processes need to be undertaken. Deep desulfurization refers to technology used to reduce sulfur content to less than 0.05 wt % sulfur (Ishihara and Kabe, 1993). When conventional hydrotreating technology is used for deep desulfurization, there is a significant reduction in the octane number. This reduction in octane is due to the saturation of olefins from fluid catalytic cracking (Ma *et al.*, 2002). This deep desulfurization uses large amounts of hydrogen, which cannot be produced alone by the catalytic reformers, as done with traditional hydrotreating (Zannikos *et al.*, 1995). Therefore, other processes are needed to reduce the fuel sulfur levels without the addition of hydrogen.

In fluid catalytically cracked gasoline (FCC gasoline) H_2S, sulfides and mercaptans appear only in trace amounts. The most abundant sulfur-containing compounds in FCC gasoline are thiophenes, benzothiophenes, and tetrahydrothiophenes. Therefore, other methods may be necessary and more efficient at removing these heavier sulfur-containing compounds. One characteristic of these heavier sulfurous compounds that is different from other compounds in a gasoline mixture is that they are slightly more polar than the hydrocarbon molecules (Zannikos *et al.*, 1995). This increases the potential of their selective removal from the gasoline.

2.1.1 Solvent Desulfurization

The purpose of this technique is to take advantage of the similar solubility characteristics between the solvent and the desired solute to be removed or separated. Solvents have been used in refining technologies for many years. Several solvents are currently used for sulfur removal. However, they are typically used for the removal of H_2S, sulfides and mercaptans. Processes that currently employ solvents include amine-treating units, the Merox process and sulfur scrubbers. For example, methyldiethanolamine (MDEA) is very selective for H_2S removal in the amine treating units (Jou *et al.*, 1997).

In order to be able to recover an analyte, such as the sulfur compounds in gasoline, the solvent needs properties similar to the analyte being extracted. The two most common properties include partition coefficients and solubility parameters (Reichardt, 1988). Our present study will focus on solubility parameters. Solvents with similar solubility properties can form mixtures; therefore being capable of predicting which solvents can be used for analyte recovery (Fitzpatrick and Dean, 2002). In order for a solvent to be effective at extracting an analyte, there must be a high degree of separation, high selectivity, no tendency to form emulsions and rapid separation (Reichardt, 1988). The extent of the separation can be determined by the density difference of the two solvents or the ratio of the partitioning coefficients (Reichardt, 1988). In order to match the chemical properties, a comparison of solubility parameters can be used to narrow the list of solvents to be used for a particular analyte.

There are several different solubility parameters with one of the most common being the Hildebrand solubility parameter. The Hildebrand solubility parameter (δ_t), or total solubility, is a measure of the internal energy of cohesion (Fitzpatrick and Dean, 2002). The total solubility is based on three separate components: hydrogen-bonding ability (δ_h), dispersion coefficient (δ_d), and polarity coefficient (δ_p) (Fitzpatrick and Dean, 2002). These solubility parameters have been determined for a variety of different solvents and can be found in the literature (Barton, 1991). Solvent extractions typically are based on hydrogen bonding or van-der-Waals interactions; however, it may be necessary for stronger chemical bonding rather than just a physical interaction to remove the desired solute.

2.1.2 Adsorption and Precipitate Desulfurization

Other chemical properties of a compound can also be used to separate it from mixtures, including its polarity. Typically, stronger chemical reactions occur with sorbent extractions. Therefore, solvent extractions are less selective and effective than most sorbent extractions.

As FCC gasoline is a complex mixture, it may be important to look at the differences between the sulfur compounds in the gasoline and the rest of the mixture. For example, thiophene has a lone pair of electrons on the sulfur; therefore, it should be possible to cause a reaction between the lone pair of electrons and an acid or metal salt. Adsorption desulfurization is the ability of a solid sorbent to selectively adsorb the sulfur containing compounds; where as precipitate desulfurization is based on the formation of an insoluble precipitate (Babich and Moulijn, 2003). The efficiency of precipitate desulfurization is low. However, sorbent desulfurization shows a lot of promise.

There is evidence that metal oxides react with alkanethiols by reacting the thiol with the metal replacing the oxygen and producing water as seen in the following reaction (Nehlson *et al.*, 2003).

$$PbO + 2RSH \rightarrow Pb(SR)_2 + H_2O \qquad (2.1)$$

In this reaction, the thiols are transformed into insoluble metal thiolates. These thiolates can then be filtered from the hydrocarbon stream (Nehlson *et al.*, 2003).

Takahashi *et al.* (2002) identified copper and silver zeolites, which could be used to remove thiophenes at room temperature. Similarly, Ma *et al.* (2002) developed a deep desulfurization method using selective adsorption onto a transition metal. There have also been examples of activated carbon and other zeolites, which cause sulfur to form a monolayer on the surface of the sorbent (Mikhail *et* al., 2002). Limestone has been used as an absorbent for coal processing in order to remove H_2S (Nakazato *et al.*, 2003). Finally, charcoal, petroleum coke, cement kiln dust and clay minerals have also been investigated as sorbents with the acidic clays being shown to be good adsorbents (Mikhail *et al.*, 2002).

2.1.3 Desulfurization using basic and acidic solutions

Typically, basic and acid solutions have been used to remove sulfur from coal. There are, however a few instances where it has been attempted for liquid fuels (Mukherjee and Borthakur, 2001). There have been several compounds studied, including chemicals such as nitric acid, sulfuric acid, hydrogen peroxide, and sodium hydroxide (Karaca and Yildiz, 2005).

In addition, sodium hydroxide is used to help sweeten fuels by removing H_2S (Meyers, 2004). There are also publications, which discuss the use of heated sodium hydroxide to desulfurize coal (Mukherjee and Borthakur, 2001). Murkherjee and Bothakur (2001) also determined that by following a sodium hydroxide treatment with a hydrochloric acid treatment, greater desulfurization could be achieved. A more recent publication discusses desulfurization by leaching the fuel with sulfuric acid (Karaca and Yildiz, 2005). This article concludes that H_2SO_4 is effective at removing thiols, sulfides and disulfides from fuel oils.

The purpose of our research is to determine if other solvents, sorbents or basic/acidic solutions can be used to remove sulfurous components from FCC gasoline. This work will focus on extractions carried out mostly under ambient conditions.

2.2 Methodology

2.2.1 FCC Gasoline Sampling and Storage

The FCC gasoline was sampled after the fluid catalytic cracking unit and Merox processing unit at Husky Energy's refinery in Prince George. A tap sampling method was used, where the tap was allowed to run for several minutes before the FCC gasoline samples were collected. The FCC gasoline was sampled into 1-litre amber, glass bottles with approximately 100 mL of headspace. Two 1-litre samples were taken on August 4, 2004 and four 1-litre samples were taken on August 27, 2004. The FCC gasoline samples were transported to UNBC and stored in a refrigerator at about 4 ^{0}C for no longer than six months, after which a new sample would be collected. As storage could cause volatile portions of the FCC gasoline to be lost a baseline sample was always taken and analyzed for the sulfur concentration with each batch of experiments performed.

2.2.2 Solvent Methodology

The ten solvents investigated were carefully selected based on their Hildebrand solubility parameter (Barton, 1991). The solubility parameters were as closely matched to the solubility of five different sulfur compounds. The five sulfur compounds are: carbon disulfide, ethyl mercaptan, diethyl sulfide, thiophene, and tetrahydrothiophene. These five compounds were selected based on a GC/SCD analysis performed on the FCC gasoline confirming the presence of these five components. The solubility parameter of a selected, potentially the most compatible, solvent was matched up directly with one of the above sulfur compounds. Once the best solvents were determined, a separatory funnel extraction was performed.

There were two different separatory funnel methods employed. The first method was a one-time addition of the solvent, while the second method was a sequential addition of the solvent. The volume of solvent was 5, 10, or 15 millilitres depending on the available volume. Once the solvent had been added, the separatory funnels were shaken vigorously for one minute. At this point, if two layers appeared, the lower layer was decanted from the separatory funnel and the remaining FCC gasoline layer was emptied into a 125 mL amber bottle for storage at 4 ^{0}C. The sulfur analysis was performed on these samples within 48 hours. If two layers were not present then the entire sample was emptied into a 125 mL flask, stoppered and placed in the freezer at a temperature of -10 ^{0}C to check the effect of temperature on the separation of the solvent and FCC gasoline. Samples remained in the freezer for 48 hours. Once placed in the freezer, if two layers formed, the FCC gasoline was decanted from the sample and placed in a 4 ^{0}C refrigerator until analysis, which was performed within 48 hours. The FCC gasoline samples that separated from the solvent were analyzed using a Horiba energy-dispersive X-ray spectrometry system.

The analysis was performed at Husky Energy's refinery in Prince George. An energy-dispersive X-ray fluorescence (XRF) system was operated according to the ASTM method D 6445 (Annual book of ASTM standards, 2003). The instrument was a Horiba Sulfur-in-Oil Analyzer (model # SLFA-1800). The instrument measured the sample for 100 seconds and this was repeated three times for each sample. A check standard was performed first in order to check the operation of the Horiba. If the check standard passed within 5 % of the actual value, the samples were then analyzed. If the standard did not pass within 5 % of the actual value, the instrument was recalibrated and another check standard was performed. Each sample was analyzed in triplicate with the average being reported in mass percent. A check standard was done every six to ten samples with a check standard being completed at the end of that day's analysis. An F-test and Student T-test were performed on the data when necessary using Microsoft Excel.

In addition, promising samples were analyzed using gas chromatography equipped with a flame ionization detector (GC/FID). This was done in order to monitor any major changes in the composition of hydrocarbons. The GC/FID used was a Hewlett Packard HP6890 series GC system with a capillary column HP1 (100.0 m in length, 250.0 μm diameter, and 0.50 μm film thickness). There was a split injection method using an injection volume of 0.2 μL. The system operated on hydrogen gas with a flowrate of 30 mL / min and a helium flow of 30 mL / min. The oven heat up was stepped up at a rate of 1 ^{0}C per minute until 50 ^{0}C, then 2 ^{0}C per minute until 130 ^{0}C and finally at a rate of 4 ^{0}C per minute until a final temperature of 180 ^{0}C. The total run time was equal to 137.5 minutes.

2.2.3 Sorbent Methodology

Three different aqueous solutions were selected for the next portion of the experiment based on the papers by Nehlson *et al* (2003) and Ma *et al* (2002). In these publications, promising results were shown with similar solutions. The three solutions were prepared in water at: 5 wt. % barium nitrate, 5 wt. % lead nitrate, and 10 wt. % zinc chloride. The first set of extractions performed was by sequential addition. First, 10 mL of the solution was added into a separatory funnel containing 50 mL of FCC gasoline. The solutions were shaken for approximately one minute, and then allowed to settle for about 15 minutes. The aqueous solution was then decanted and the procedure was repeated two more times, for a total of 30 mL of aqueous solution. The remaining FCC gasoline was then placed in the refrigerator until sulfur analysis of the FCC gasoline could be performed, which was usually within 48 hours.

Another method was also used for the 5 wt. % barium nitrate and 5 wt. % lead nitrate solutions. In this method, 30 mL of the solution was added to 50 mL of FCC gasoline and then it was stirred vigorously for one hour on a stirring plate. The samples were then allowed to settle for 15 minutes and the aqueous solution was decanted. The remaining FCC gasoline was placed in the refrigerator; analysis was performed within 48 hours.

Again, the analysis was performed at Husky Energy's refinery in Prince George. Some samples in the sorbent experiments were analyzed using an XRF system, which was operated according to the ASTM method D 6445 (Annual book of ASTM standards, 2003). Other samples were analyzed using the Ultraviolet fluorescence (UVF) method. The Ultraviolet fluorescence method used an Antek Elemental Analyzer 9000 operated according to the ASTM method D 5453 (Annual book of ASTM standards, 2003). The oxidative furnace was operated at 1075 ^{0}C. A check standard was performed first in order to check the operation of the Antek. If the check standard passed within 5 wt. % of the actual value, the samples were then analyzed. If the check standard failed then the instrument was recalibrated and another check standard was performed to make sure the new calibration was accurate. Each sample was analyzed in triplicate with the average being reported in parts per million. A check standard was analyzed after every six to ten samples with a check standard being completed at the end of that day's analysis.

2.2.4 Basic and Acidic Methodology

The solutions in this portion were chosen based on publications by Karaca and Yildiz (2005), and Murkherjee and Bothakur (2001), which showed promising results with similar solutions. This methodology was exactly the same as the sequential method attempted for the sorbents in the previous section. A basic solution of 5 wt. % sodium hydroxide and an acidic solution of 10 vol. % sulfuric acid were used for this portion of the experiments. The samples were analyzed using either XRF or UVF described in the previous section.

2.3 Results

2.3.1 Solvent Results

First, the ten solvents identified to be tested are listed in Table 2.1. These solvents were chosen from the CRC Handbook of solubility parameters and other cohesion parameters (Barton, 1991). They were purchased from a variety of suppliers with each having 97 % or better purity. The table also shows that the ten solvents had similar solubility parameters to one of the five sulfur compounds: carbon disulfide, ethyl mercaptan, diethyl sulfide, thiophene and tetrahydrothiophene. As seen, the solubility parameters of the five sulfur compounds do not differ by more than 3.1 units.

Table 2.1: Ten solvents selected based on solubility parameters similar to five selected sulfur compounds (Barton, 1991).

Sulfur Compound	**Solvent**	**Supplier and Purity**	**Solubility Parameter**
Carbon Disulfide			20.3
	Diethyl maleate	Aldrich, 97 %	20.3
	2,3-Butanedione	Aldrich, 97 %	20.3
	Diethylene glycol monomethyl ether	Alfa Aesar, 99 %	20.3
Ethyl Mercaptan			18.6
	Butyraldehyde	Aldrich, 99 %	18.6
	Diethyl pimelate	Alfa Aesar, 98 %	18.6
	3-(Dimethylamino)propylamine	Aldrich, 99 %	18.6
Diethyl Sulfide			17.4
	Heptylbenzene	Acros Organics, 97 %	17.4
Thiophene			20.0
	Dimethyl pimelate	Aldrich, 99 %	20.0
Tetrahydro-thiophene			20.5
	1-Decanol	Baker, 99 %	20.5
	o-dichlorobenzene	Lancaster, 99 %	20.5

The results of the individual solvent tests can be separated into two categories: those that showed a separation, and those that did not show a separation. A summary of the results for the ten different solvents can be seen in Table 2.2. Table 2.2 shows that only 1-decanol separated and this separation occurred only at low temperatures when the 1-decanol froze. Approximately half of the sample was frozen on the bottom of the sample container. It was determined that the frozen section was the solvent as 1-decanol has a melting point of 7 ^{0}C.

The remaining liquid was decanted and approximately 34 mL was recovered. The sample was analyzed using XRF. The original FCC gasoline contained a sulfur concentration of 208 ppm while the 1-decanol extracted sample contained a sulfur concentration of 191 ppm. This was an 8 % reduction in the sulfur concentration.

Table 2.2: Summary of the separation between the solvent and FCC gasoline.

Solvent	**Separation**	**Observations**
diethyl maleate	None	None
dimethyl pimelate	None	None
diethyl pimelate	None	Amber Colour
1-decanol	Froze	None
diethylene glycol monomethyl ether	None	None
3-dimethylaminopropylamine	None	None
Butyraldehyde	None	Yellow Colour
2,3 butanedione	None	Red precipitate
1,2 dichlorobenzene	None	None
Heptylbenzene	None	None

Since 1-decanol showed a reduction in the sulfur concentration, further tests were performed. The first test performed was to determine if one-time addition or sequential addition was more effective for removing sulfur. The one-time addition used 15 mL of 1-decanol; the sequential addition used 5 mL aliquots of 1-decanol for a total of 15 mL. The samples were placed in the freezer to allow the 1-decanol to freeze and separate. The samples were partially frozen within 24 hours of extraction, however if left for another 24 hours the sample became completely frozen. In both samples, approximately 35 mL of FCC gasoline was recovered from the frozen samples. The samples were analyzed using XRF to determine the sulfur concentrations. The initial concentration of the FCC gasoline was 236 ± 10 ppm. The one-time addition sample had a concentration of 227.8 ± 6.8 ppm, while the sequential addition had a concentration of 224.7 ± 6.5 ppm. Analysis showed that the two samples were within the standard deviations of the original sample therefore, it was concluded that no sulfur was removed.

An F-test was performed that determined the F-value to be 1.09 and the F-critical value to be 5.05 for a 95 % confidence interval with 5 degrees of freedom for each value. As the F-value is less than the F-critical value, no distinction in the variances can be determined. Next, a Student T-test determined that there was also no significant difference between the two mean values within a 95 % confidence interval.

The final analysis using 1-decanol involved adding 30 mL of 1-decanol to 50 mL of FCC gasoline, covering it and stirring using a stirrer plate for one hour. This resulted in 66 mL of sample being recovered from the initial 80 mL. The sample was placed in the freezer overnight; similarly, if the sample were in the freezer for too long the entire sample would freeze solid. The analysis was again performed using XRF. The original FCC gasoline had a concentration of 268 ± 7.7 ppm while the 1-decanol extracted sample had a concentration of 200 ± 7.7 ppm. This was approximately a 25 % reduction in sulfur concentration. However, as the entire sample freezes when left long enough, it is possible that the sample was simply a mixture of FCC gasoline and 1-decanol and the sulfur concentration decreased due to dilution. In order to investigate if any 1-decanol remained in the sample a GC/FID analysis was performed. Figure 2.1 is the original hydrocarbon analysis of FCC gasoline using GC/FID while Figure 2.2 is the GC/FID analysis of the FCC gasoline extracted with 1-decanol. It was apparent from the chromatograms that there was a large unidentified peak at the end of the analysis in Figure 2.2 compared to the lack of a peak in Figure 2.1.

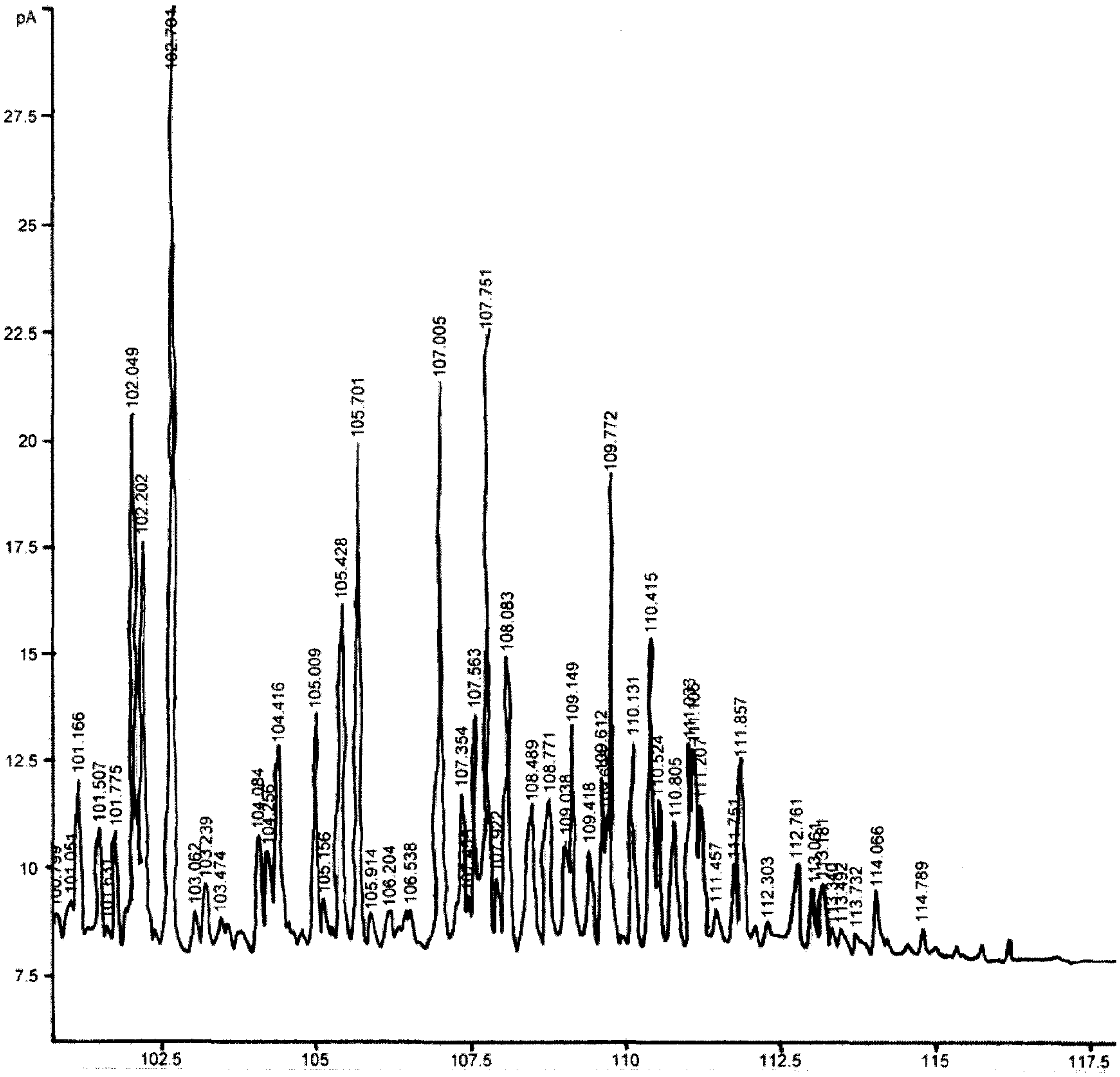

Figure 2.1: **GC/FID analysis of original FCC gasoline.**

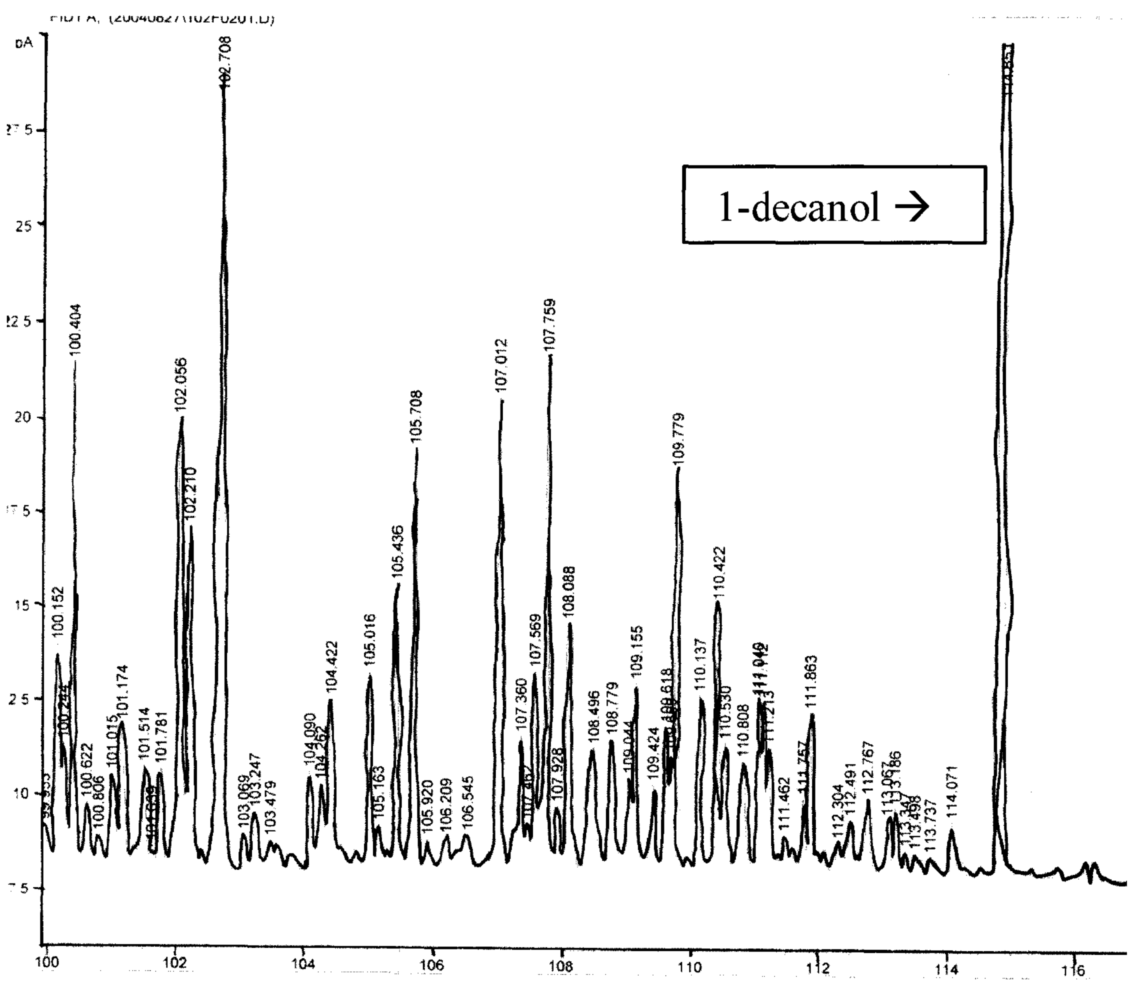

Figure 2.2: **Analysis of FCC gasoline extracted with 1-decanol using GC/FID.**

The rest of the ten solvents did not show any significant separation, however some changes in three of the samples were observed. The solution of diethyl pimelate and FCC gasoline, when placed in the freezer overnight, showed a colour change from colourless to amber, but there was still no separation. A small sample of this mixture was placed in the fumehood to evaporate to see if the colour change was the result of a non-volatile compound. Once the sample evaporated, there was no evidence of a precipitate, so 25 mL of the partially frozen sample was heated at a temperature of 25 ^{0}C and there was still no change. No change was observed until the sample was heated to 130 ^{0}C when the sample became a brighter yellow colour. At a temperature of 150 ^{0}C, a portion of the FCC gasoline should have boiled off and as the boiling point of the solvent is 192 ^{0}C, the solvent, assuming ideal behaviour, should have remained in the liquid solution as its boiling point was not reached. This would not allow the diethyl pimelate to change into the gaseous phase.

Next, the butyraldehyde extracted sample was placed in the freezer and twelve hours later, it appeared to be more yellow than the original FCC gasoline. Twenty-five millilitres of the sample was heated in the fumehood. The boiling point of butyraldehyde is 75 ^{0}C so the sample was heated to 70 ^{0}C. At approximately 51 ^{0}C, the sample began to appear more yellow in colour.

Finally, 2,3-butanedione showed no separation, however a small reddish precipitate was visible on the sides of the separatory funnel after shaking. Fifty millilitres of additional FCC gasoline was used in an attempt to rinse the crystals from the sides of the separatory funnel into the sample beaker. This, however, did not work so acetone was used to rinse the crystals into a separate beaker; the crystals dissolved in the acetone. Both the original sample and the acetone containing the crystals were placed in the freezer. After 12 hours, more precipitate was visible on the bottom of the sample container. There was no change in the acetone sample so it was transferred onto a watch glass and placed in the fumehood to evaporate the acetone. After approximately 10 minutes in the fumehood, the sample became a pinkish colour and was more viscous. After 20 minutes, the sample was still pink with noticeable granules suspended in the liquid. After 2 hours, a syrup-like liquid was left that was red in color. The sample was left for two days and it was found that there was a sticky red residue left on the watch glass. Although this residue could be re-dissolved in methanol, no further analysis into its identity or structure was attempted at this time. These results indicate that another chemical approach is needed to remove sulfur-containing compounds from FCC gasoline rather than just by using solvents.

2.3.2 Sorbent Results

First, the layer containing barium nitrate separated from the FCC gasoline. The sample was analyzed using XRF. The original FCC gasoline had a sulfur concentration of 230 ± 5 ppm and the barium nitrate extracted sample had a sulfur concentration of 236 ± 12 ppm. No significant difference between the mean value of the original FCC gasoline and the barium nitrate extracted sample was found.

The layer containing lead nitrate separated from the FCC gasoline so it was analyzed using XRF. The original FCC gasoline had a sulfur concentration of 230 ± 5 ppm and the lead nitrate extracted sample had a sulfur concentration of 243 ± 6 ppm. The student T-test again showed that there is no significant difference between the means of the two samples at a 95 % confidence limit.

The samples involving a one-time addition of the solution and stirring for one hour showed interesting results. When the samples were analyzed after the one-time addition the sulfur concentration was much higher in all cases than the original concentration. The original concentration of the FCC gasoline was 258 ± 8 ppm however, the concentration of sulfur in the extracted samples was 498 ± 3 ppm for the barium nitrate sample and 504 ± 8 ppm for the lead nitrate sample. Using a student T-test, these values are significantly different than the original concentration based on a 95 % confidence level. The large values are not logical; however, the XRF method is known to typically have problems such as matrix interference. To test this, a sample of the barium nitrate extracted sample was sent to Core Laboratories in

Calgary for analysis using a gas chromatography / sulfur chemiluminescence detector. The sample showed an increase in sulfur concentration to 310 ± 10 ppm from 268 ± 10 ppm. It was not significantly different than the original FCC gasoline. The matrix interference appeared to be less with GC/SCD than with the XRF.

The sample extracted with a 10 wt. % zinc chloride solution showed a separation from the FCC gasoline. The FCC gasoline originally had a concentration of 243 ± 12 ppm while the extracted sample had a sulfur concentration of 242 ± 8 ppm. The UVF method was used as matrix interference is not a problem and the method became available as well. The Student T-test showed that there is no significant difference between the mean of the original sample and the mean of the extracted sample.

2.3.3 Basic and Acidic Results

A separation occurred for the sequential addition of sodium hydroxide, the sodium hydroxide solution was then separated from the FCC gasoline. The sample was placed in the refrigerator with analysis being performed within 48 hours. The sample was analyzed using XRF. The original FCC gasoline showed a sulfur concentration of 230 ± 5 ppm while the extracted sample showed a concentration of 241 ± 3 ppm. When a Student t-test was performed, there was no significant difference between the mean of the original FCC gasoline and the sodium hydroxide extracted sample.

The solution of 10 vol. % sulfuric acid also separated from the FCC gasoline. In Table 2.3, the results from a variety of sulfuric acid tests are given. The difference in the samples was the type of rinse performed after the initial extraction with sulfuric acid. Once the original sample was analyzed using UV fluorescence, it was apparent that not all the sulfuric acid had been removed from the sample. Therefore, further rinsing was needed to ensure all the sulfuric acid had been removed from the FCC gasoline, including a rinse with a solution of acid cadmium chloride that has been shown to remove hydrogen sulfide from gasoline samples (UOP, 1980).

Table 2.3: Summary table of the four levels of rinsing performed on a sample extracted with 10 % sulfuric acid.

10 % Sulfuric Acid	**Rinsing Method**	**Mean**	**Standard Deviation**	**Student T-test Value**
1.	20 mL 10 wt. % NaOH	254.36	6.70	0.12
2.	50 mL 10 wt. % NaOH	251.72	5.31	0.10
3.	50 mL 10 wt. % NaOH	248.44	9.11	0.05
4.	20 mL 100 wt. % acid cadmium chloride	237.80	10.46	0.04

The initial sample was rinsed with 20 mL of 10 wt. % NaOH and then it was analyzed. After analysis, it was necessary for additional rinses to be performed on the sample. Table 2.3 shows the decrease in sulfur concentration with each subsequent rinse. The Student T-test showed that there is no difference between the mean values of the four different rinses for a 95 % confidence interval. Therefore, there was no reduction in the sulfur concentration with the use of a sulfuric acid solution.

2.4 Discussion

2.4.1 Solvent Desulfurization

The ten solvents chosen for this experiment showed less than 3.1 units difference in solubility parameters between all solvents and all five sulfur compounds. According to

Reichardt (1988) two liquids will be miscible in each other if their Hildebrand solubility parameter differs by no more than 3.4 units. Therefore, the ten solvents should have been effective for any of the five sulfur compounds. However, this is only true for pure mixtures. As FCC gasoline contains over 200 compounds, it is considered to be a complex solvent mixture, which is miscible in many other solvents as seen in Table 2.2.

The only solvent, which showed a promising result, was 1-decanol. The separation, which occurred due to the high melting point of 1-decanol allowed for further tests to be performed. Although a decrease in the sulfur concentration was determined for both the one-time addition and the sequential addition, there was no statistical difference in the values as shown by the Student T-test. However, as was stated above, the entire sample would freeze if it remained in the freezer for an extended period of time.

A gas chromatography analysis showed that the 1-decanol extracted sample had a large peak at near 115 minutes. This large peak is not present in the original FCC gasoline and is most likely the 1-decanol solvent or possibly a new compound formed through the extraction process. Therefore, the reduction in sulfur concentration seen in all the experiments using 1-decanol was most likely a result of the sample being diluted by the 1-decanol, with a portion of the FCC gasoline remaining in the frozen 1-decanol. Therefore, 1-decanol was not effective at desulfurizing FCC gasoline.

The three solvents, which showed signs of a reaction during the extraction, can be seen in Table 2.2. Diethyl pimelate showed a colour change when left overnight in the freezer. It was determined that the color change was not a result of a precipitate as when the sample was evaporated there was no precipitate found. However, a distillation would need to be performed to determine if the sulfur is remaining in the solvent. The solvent butyraldehyde also showed a colour change when placed in the freezer overnight, which was most likely due to a similar mechanism as the diethyl pimelate. Therefore, potentially more work could be done with these two solvents to determine if there is a possible distillation or other separation method, which could occur in order to separate the solvent from the FCC gasoline.

Finally, the solvent 2,3-butanedione, formed a red precipitate when it was mixed with the FCC gasoline. In order to identify the red, viscous compound it was analyzed using GC/MS, however it was not possible to identify, as it was not volatile enough. However, it was observed during the experiments that the caustic solution added to FCC gasoline during the Merox process does form a red precipitate with certain fuels. Therefore, it is possible that the red precipitate observed was just a reaction between the caustic solution in the FCC gasoline and the solvent.

The fundamental objective that was being searched for was a separation between the solvent and the FCC gasoline. However, since gasoline is a complex mixture, there was no separation for the ten solvents with the exception of 1-decanol at cooler temperatures. In each case of solvent-solvent extraction, it appears that simple van-der-Waals forces are not enough to remove the sulfur from the FCC gasoline. However, a 'solvent cocktail' has been shown to remove sulfur compounds from refinery streams and therefore a mixture of solvents may be required for desulfurization of FCC gasoline (Babich and Moulijn, 2003). As there were no promising results seen with the use of the solvents selected, it is possible that a stronger interaction may be needed to remove sulfur-containing compounds from FCC gasoline. Therefore, some sorbent reactions were attempted which should have stronger interactions/reactions as they are based on the reaction of the lone pair of electrons on thiophenes with the sorbent.

2.4.2 Adsorption and Precipitate Desulfurization

There have been publications where metal salts or metal oxides have been used to convert thiols into metal thiolates (Nehlson *et al.*, 2003). Therefore, three solutions with metal ions in aqueous solutions were attempted. However, in all three cases there was no reduction in the sulfur levels observed. It is interesting to note that the energy-dispersive X-ray spectrometry consistently measured the extracted samples higher than the original samples. This was especially apparent in the metal samples that were stirred for one hour. A potential reason for this is that the energy-dispersive X-ray system can have problems such as matrix interference when solvents are used and are not fully removed from the samples before analysis (ASTM, 2003). Therefore, if some of the metal solution remained in the sample, the matrix is different from the FCC gasoline matrix, which it is calibrated for (ASTM, 2003). This difference in the matrix may cause false values to be reported. This can occur when the sample is exposed to the X-ray the solvent may emit radiation at the same wavelength as sulfur causing the instrument to believe the solvent is also sulfur, thus giving a false reading. For this reason a sample was sent to be analyzed using GC/SCD at Core laboratories. However, a significant difference could not be established using a Student T-test.

Finally, in order to prevent this problem in the future, a UV fluorescence method was made available. This method does not have matrix interference problems, as the sample is combusted so everything in the sample is converted into CO_2, H_2O, or SO_2. Therefore, when the sample containing zinc chloride was analyzed, the values were very similar with no significant difference being identified.

The reaction of the aqueous metal salts was not effective at removing sulfur from the FCC gasoline. Although other papers have shown metal compounds to be effective, it may be important that the metal contain an oxide component. A publication by Nehlson *et al* (2003) used a variety of metal oxides and metal salts and they concluded that oxides or hydroxides of Pb, Hg(II), and Ba were the most effective. Therefore, the sample extracted using barium nitrate should have shown a promising result, but did not possibly due to the lack of oxides or hydroxides. It should be noted in Nehlson *et al* (2003) that the experiments did not use an actual fuel sample but instead a mixture of 1-octanethiol was used. Therefore, the complex mixture of FCC gasoline may not show the same results. An attempt was then made to react the more polar sulfur compounds with a basic or acidic solution.

2.4.3 Desulfurization using basic and acidic solutions

The final experiment of a separatory funnel extraction was attempted using a basic solution of sodium hydroxide and an acidic solution of sulfuric acid. Sodium hydroxide has been used for many years to remove hydrogen sulfide using the Merox process (Meyers, 2004). As this sample was analyzed before the UV fluorescence method was available, a similar matrix interference problem was found. However, the Student T-test showed that there was still no significant difference evident between the original FCC gasoline's sulfur concentration and that of the extracted sample. There is a publication about the use of sodium hydroxide in reducing the sulfur concentration in coal (Mukherjee and Borthakur, 2001). In coal samples it was found that the sodium hydroxide solution needed to be heated to 190-200

^{0}C in order to remove sulfur (Mukherjee and Borthakur, 2001). However, at these temperatures, most of the FCC gasoline would all have been boiled off, as the final boiling point of the FCC gasoline is 210.5 ^{0}C.

Finally, the experiments with sulfuric acid determined that much of the sulfuric acid remained in the sample after decanting the aqueous solution. This was shown by the large increases in sulfur concentration in the extracted FCC gasoline samples. As these samples were analyzed using the UV fluorescence method, there was no matrix interference problem. Therefore, a stronger rinsing method was required in an attempt to remove all of the remaining sulfuric acid. As seen in Table 2.3, with each rinse of sodium hydroxide, there was a decrease in the sulfur concentration, but none were significantly different from the original FCC sample. The final rinse using an acidic cadmium chloride solution has been known to remove H_2S from gasoline samples before analysis (UOP Laboratory Test Methods, 1980).

2.5 Conclusion

In conclusion, it is apparent that the ten above-mentioned solvents are all somewhat soluble in FCC gasoline and therefore cannot be used in a simple shake flask extraction method for sulfur. This is most likely due to the complex mixture of FCC gasoline and its solubility in most organic solvents. Perhaps trials with aqueous solutions would be more effective as aqueous solutions are not as soluble in FCC gasoline. The experiments with the metal salts showed more promise because separation occurred between the aqueous salt solutions and the FCC gasoline. However, the metal salt extractions showed no significant reduction in sulfur concentration. The basic and acidic solutions also separated from the FCC gasoline; however there was again no significant difference in the sulfur concentration.

Therefore, in this work, a simple shake flask extraction using a single solvent or solution is not effective for desulfurization of FCC gasoline. This study shows that intermolecular forces such as van-der-Waals interactions are normally not strong enough to remove sulfur from FCC gasoline. Due to time constraints and limited resources, there is room for future research with each of these compounds, particularly secondary solvents. However, it may be more suited to a person with significant knowledge of solvent chemistry. A stronger chemical interaction seems to be required to desulfurize FCC gasoline at ambient conditions, perhaps through a catalytic reaction or through reactive adsorption.

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Chapter 3: Activation Methods for Raney Nickel in the Desulfurization of Gasolines

3.1 Introduction

As the previous chapter determined it is necessary to have a more selective and stronger molecular interaction or reaction in order to remove the less reactive sulfur compounds, such as thiophene. This can be seen in other sulfur removal technologies such as the Claus process, which uses iron oxides or chromium oxides supported on alumina and hydrotreating, which uses a variety of supported zeolites (Ertl *et al.*, 1999). In both of these technologies, catalysts are used to remove the sulfur-containing compounds from the feeds (Meyers, 2004).

Within a refinery, both water and gas streams can contain H_2S, respectively called "sour water" and "acid gas" (Meyers, 2004). Sour water is produced when steam is used as a stripping medium in distillations or from the reduction of hydrocarbon partial pressure in catalytic cracking. Acid gas is usually formed in the amine regeneration and sour water stripping units (Meyers, 2004).

A schematic of the Claus process is shown previously in Figure 1.7. In this process, acid gas is added into a reaction furnace with air to combust a portion of the H_2S as seen in reaction 3.1 below. The SO_2 produced from the combustion reacts with the uncombusted H_2S to form elemental sulfur as seen in reaction 3.2 (Meyers, 2004). The second part of the Claus process involves two or three catalytic reactors. These reactors reheat the acid gas, converting a portion of it to SO_2; the stream is then cooled causing any remaining H_2S to be converted to elemental sulfur by reacting with SO_2. The catalyst is typically a bauxite catalyst (Matar and Hatch, 2001).

$$H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + H_2O \qquad (3.1)$$

$$H_2S + \frac{1}{2}SO_2 \rightleftharpoons \frac{3}{2}S + H_2O \qquad (3.2)$$

A schematic diagram of the hydrotreating process can be seen previously in Figure 1.8. The hydrotreating catalysts are typically Co(Ni)Mo or NiW supported by aluminum oxide (Coulier *et al.*, 2002). The development of new hydrotreating catalysts other than the typical Co(Ni)Mo catalysts is fast growing. Oyama *et al* (2002) have developed a new type of nickel catalyst, which uses phosphide. The catalyst, Ni_2P, has shown promise as 98 % of the sulfur was removed from petroleum feedstocks compared to only 78 % with NiMo. The lack of a layered structure, the moderate preparation temperatures, and inexpensive precursors make this new catalyst promising. Other processing and analytical methods also use nickel-based catalysts for desulfurization.

Raney nickel is one of the most common skeletal metal catalysts and is prepared by adding sodium hydroxide to a powdered nickel-aluminum alloy. This reaction causes the nickel to form a porous structure so it is sometimes referred to as “spongy nickel” (Freel *et al.*, 1969). The porous structure creates a high surface area, increasing the reaction surface (Augustine, 1996). Raney nickel can be used to effectively remove sulfur-containing compounds by cleaving the carbon-sulfur bond and replacing the sulfur with hydrogen, the result is a nickel sulfide precipitate. Also, Raney nickel has been used as part of an analytical method or purification method for years.

3.1.1 Activation of Raney Nickel

The activation of Raney nickel with sodium hydroxide has been extensively studied with a variety of activation procedures identified. These procedures were summarized earlier. Through the activation process, large amounts of hydrogen are adsorbed through Van der Waals forces by leaching the aluminum off the nickel (Beigi *et al.*, 1999). The activation reaction can be seen in Reaction 3.3 (Devred *et al.*, 2003):

$$2(Ni - Al)_{(s)} + 2OH^{-} + 6H_2O_{(l)} \rightarrow 2Ni - H_{2Raney} + 2Al(OH)^{-}_{4(aq)} + H_{2(g)} \quad (3.3)$$

The amount and temperature of the sodium hydroxide can greatly affect the activity of the Raney nickel (Augustine, 1996). The three methods of activation were based on the information gathered from the literature. This includes the activation methods used by Granatelli (1959), Beigi *et al.* (1999), Srivastava *et al.* (1985), and Bartok *et al.* (1987). The activation process can have a variety of effects on the structure of the activated Raney nickel.

3.1.2 Structure

The leaching of Raney nickel creates a large surface area with the preparation temperature having an impact on the porous structure and therefore, the surface area (Fouilloux, 1983). At low preparation temperatures the pores have a narrower diameter, whereas at higher preparation temperatures the pores are more cylindrical and create a higher pore volume (Fouilloux, 1983). In general, Raney nickel is comprised of sponge-like particles and, it is this porous structure that makes Raney nickel a high capacity catalyst or rapid reactant for the removal of sulfur.

3.1.3 Desulfurization with Raney nickel

There are two reaction mechanisms by which Raney nickel can be used to remove sulfur. The two mechanisms are as follows (Beigi *et al.*, 1999):

$$3RSR' + 3Ni - H_{2Raney} \rightarrow RR' + RR + R'R' + 3NiS + 3H_{2(g)} \quad (3.4)$$

$$RSR' + Ni - H_{2Raney} \rightarrow RH + R'H + NiS \qquad (3.5)$$

With the thiols and thiophenes, a cleavage of the carbon-sulfur bond with formation of a carbon-hydrogen bond is the most common mechanism (Pettit and van Tamelen, 1962). The effectiveness of Raney nickel, for removing sulfur makes it a promising option for desulfurization of FCC gasoline.

The purpose of this chapter is to identify the best form of activated Raney nickel to remove sulfur from FCC gasoline. In order to determine the most effective activated Raney nickel the chosen method will need to use the smallest amount of Ni-Al alloy possible and the lowest activation temperature possible to make it cost effective for large scale operations.

3.2 Methodology

3.2.1 FCC Gasoline Sampling and Storage

The FCC gasoline was sampled as described in Chapter 2 at Husky Energy's refinery in Prince George. Two 1-litre samples were taken on March 07, 2005 and six 1-litre samples were taken on June 14, 2005. The FCC gasoline samples were transported to UNBC and stored as described in Chapter 2.

3.2.2 Raney Nickel Activation

Six activation experiments were studied in order to determine the most effective and rapid activation method for Raney nickel. One experiment of each of the following leaching processes was performed. The first experiment was low temperature activation similar to the process used by Beigi *et al* (1999). This process used 3.7 ± 0.01 g of nickel-aluminum alloy (Alfa Aesar / Lancaster, 50/50 %) and 10 mL of 10 % sodium hydroxide solution in a 100 mL beaker. The solution was allowed to react until the vigorous evolution of hydrogen ceased. The mixture was covered with Parafilm and allowed to react further for approximately 20 hrs. After 20 hrs, the mixture was rinsed three times with distilled water and then three more times with isopropanol, decanting between rinses. 10 mLs of isopropanol was then added to the activated mixture.

The next three activation experiments were similar except the amount and concentration of sodium hydroxide was altered. The second experiment used 20 mL of 10 % sodium hydroxide, the third experiment used 5 mL of 20 % sodium hydroxide and the fourth experiment used 10 mL of 20 % sodium hydroxide. It should be noted that the Raney nickel had to be used for the experiments on the same day it was prepared.

The next two experiments were performed at high temperatures. The fifth experiment was similar to a method used by Bartok *et al* (1987). This method used 3.0 ± 0.01 g of nickel-aluminum alloy (Ni-Al) added to 60 mL of 20 % sodium hydroxide that had been heated to 80 ^{0}C. The solution was stirred continuously at 80 ^{0}C for 45 minutes. The solution was then rinsed four times with 40 mL of distilled water and once with 40 mL of isopropanol. Finally, 10 mL of isopropanol was added to the activated Raney nickel.

The sixth experiment and the second high temperature method were similar to a method used by Srivastava *et al* (1985). This sixth experiment involved cooling 150 mL of 20 % sodium hydroxide in a refrigerator to a temperature of 4 ^{0}C, followed by addition of 3.0 ± 0.01 g of nickel-aluminum alloy while stirring continuously. The mixture was then gradually heated to 100 ^{0}C; the heating process took approximately 35 minutes. The activated Raney nickel was then removed from the heat and rinsed twice with 5 % sodium hydroxide, four times with distilled water and once with 20 mL of isopropanol. Finally, 10 mL of isopropanol was added to the activated Raney nickel.

A Student T-test was used to determine if a significant difference was present between the original concentration of sulfur and the final concentration of sulfur in the reacted samples. A one-way ANOVA was then used to determine any significant differences between the six different activation methods (Miller and Miller, 1993). Finally, an F-test was used to determine the relative precision of the methods and another Student T-test was performed to determine which methods had a significant difference from each other.

A scanning electron microscope (SEM) was used to observe any differences in the surface of Raney nickel, activated under different conditions. A beam of accelerated electrons (30 kV) is condensed to 50 – 200 Å diameters scanning the surface of the Raney nickel. The interaction between the electrons and atoms produces transitions between energy levels in the atom. The energy is released as X-ray photons giving a fingerprint of the composition of the Raney nickel (Reeder, 1983). A Philips XL30 SEM equipped with an energy dispersive spectrometer (EDS) was used for the analysis. The EDS is capable of chemical analysis with an element range from boron to uranium. The elemental analysis was performed to determine differences in the composition of elements found in Raney nickel that is activated under varying conditions. The samples of Raney nickel were placed on an Al pin-type stub and cemented with a carbon-based glue. Then they were coated with a 25 nm layer of gold in a Denton Desk II sputter coater.

3.2.3 Methodology for the Amount of Raney Nickel

As it was important that the amount of Raney nickel be minimized, a test on the amount of Raney nickel needed to cause a sufficient reaction was necessary. The method for this was that a sample of Raney nickel was prepared using the second activation method described above. The nickel-aluminum alloy solutions were prepared using 1.0, 2.0, 3.0 and 4.0 g of nickel-aluminum alloy. The volume of sodium hydroxide was also decreased or increased appropriately. A Student T-test was used to determine any significant differences between the amount of Ni-Al alloy used and the amount of sulfur removed.

3.2.4 Methodology of Desulfurization of FCC Gasoline

For all of the above methodologies the same reaction procedure was employed using the FCC gasoline. Each sample of activated Raney nickel had 50 mL of FCC gasoline added. The samples were then covered and stirred continuously at 20 ^{0}C for 30 minutes. At the end of the 30 minutes, the samples were filtered through Whatman No.2 filter paper and placed in a 4 ^{0}C refrigerator until the analysis could be completed.

The analysis was performed using UV fluorescence spectrometry according to the ASTM method D5453 (ASTM, 2003). The instrument was an Antek 9000 series elemental analyzer with an oxidative furnace that operated at 1075 ^{0}C (see chapter 2 for more information).

A check standard was analyzed first in order to check the operation of the Antek instrument. If it passed the check standard within 5 % of the actual value, the samples were then analyzed. If it did not pass then it was recalibrated before another check standard was performed. Each sample was analyzed in triplicate with the average being reported in parts per million.

3.2.5 Repeatability of Method 5

Finally, a repeatability test was performed to ensure that the test could produce similar results during multiple tests. The repeatability test involved using method 5 for the activation method of Raney nickel. Each batch of Raney nickel was prepared separately using the exact same method so that the amount of Raney nickel was consistent among each of the samples. Then 50 mL of FCC gasoline was added to each individual sample and reacted at 20 ^{0}C for 30 minutes. The individual samples were analyzed using the UV fluorescence method. A preliminary test of 5 samples was needed in order to determine an appropriate sample size. The sample size was determined using the following equation (Caulcutt and Boddy, 1983):

$$n \cong \left(\frac{t\sigma}{c}\right)^2 \qquad \text{(e.3.1)}$$

Where, t is the t-statistic value for given sample size, s is the standard deviation, and c is the confidence interval. Once the sample size was determined, the appropriate numbers of samples were prepared and analyzed. The values obtained were used to determine the standard deviation. These values were then placed into the equation for repeatability (Farrant, 1997):

$$r = t * \sqrt{2} * \sigma_r \qquad \text{(e.3.2)}$$

Where σ_r = the standard deviation obtained when the same method is used under the same conditions and t = the constant value for a Student T-test.

3.3 Results

3.3.1 Results of the Six Different Activation Methods

The results from the six different activation methods can be seen in Table 3.1. Methods 2, 3, 5 and 6 showed a significant difference from the initial sulfur concentration. Methods 5 and 6 had the largest decrease in sulfur concentration compared to activation methods 2 and 3. It should be noted that the initial sulfur concentrations were different between the first four methods and the last two methods, because two different samples of FCC gasoline were used as we ran out of the first.

Table 3.1: Summary of Raney Nickel Activation Methods.

Method Name	**Conditions**	**Initial Sulfur Conc. (ppm) ± 5.0 ppm**	**Final Sulfur Conc. (ppm) ± 5.0 ppm**	**Significant Difference**
Method 1	3.7 g Ni-Al alloy, 10 mL 10 % NaOH 20 ^{0}C	163.53	160.22	No
Method 2	3.7 g Ni-Al alloy, 20 mL 10 % NaOH 20 ^{0}C	163.53	112.31	Yes
Method 3	3.7 g Ni-Al alloy, 5 mL 20 % NaOH 20 ^{0}C	163.53	123.40	Yes
Method 4	3.7 g Ni-Al alloy, 10 mL 20 % NaOH 20 ^{0}C	163.53	161.63	No
Method 5	3.0 g Ni-Al alloy, 60 mL 20 % NaOH 80 ^{0}C	183.99	52.42	Yes
Method 6	3.0 g Ni-Al alloy, 150 mL 20 % NaOH 100 ^{0}C	183.99	49.00	Yes

The ANOVA showed that there was a significant difference between the means using the six different activation procedures as can be seen in Table 3.2, each method had a sample size of 3. As the calculated F-value is higher than the critical value, the standard deviations are therefore significantly different. Since the ANOVA showed there was a significant difference, further analysis was needed to determine exactly where the significance lies.

Table 3.2: ANOVA table for the Comparison of Six Different Activation Methods.

	Variance			
Method 1	1.73			
Method 2	1.72			
Method 3	3.45	**Sample Mean Variance**		1030.85
Method 4	0.72			
Method 5	0.09			
Method 6	0.04			
		Degrees of Freedom	**F-value**	**Critical Value (95 %)**
Within-Sample variance	1.29	12	3988.73	3.106
Between-sample variance	5154.27	5		

An F-test was performed in order to show the more precise methods. The F-test determined that methods 5 and 6 were more precise than methods 1, 2 and 3 however; the precision was not significantly different than method 4. Also, the precision between method 5 and 6 was not significantly different. Next, a Student's T-test was used to determine the differences between the six methods. The data showed that there was a significant difference between each of the methods except for when method 1 was compared to method 4. In this case no significant difference was determined. Even though there was a significant difference between the means of each of the methods, methods 5 and 6 showed the largest significance of the six methods.

The differences in the structure of the activated Raney nickel can be seen in the SEM images of the different methods. Using activation method 2, Figure 3.1 shows that the Raney nickel is covered with a crystalline material and the structure was cylindrical with rounded edges. Using activation method 5, Figure 3.2 shows a slightly different structure. In Figure 3.2 the Raney nickel has fewer crystals on the surface. In addition, the structure had sharper edges, with more surface area visible due to the lack of the crystals. Finally, Figure 3.3 shows the structure produced when method 6 was used for activation. In Figure 3.3 it can be seen that there were fewer crystals on the surface than for method 5 and the structures have even more sharp edges. The elemental analysis shows the chemical differences between the different types of Raney nickel.

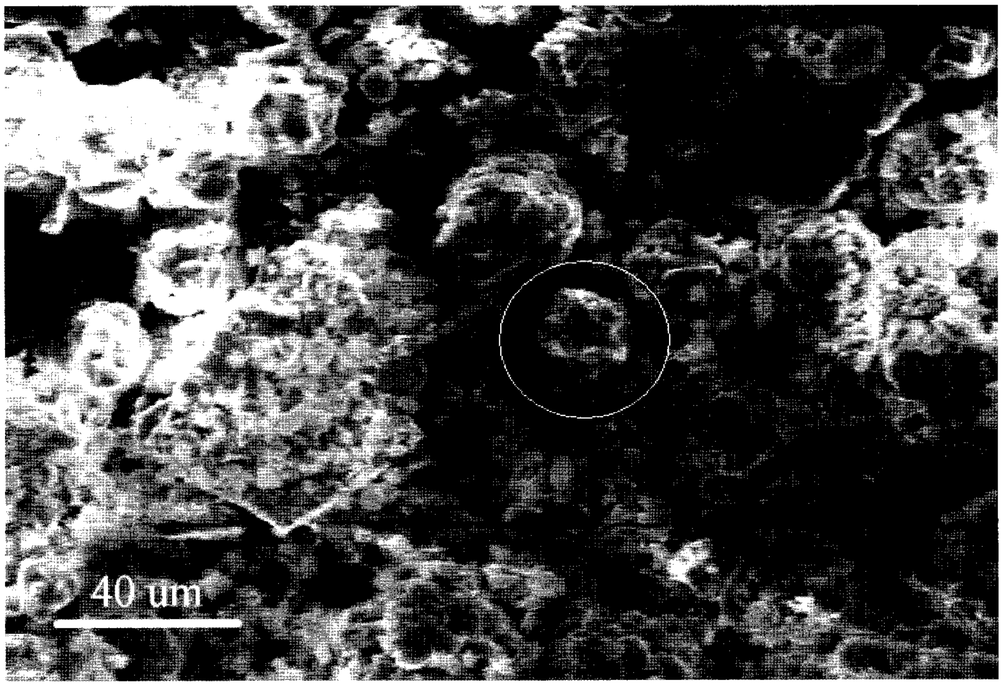

Figure 3.1: **SEM image of Raney nickel prepared using Method 2 (20 ^{0}C).**

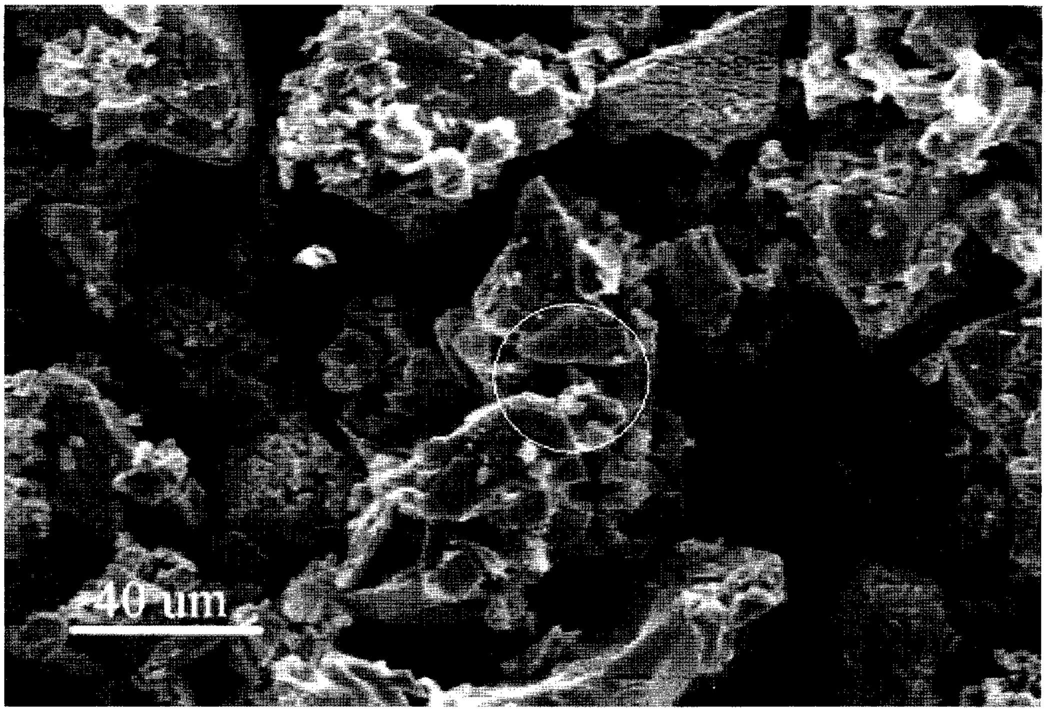

Figure 3.2: **SEM image of Raney nickel prepared using Method 5 (80 ^{0}C).**

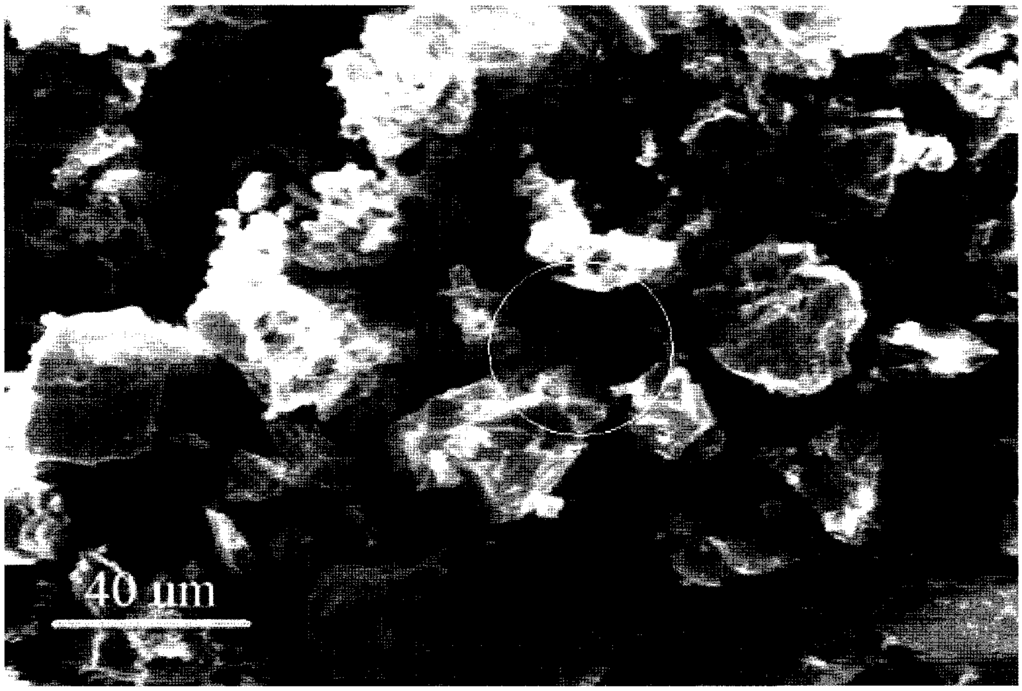

Figure 3.3: **SEM image of Raney nickel prepared using Method 6 (100 ^{0}C).**

The elemental analysis of the lower temperature activation method 2 shows that there was a large portion of aluminum and nickel in the sample as seen in Figure 3.4, the target location can be seen in Figure 3.1. This can be compared to Figures 3.5 and 3.6 from the two higher temperature activation methods where there was very little aluminum present, the target positions can be seen in Figure 3.2 and 3.3 respectively. Other than the difference in the amount of aluminum and oxygen, the elements present were very similar. There are small differences in the amount of nickel present in each of the Figures 3.4, 3.5 and 3.6. This difference is simply due to the presence of aluminum. The aluminum peak seen in Figure 3.4 is larger than in Figures 3.5 and 3.6 so it masks the nickel peaks within close proximity. Also, one can notice that gold appears in the energy spectrum, due to the conductive gold coating on the Raney nickel.

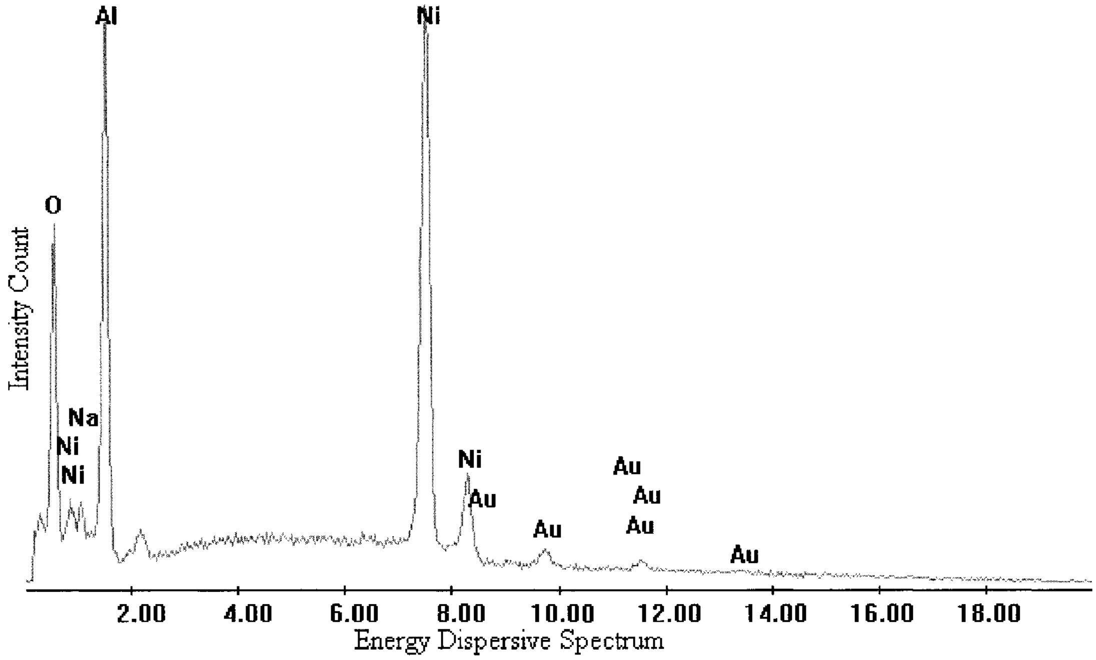

Figure 3.4: **Elemental Analysis of Raney nickel prepared using method 2 (20 ^{0}C).**

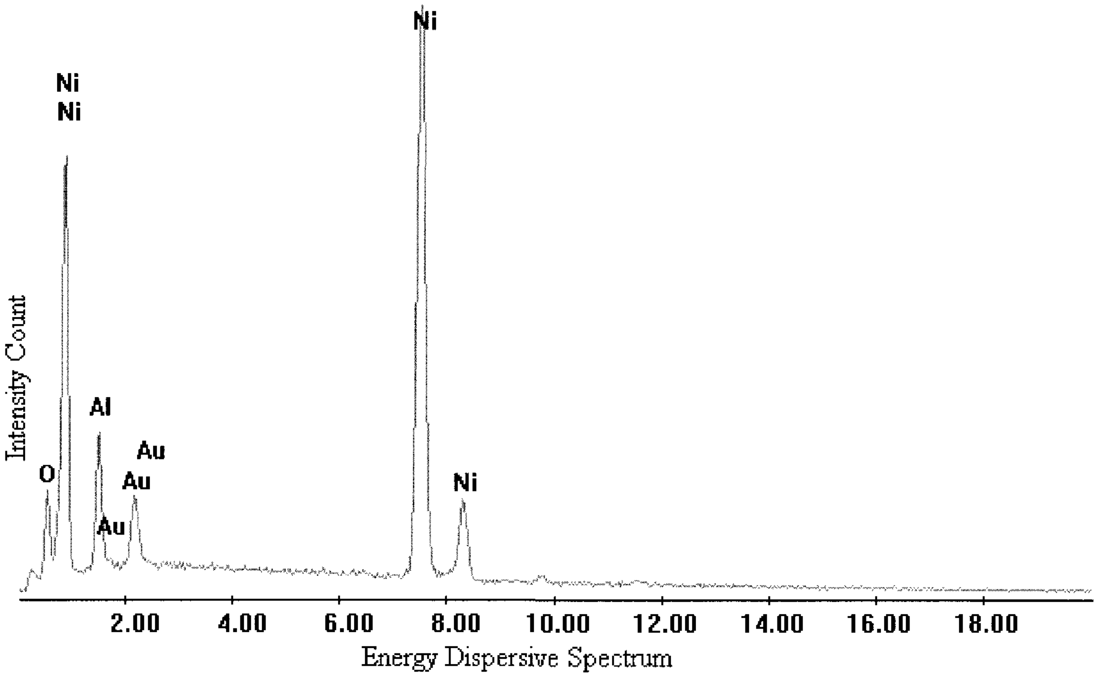

Figure 3.5: **Elemental Analysis of Raney nickel prepared using method 5 (80 ^{0}C).**

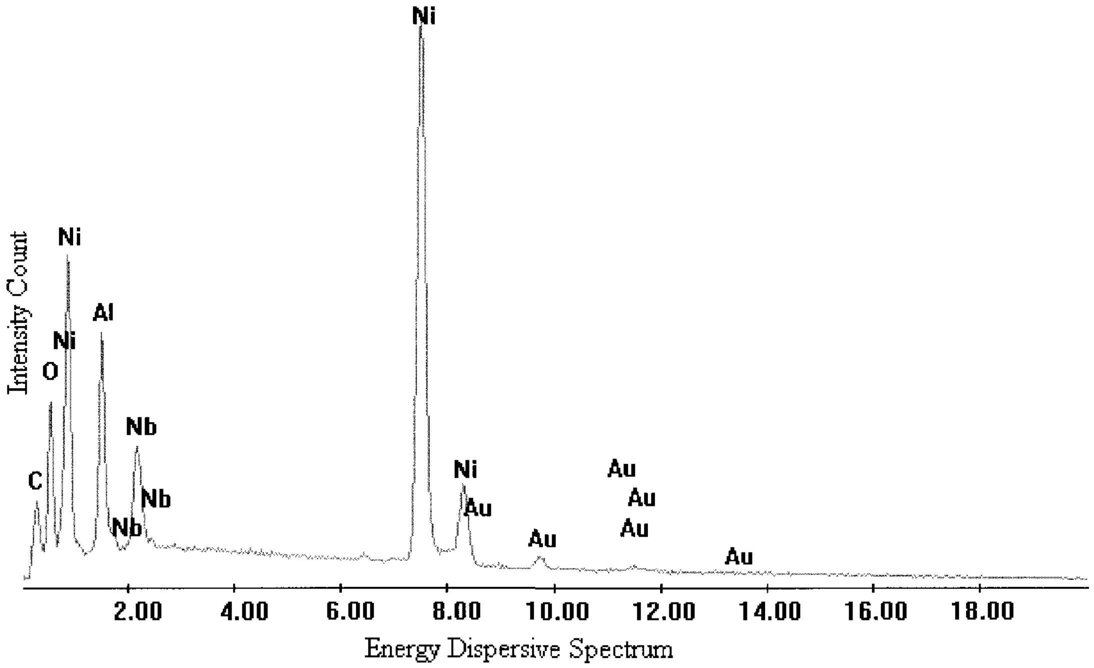

Figure 3.6: **Elemental Analysis of Raney nickel prepared using method 6 (100 ^{0}C).**

3.3.2 Results for the Amount Nickel-Aluminum Alloy

The results from varying the amount of Ni-Al alloy used during the method 2 activation processes can be seen in Table 3.3. The table shows that each amount of Ni-Al alloy decreased the sulfur concentration. However, the Student t-values show that 3.0 and 4.0 g of alloy had a much more significant effect on the final sulfur concentrations. However, there is no significant difference between 3.0 and 4.0 grams.

Table 3.3: Summary of the Difference in Desulfurization Based on the Amount of Ni-Al Alloy.

Mass of Ni-Al alloy (g)	**Initial Sulfur Concentration (ppm)**	**Final Sulfur Concentration (ppm)**	**Standard Deviation (ppm)**	**T-value**	**T-critical**	**Significant Difference**
1	179	168	2.5	7.62	2.92	Yes
2	179	170	2.5	6.24	2.92	Yes
3	179	151	2.5	19.40	2.92	Yes
4	179	152	2.5	18.71	2.92	Yes

3.3.3 Repeatability of Method 5

As was demonstrated in the previous sections, the most effective method for activation was method 5, using an optimal amount of 3.0 grams of Ni-Al alloy to get the most desulfurization. A preliminary test of 5 samples showed that a sample size of 15 samples would be sufficient for determining the repeatability using equation e.3.1. This is for a 5 ppm confidence interval and 95 % confidence. Once this was determined, the test was repeated for a total of 15 samples. The summary statistics are shown in Table 3.4.

Table 3.4: Summary Statistics for 15 Identical Samples.

Mean	44.00 ppm
Variance	3.99 ppm^2
Standard Deviation	2.00 ppm
Repeatability	6.06 ppm
Original FCC Sulfur Concentration	186 ± 4.12 ppm

This shows that from the original concentration of 186 ppm, there is a 76 % reduction in the sulfur concentration. In addition, the repeatability of the method is approximately 6 ppm. The scatter of the measurements can be seen in Figure 3.7.

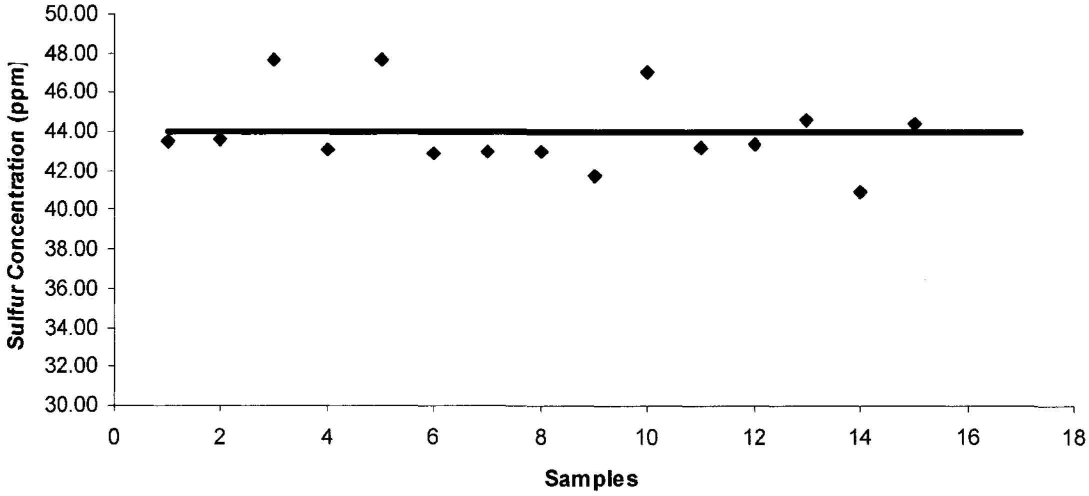

Figure 3.7: **Determination of Sulfur Concentration in 15 Uniquely Prepared Samples of Raney Nickel Using Activation Method 5 and 3.0 grams of Ni-Al Alloy.**

3.4 Discussion

3.4.1 Raney Nickel Activation

The results in Table 3.1 show that the two high temperature activation methods produce the greatest reduction in sulfur concentration. This is supported by literature where the activation procedures performed at higher temperatures were reported to produce more reactive Raney nickel (Devred *et al.*, 2003; Lieber and Morritz, 1953; Fouilloux, 1983). This can be explained by observing the SEM micrographs and elemental analysis results. The elemental analysis results for the low temperature activation, Figure 3.4, show a large amount of aluminum remaining on the Raney nickel. This aluminum is in the form of bayerite $(Al_2O_3 \bullet H_2O)$, which can be seen in Figure 3.1 as the crystals covering the surface of the Raney nickel. A crystal of similar structure was reported by Kiyohara *et al* (2000) for a variety of aluminas. A similar result was also reported by Devred *et al* (2003) for low temperature leaching processes, which did not use an excess of sodium hydroxide. Bayerite covers the surface of the nickel using up the active sites. This reduces the amount of contact the FCC gasoline can have with the Raney nickel and its active sites. However, at excess concentrations of sodium hydroxide and higher activation temperatures, the elemental analysis shows a lower amount of aluminum or bayerite present (Figures 3.5 and 3.6) this was also supported by Devred *et al* (2003). This is supported by the SEM images in Figures 3.2 and 3.3, which show much less of the bayerite on the surface of the nickel. Therefore, there is a greater chance for the FCC gasoline to contact the surface of the nickel, making methods 5 and 6 the most effective methods for removing sulfur from FCC gasoline. The Student T-test shows that they had the largest significant difference when compared to the other methods.

There was only a 3 ppm difference between the 80 ^{0}C and 100 ^{0}C method. This was within the standard deviations of the two samples so it is not necessary to heat the sample the extra 20 ^{0}C. Also, the F-test showed that there was no significant difference in the precision of the two methods. Therefore, method 5 was the most effective activation method for producing the most reactive Raney nickel for removal of sulfur from FCC gasoline.

3.4.2 Raney Nickel Amount

The tests investigating the amount of Ni-Al alloy that was most effective at removing the sulfur from FCC gasoline showed that 3.0 grams was enough to effectively remove sulfur. As Table 3.3 shows both 3.0 and 4.0 grams had very significant reductions in sulfur concentration. However, there was not a significant difference between 3.0 and 4.0 grams. Therefore, 3.0 grams is the least amount of Ni-Al alloy that could be used to remove the most amount of sulfur from FCC gasoline based on 50 mL of FCC gasoline.

3.4.3 Repeatability

As the previous sections have determined, method 5 was the best activation method and 3.0 grams of Ni-Al alloy was enough to show significant results. Therefore, the repeatability of this method was tested. The results of 15 identically prepared samples can be seen in Table 3.4. The method had a standard deviation of 2.0 ppm and had a repeatability of 6.0 ppm.

3.5 Conclusion

In conclusion, the higher temperature methods were more effective at producing activated Raney nickel for removing sulfur from FCC gasoline. The higher temperature activations combined with an excess of sodium hydroxide produced less bayerite, allowing more of the nickel surface to come in contact with the FCC gasoline. In addition, the difference between the two higher temperature methods, method 5 and 6, was not significant enough to warrant heating the sodium hydroxide the extra 20 ^{0}C. Therefore, method 5 is the most effective activation method. Next, the amount of Ni-Al alloy necessary to cause the largest reduction in sulfur concentration was found to be 3.0 grams. The 4.0 grams of Ni-Al alloy caused the same reduction as the 3.0 grams so the lesser amount of 3.0 grams contained enough Ni-Al alloy to achieve the desired result. Therefore, the final experiment was an activation method 5 where the sodium hydroxide was heated to 80 ^{0}C using 3.0 grams of Ni-Al alloy. The repeatability of this method was determined to be 6.0 ppm.

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Chapter 4: Optimization of the Reaction Conditions for Raney Nickel for the Desulfurization of FCC Gasoline

4.1 Introduction

As described in chapter 3 the most active Raney nickel was produced by leaching 3.0 grams of nickel-aluminum (Ni-Al) alloy with an 80 ^{0}C solution of 20 % sodium hydroxide for 45 minutes (Devred *et al.*, 2003). This method had a repeatability of 6 ppm when reacted for 30 minutes with FCC gasoline. The activation process oxidizes the aluminum and generates hydrogen gas, which activates the nickel portion of the catalyst (Fouilloux, 1983).

$$2(Ni-Al)_{(s)} + 2OH^{-} + 6H_2O \rightarrow 2Ni-H_{2Raney} + 2Al(OH)^{-}_{4(aq)} + H_{2(g)} \qquad (4.1)$$

Some of the hydrogen remains adsorbed on the nickel, making it a low temperature hydrogenation catalyst. Therefore, nickel catalysts have been used widely in hydrogenation, hydrotreating, and in steam-reforming reactions (Wojcieszak *et al.*, 2004). In particular, Raney nickel has been used in industry for the hydrogenation of organic compounds and the determination of trace amounts of sulfur in organic mixtures (Devred *et al.*, 2003; Granatelli, 1959).

This chapter focuses on optimizing the reaction between Raney nickel and FCC gasoline in order to remove as much sulfur as possible; as such optimizing the reaction can reduce the amount of Raney nickel required and therefore reduce costs. In order to further reduce the costs of Raney nickel, the recovery of nickel from the spent Raney nickel will also be assessed and discussed.

To the best of our knowledge, the use of a Raney nickel catalyst has never been attempted for desulfurization of FCC gasoline although it has been used for the desulfurization of other fuels and solvents (Augustine, 1996; Granatelli, 1959; Fouilloux, 1983). Beigi *et al* (1999) determined that at lower temperatures and with newly prepared catalysts, the desulfurization occurs according to reaction 4.2, whereas at higher temperatures the desulfurization occurs according to reaction 4.3. In both cases, the sulfur forms a covalent, alloy-like, non-stoichiometric compound with the nickel (Beigi *et al.*, 1999).

$$RSR' + Ni - H_{2Raney} \rightarrow RH + R'H + NiS \qquad (4.2)$$

$$3RSR' + 3Ni - H_{2Raney} \rightarrow RR' + RR + R'R' + 3NiS + 3H_2 \qquad (4.3)$$

These reactions occur at the Raney nickel surface and therefore the Raney nickel is acting as a heterogeneous catalyst. On the surface, there are two main types of adsorption: physical adsorption and chemisorption. Physical adsorption involves van der Waals forces, which cause relatively weak adsorption. Chemisorption involves covalent forces, which are similar to the forces occurring between bound atoms in molecules (Laidler, 1987). Chemisorption causes a single layer of adsorbed molecules to cover the surface of the Raney nickel. Once the surface of Raney nickel is covered with a single layer of reactant it is saturated and no more molecules can be adsorbed. The only way more molecules can be absorbed is if they are physically adsorbed to the single layer already formed (Laidler, 1987).

The kinetics of these surface reactions can be affected by temperature. The amount of a compound adsorbed to a surface is dependent on a variety of factors, including temperature and pressure (Laidler, 1987). The rate constant (k) is dependent on temperature; therefore temperature will affect the rate at which a reaction occurs (Laidler, 1987). The surface reactions occur in five steps (Laidler, 1987):

1. Diffusion of the reactants to the surface
2. Adsorption on the surface
3. Reaction on the surface
4. Desorption of the products
5. Diffusion of the desorbed products into solution

The slowest of these five steps determines the overall rate of the process. In most cases reactions on the surface and/or desorption of the products are the rate determining steps (Campbell, 1988). However, there are many factors that affect the reaction process. Olefins are a large component of FCC gasoline and are a key source of octane rating. During hydrogenation reactions the olefins can become saturated causing a possible loss in octane. Olefins affect the recovery of sulfur with Raney nickel by forming an addition reaction between the hydrogen sulfide and an olefin as seen in reaction 4.4 (Beigi *et al.*, 1999):

$$H - S - H + R = R' \leftrightarrow R - SH + R' - SH \qquad (4.4)$$

Beigi *et al* (1999) also found that in samples with greater than 10 wt. % of olefins, the double bonds interact with the active sites of the Raney nickel, interfering in the desulfurization step. Therefore, olefins are competing with the sulfur-containing compounds to occupy the active sites of the Raney nickel.

In order to determine the effectiveness of Raney nickel on desulfurization of FCC gasoline, a variety of experiments were performed. The experiments investigated the effects of time, temperature, and the sequential use of Raney nickel. In addition, analysis was performed in order to determine any chemical changes in the FCC gasoline due to its reaction with Raney nickel.

Finally, the ability to recover nickel from the spent Raney nickel was assessed. A variety of methods have been shown to remove sulfur from nickel. For example, Granatelli (1959) used a hydrochloric acid solution in order to remove sulfur in the form of hydrogen sulfide. Other methods include nickel roasting, which is used extensively in mineral extraction processes. Nickel roasting involves heating the nickel-containing compound to high temperatures (600 – 800 ^{0}C) causing oxidation.

The objectives of the work presented in this chapter then are to first determine the most effective laboratory conditions for Raney nickel to desulfurize FCC gasoline. The second objective is to determine any effects that Raney nickel may have on the FCC gasoline composition. Thirdly, if the nickel can be recovered from the nickel sulfide for re-use.

4.2 Methodology

4.2.1 FCC Gasoline Sampling and Storage

The FCC gasoline was sampled as described in Chapter 2 at Husky Energy's refinery in Prince George. Six 1-litre samples were taken on June 14, 2005 for use with the following experiments. The FCC gasoline samples were transported to UNBC and stored as described in Chapter 2.

4.2.2 Preparation of the Raney Nickel

First, 60 mL of 20 % sodium hydroxide was heated to 80 ^{0}C on a hot plate stirrer this took approximately 15 minutes. Next, 3.0 ± 0.01 g of nickel-aluminum alloy (50-50 Ni/Al wt.

%, Alfa Aesar) was gradually added over approximately 5 minutes to the heated sodium hydroxide. The reaction was stirred continuously for 45 minutes at 80 ± 5 ^{0}C once all the Ni-Al had been added. The Raney nickel was then rinsed four times with 40 mL of distilled water, letting the Raney nickel settle between rinses, and then decanting the distilled water and hydroxide mixture. The Raney nickel was then rinsed once with 40 mL of isopropanol, to remove any remaining water. Finally, 10 mL of isopropanol was added to the Raney nickel in order to keep it active and aid in the mixing of the Raney nickel with FCC gasoline (Lieber and Morritz, 1953; Granatelli, 1959).

4.2.3 Time Trial Experiments

To determine the effect of time on the removal of sulfur, twelve samples were prepared by adding 50 mL of FCC gasoline to the Raney nickel. The reactions occurred at an ambient temperature of 20 ^{0}C. Duplicate samples were stirred continuously for each of the following reaction times: 0.5, 30, 60, 90, 120, and 180 minutes. In order to stop the reaction the samples were filtered, using No. 2 Whatman filter paper, immediately upon removal from the stirring plate. The filtered FCC gasoline was then stored in 125 mL amber glass bottles at 4 ^{0}C for further analysis.

4.2.4 Temperature Trial Experiments

To determine the effect of temperature on the removal of sulfur, ten samples were prepared by adding 50 mL of FCC gasoline to the Raney nickel. Duplicate samples were performed at each of the following temperatures: 5, 20, 30, 40 and 50 ^{0}C. The samples were stirred continuously for 30 minutes.

The samples used a reflux condenser with a hot plate stirrer as the heater and mixer as shown in Figure 4.1. In this set of experiments the FCC gasoline was first heated to the desired temperature then added to the Raney nickel and held at a constant temperature while stirring continuously for 30 minutes. In each case, after 30 minutes, the samples were removed and filtered using No. 2 Whatman filter paper. The filtered FCC gasoline was then stored in 125 mL amber glass bottles at 4 ^{0}C until analysis.

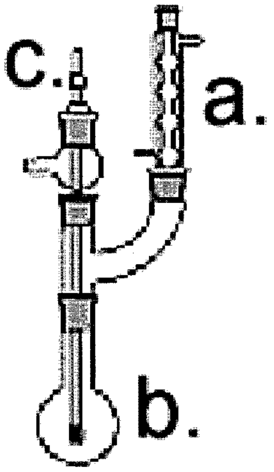

Figure 4.1: **Reflux condenser apparatus for temperature experiments: a. condenser, b. round bottom flask, e. thermometer.**

4.2.5 Sequential Addition Runs

The sequential trials involved reacting 50 mL of FCC gasoline with Raney nickel for 30 minutes at 20 ^{0}C with continuous stirring. The FCC gasoline was then filtered through No. 2 Whatman filter paper then reacted again for 30 minutes with a fresh batch of Raney nickel. The FCC gasoline was again filtered and then stored in 125 mL amber glass bottles at 4 ^{0}C until analysis.

4.2.6 Method of Analysis

The samples were analyzed using an Antek 9000 sulfur/nitrogen system. This system was setup according to the ASTM method D5453 (Annual Book of ASTM Standards, 2003). The system injects 5 μL of sample, which is then completely oxidized at a temperature of approximately 1000 ^{0}C. The combustion gases are dried, removing any water formed. The sample gases then move to the detector module where the fluorescence SO_2 is recorded. The fluorescent emission is specific for sulfur dioxide and is also proportional to the amount of sulfur in the sample.

Two samples of the original FCC gasoline were analyzed as the baseline for the test samples. Each of the samples was injected three times. The standard deviation and mean values were also determined for each of the samples. The samples were analyzed in triplicate and average values determined.

4.2.7 Statistical Analysis

The data from the time and temperature trials were subjected to a statistical analysis consisting of a one-way ANOVA and a Student's T-test. The one-way ANOVA was performed first in order to determine if a significant difference existed between the means of any of the values. The ANOVA was a one-tailed test using a 95 % confidence interval. Once a significant difference was determined, a Student's T-test was performed to determine exactly where the significant differences occurred. The Student's T-test established differences at the 99 % confidence interval.

4.2.8 Hydrocarbon Analysis

A hydrocarbon analysis was performed on a few samples to determine the effect that the reaction with Raney nickel has on FCC gasoline. The hydrocarbon analysis was performed using gas chromatography with a flame ionization detector (GC/FID). A Hewlett Packard HP 6890 series GC system was used. It was operated with an HP 1 dha column at a maximum temperature of 280 ^{0}C for a run time of 138 minutes, see chapter 2 for more information.

4.2.9 Recovery of Nickel

The final step was to assess the recovery of nickel from the nickel sulfide formed during reaction with FCC gasoline. It was first necessary to determine that the sulfur was present within the spent Raney nickel. A sample of the spent Raney nickel was reacted with 50 mL of 20 vol. % HCl (Reagant A.C.S, Lot No. 204173) in a 100 mL flask. Once bubbles started to form in the solution, a GASTEC (Levitt-Safety Limited, model 801) was used to determine if hydrogen sulfide was being produced. The GASTEC apparatus uses detector tubes (No. 4LT), which change colour to indicate the presence of hydrogen sulfide. The GASTEC requires 50 mL of air to be drawn and forced through the detector tube.

Once it was determined that the spent Raney nickel contained sulfur, the following roasting method was used to remove the sulfur, in order to recover the nickel. In this method 3.0 ± 0.01 grams of spent Raney nickel was added into a ceramic crucible. The crucible was then inserted into a muffle furnace and stepped up gradually to 800 ^{0}C over a period of 6 hrs. The crucible was then removed from the furnace and allowed to cool for 18 hrs.

X-ray diffraction (XRD) was then used to analyze the sample for different phase compositions. A Bruker D8 X-ray diffractometer, with a 2θ X-ray diffraction system and Co-K_α X-ray source was used for the data collection. The system was operated at 40 kV and 25 mA. The XRD recorded powder diffraction patterns for 180 seconds at three different angles. The patterns were then compared to a DIFFRAC^{Plus} EVA mineral powder diffraction file.

The samples were prepared for XRD analysis using a thin smear method. This requires mixing the sample with a small amount of distilled water to form a paste (Poppe *et al.*, 2002). This paste is then smeared onto the corner of glass slides. The XRD can only detect compounds that are greater than 1 wt % of the sample.

4.3 Results

4.3.1 Time Trials

The results of the time trial experiments can be seen in Figure 4.2, with the sulfur concentration on the subordinate and time on the ordinate. The time data follows a power function with the fitted line having an R-squared value of 0.9942 and a function of equation e.4.1:

$$y = 78.507x^{-0.1768} \qquad \text{(e.4.1)}$$

The baseline sulfur concentration was 186 ppm indicating there is an immediate removal of sulfur within the first 30 seconds of contact with the Raney nickel. The data showed that even at a short reaction time of 30 seconds only 80 ppm remained. The largest reduction was found at 180 minutes with 32 ppm remaining. However, the same maximum reduction was found at 120 minutes, so an ANOVA was performed to determine if the differences were statistically significant.

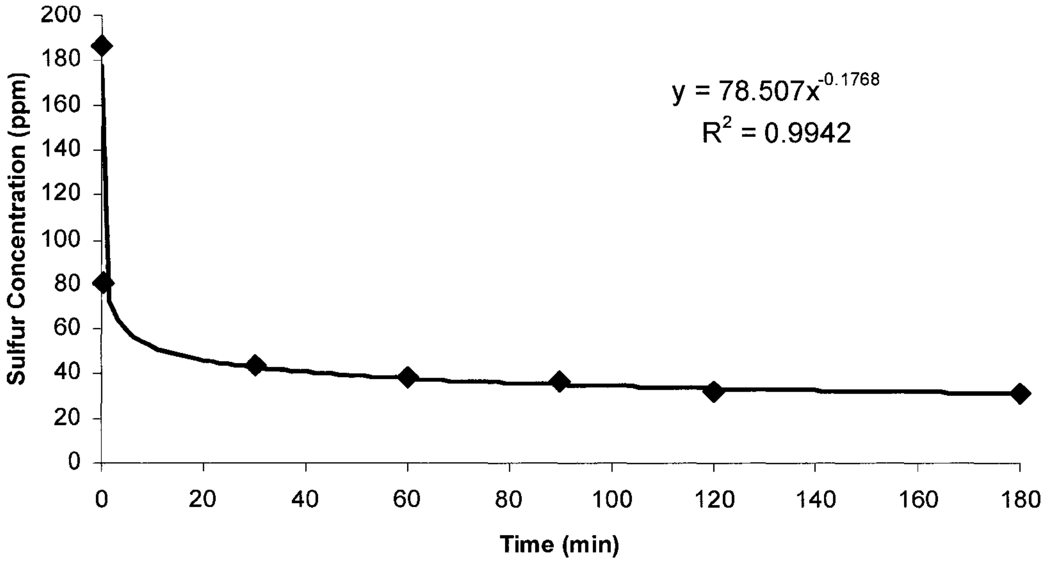

Figure 4.2: **Sulfur Concentration in FCC Gasoline with Time of Treatment at 20 ^{0}C.**

The ANOVA showed that there was a significant difference between the values at different reaction times. Further analysis indicated that there were significant differences up to a reaction time of 60 minutes, with the most significant occurring within the first 30 minutes. After 60 minutes there is no longer a significant decrease in the sulfur concentration.

4.3.2 Temperature Trials

The results from the temperature trial experiments can be seen in Figure 4.3. As seen, there is a decrease in sulfur concentration at all temperatures tested in this work. However, the decrease in sulfur concentration is much higher at the higher temperatures. The minimum reduction in sulfur concentration was found at 5 ^{0}C with only 53 ppm remaining from a starting concentration of 213 ppm. The maximum reduction was found at 50 ^{0}C with 2 ppm remaining. The effect of temperature on the rate of the reaction can be seen in the large concentration decreases in Figure 4.3.

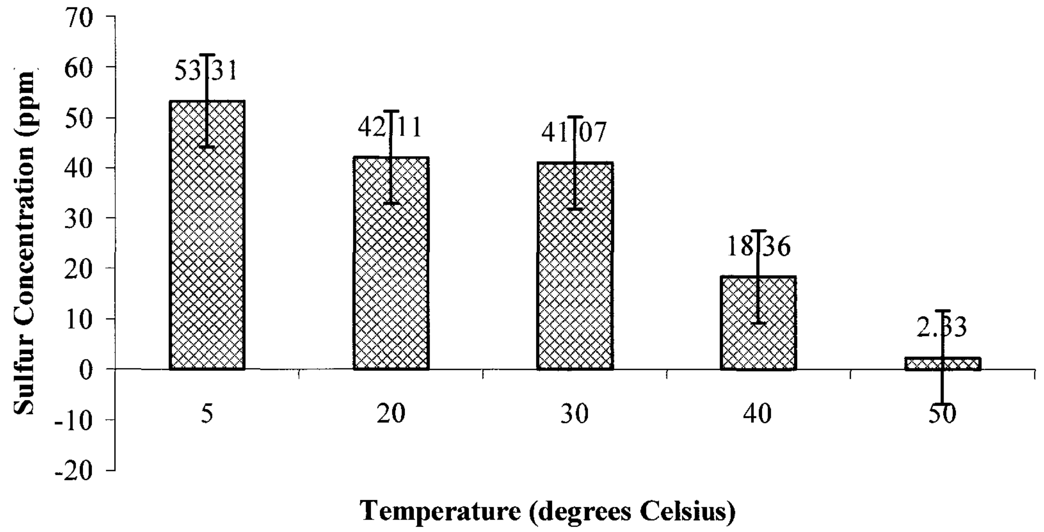

Figure 4.3: Effect of Temperature on the rate of Reduction in sulfur concentration in FCC gasoline over 30 minutes of reaction time.

The ANOVA was performed and determined that there was a significant difference between the average values determined for the five temperatures used in this study. The Student's T-test further confirmed that the significant difference was between the values obtained at 30, 40 and 50 ^{0}C. There were no significant differences seen between the results using the lower temperatures of 5 and 20 ^{0}C.

4.3.3 Sequential Addition Runs

The sequential reaction results showed that with a total of two additions of Raney nickel, the starting concentration of 213 ± 6.68 ppm for total sulfur compounds could be lowered to 7 ppm with a standard deviation of 1 ppm. This is equivalent to a 97 % reduction in the sulfur concentration at 20 ^{0}C.

4.3.4 Hydrocarbon Analysis Results

The hydrocarbon analysis showed a drop in the paraffins, I-paraffins, naphthenes, aromatics and multisubstituted aromatics. It should be noted that the multisubstituted aromatics are calculated separately during the GC/FID process so the below values may not sum to 100 %. The olefin percentage increased independent of the reaction time as can be seen in Table 4.1. The decrease in percent volume of the paraffins, I-paraffins, naphthenes, aromatics and multisubstituted aromatics was equivalent to 10 % with the largest drop seen in the I-paraffins. This drop was equal to the 10 % increase seen in the olefins. Part of the loss in volume may be a result of evaporation during the experiments, although no large volume loss was found.

Table 4.1: Comparison of hydrocarbon component concentrations for a variety of time intervals (± 5 %).

Hydrocarbon Components (Vol %)	**Original FCC Gasoline**	**0.5 mins**	**30 mins**	**60 mins**	**90 mins**	**120 mins**	**180 mins**
Paraffins	5.6	4.0	3.9	3.9	3.9	4.0	4.0
I-paraffins	25.7	20.0	20.4	20.1	20.4	20.3	20.5
Olefins	43.4	54.5	53.5	53.1	53.2	53.5	52.6
Naphthenes	10.4	8.8	8.8	9.6	9.0	9.3	9.4
Aromatics	13.7	12.0	12.1	12.3	12.4	12.0	12.6
Multisubstituted Aromatics	4.3	3.8	3.9	3.9	4.0	3.8	4.1

The temperature trials showed similar results as to the time trials. There was an average decrease in the percent volume of all components except the olefins as seen in Table 4.2. The decrease was equivalent to an average of 6 % with an average increase of 10 % for the total olefins. However, the data shows that the C_5 olefin compounds were the only olefins that increased in volume percent.

Table 4.2: Comparison of hydrocarbon component concentrations for a variety of temperatures (± 5 %).

Hydrocarbon Components (Vol %)	Original FCC Gasoline	5 ^{0}C	20 ^{0}C	30 ^{0}C	40 ^{0}C	50 ^{0}C
Paraffins	5.5	4.4	4.4	3.5	4.1	4.4
I-paraffins	27.2	22.3	21.8	18.4	21.0	22.1
Olefins	36.4	47.8	47.6	43.5	47.4	44.3
Naphthenes	9.6	7.8	8.0	7.0	8.2	8.7
Aromatics	18.6	16.8	17.1	15.5	18.1	19.2
Multisubstituted Aromatics	6.6	6.0	6.1	5.5	6.5	7.0

Finally, Table 4.3 shows the hydrocarbon components for the sequential addition experiments. As seen in Table 4.3, there is a decrease in each of the hydrocarbon components except for the olefins, which again showed an increase. The hydrocarbon components showed a total decrease of 20.4 % with the largest decrease seen in the I-paraffins. The olefin increase was equivalent to 20.1 %, which is just slightly less than the total decrease in the other components.

Table 4.3: Comparison of hydrocarbon component concentrations for sequential addition (± 5 %).

Hydrocarbon Components (Vol %)	Original FCC Gasoline	Sequential Addition
Paraffins	5.5	3.0
I-paraffins	27.2	16.1
Olefins	36.4	56.5
Naphthenes	9.6	7.1
Aromatics	18.6	15.3
Multisubstituted Aromatics	6.6	5.5

4.3.5 Recovery of Nickel

The GASTEC apparatus showed the production of hydrogen sulfide in the spent Raney nickel on addition of acid indicating the presence of sulfur. The detector tubes in both cases changed from yellow to a pinkish colour as soon as it was exposed to air from the headspace of the reaction beakers. Also, when the reaction occurs between the spent Raney nickel and HCl, the solution turns a green colour indicating that the nickel is dissolving into the solution and forming nickel chloride, implying that there was oxidation of nickel.

Using the nickel roasting method, the spent Raney nickel changed from an almost black colour to a green colour by the end of the 6 hour roasting process. The spent nickel also had an average increase in weight of 0.06 grams suggesting formation of nickel oxide, which is the product formed during industrial roasting processes. The production of nickel oxide was further supported by XRD analysis. In Figure 4.4 the diffraction pattern is perfectly aligned with the index diffraction pattern for nickel oxide. This indicates the sample is largely nickel oxide as no other diffraction peaks are present.

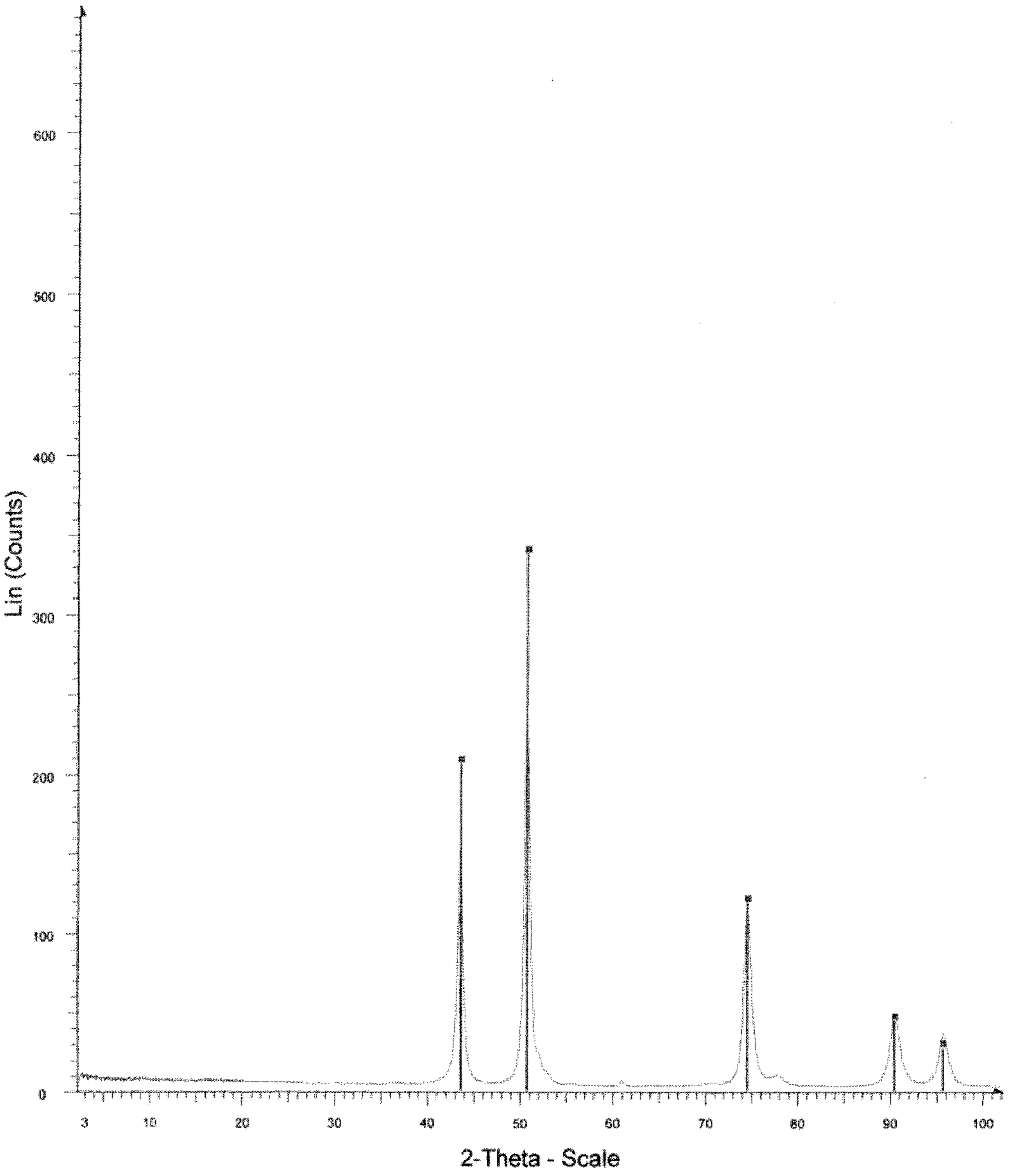

Figure 4.4: XRD diffraction pattern for spent Raney nickel roasted at 800 ^{0}C for 6 hrs and NiO indexed diffraction pattern.

4.4 Discussion

4.4.1 Effect of Time on the Removal of Sulfur

This study demonstrates that it is possible to remove sulfur from gasoline using Raney nickel. From the time trial data shown in Figure 4.2, it is evident that as the length of reaction time increases so does the reduction in sulfur concentration until after a certain time. Over 50 % of the sulfur is removed from the FCC gasoline during the first 30 seconds of reaction. However, in order to remove the maximum amount of sulfur removed, a longer contact time is necessary. The most significant reduction in sulfur concentration occurs within the first 30 minutes. It can be concluded then that 30 minutes is a sufficient reaction time as at this point, 76 % of the sulfur is removed from the FCC gasoline at 20 ^{0}C. However, an extra 4 % can be removed if left for another 30 minutes, ie. a total reaction time of 60 minutes.

After 60 minutes, there are no significant changes in the sulfur concentration. Without an in depth investigation into the exact reaction kinetics, there are several possible explanations for this result. The most probable result is due to the sulfur being adsorbed to the entire nickel surface available, leaving no additional reaction surface. Finally, it is also possible that the olefins in FCC gasoline are competing for the reaction sites on the surface of Raney nickel, making these sites unavailable for sulfur reactions (Campbell, 1988). Existing research has reported that $C_6 - C_{10}$ olefins strongly inhibit the hydrodesulfurization of thiophene (Hatanaka and Yamada, 1998).

The concentration of sulfur still decreases after 60 minutes, but by very small amounts so it is insignificant. The reaction may still be occurring at a much slower rate, the thiophenes may need a longer reaction time to give the less labile olefins an opportunity to desorb, making room for more sulfur on the surface of the Raney nickel. Another possible explanation is that all the highly active sites on the Raney nickel may be full and only the less reactive sites remain available so the reaction times may be longer. As the reaction slows after 60 minutes, this is sufficient amount of time to remove as much sulfur as possible from the

FCC gasoline used in this study. It is apparent that additional work needs to be done in order to look at the reaction kinetics.

4.4.2 Effect of Temperature on the Removal of Sulfur

The temperature runs indicated that the reaction rate is higher at higher temperatures. This is due to temperatures relation to the rate laws. Interestingly, even at 5 ^{0}C, it is seen that 75 % of the sulfur is removed after 30 minutes. There was very little difference in the amount of sulfur removed up to 30 ^{0}C. However, above 30 ^{0}C there was a large difference in the amount of sulfur removed after 30 minutes.

However, the Student's T-test confirmed that there were only significant differences in the sulfur concentrations at temperatures higher than 30 ^{0}C. Therefore, heating did not make a significant difference in the removal of sulfur using Raney nickel unless the samples were heated to above 30 ^{0}C. By increasing temperature the bonds in thiophene may be more easily broken or the desorption of the products off the Raney nickel surface may occur at a faster rate. These are some possible explanations as to why a greater rate of sulfur removal occurs at higher temperatures.

4.4.3 Effect of Sequential Addition on the Removal of Sulfur

The sequential use of Raney nickel was found to remove a total of 97 % of the sulfur from FCC gasoline. This method seems to be more effective at removing sulfur than most of the other experiments, except for the sample at 50 ^{0}C. The sample at 50 ^{0}C showed over 99 % removal of sulfur. The 97 % reduction seen during the sequential addition is due to the amount of Raney nickel being used. This method uses double the quantity of Raney nickel, more than in other trials, and a 60 minute reaction time was used. This method is very effective because after the first 30 minutes a new batch of Raney nickel is added. This new batch of Raney nickel is not poisoned by the sulfur or olefins as the previous batch thus allowing more sulfur to be adsorbed on the surface. In addition, there is the maximum number of active sites available with a fresh batch of Raney nickel. Therefore, by performing a sequential addition of Raney nickel, the spent Raney nickel is removed and fresh Raney nickel is added, allowing for more sulfur to be removed in the 60 minute period than if a single batch of Raney nickel were used.

4.4.4 Hydrocarbon Components Analysis

The hydrocarbon components analysis showed that there is a small change in the FCC gasoline composition due to its reaction with Raney nickel. The reaction results in an increase in the percent volume of olefins and a decrease in the percent volume of all other components. Olefins have double bonds and are considered good for fossil fuels as they contribute to the octane number. The increase in olefin content may not actually be an increase. The analysis shows each of the components as a percentage of the volume, therefore the resulting increase in olefins may be due to a decrease in the rest of the components. The decrease in the rest of the components may be through evaporation or conversion of the sulfur containing compounds into other such hydrocarbon components. It is also possible that sulfur is being removed from aromatics to produce some of the increase in olefin concentration. This could be due to the cleaving of the sulfur-carbon bond in the thiophene resulting in the breakage of the ring, forming a C5 olefin. There is definitely a need for more research to determine the exact effects these changes will have on the end products.

4.4.5 Recovery of Nickel for Possible Re-Use

The production of hydrogen sulfide when the spent Raney nickel is reacted with hydrochloric acid suggests that NiS is indeed formed during the reaction of FCC gasoline with Raney nickel. Since hydrochloric acid is effective at liberating the sulfur from nickel in the form of hydrogen sulfide, this is a possible recovery method for the nickel. As the sulfur is removed in the form of hydrogen sulfide, the nickel goes partially into solution as nickel II chloride. An example of this reaction can be seen in reaction 4.5. Once the nickel is in solution, it may be possible to use an electroplating method to retrieve pure nickel.

$$NiS_{(s)} + 2HCl_{(aq)} \rightarrow NiCl_{2(aq)} + H_2S_{(g)} \qquad (4.5)$$

Another possible method for the recovery of nickel is through nickel roasting. As we know that sulfur is present in the spent Raney nickel, it is possible to remove it as SO_2. When the spent Raney nickel was heated to 800 ^{0}C the components of the spent Raney nickel were oxidized. Oxidation causes the sulfur to form SO_2 and the nickel to partially convert into NiO. The formation of nickel oxide can be seen in the change from a black colour to a green colour. Also the XRD diffraction pattern shows the sample contains only nickel oxide all other components are less than 1 wt % as they are not seen in the diffraction pattern. An example of the reaction can be seen in reaction 4.6, which may also explain the increase in weight once roasted. As all the nickel may not be in the form of nickel sulfide, some may still be in the form of Raney nickel which also oxidizes during the roasting process. Therefore, this may also be another option for nickel recovery. There were conflicting results obtained as small increases in the mass do not fit with the full conversion of the spent Raney nickel into NiO, even though the XRD pattern shows only nickel oxide in the roasted samples. Fouilloux

(1983) reports that some authors believe there is hydride formation on Raney nickel, however XRD data was not consistent with this theory. If the spent Raney nickel was hydrated it may explains the small mass difference. Further research will be needed to determine the exact course of the reaction.

$$NiS_{(s)} + Ni - H_{2Raney} + \frac{3}{2}O_2 \xrightarrow{800^0C} 2NiO_{(s)} + SO_{2(g)} + H_2O_{(g)} \qquad (4.6)$$

4.5 Conclusions

This study demonstrates that Raney nickel is effective at removing sulfur compounds from FCC gasoline. A variety of reaction times and temperatures were attempted which showed that a variety of amounts of these compounds could be removed. Therefore, the amount of sulfur, which needs to be removed from a FCC gasoline stream, will help determine the most appropriate method to be employed. For example, if only 80 % of the sulfur needs to be removed, then allowing the reaction to occur for 90 minutes at 20 ^{0}C is sufficient. However, if greater than 90 % removal is needed, then the samples should be heated to 40 or 50 ^{0}C and allowed to react for 30 minutes. Over 90 % removal of sulfur can also be achieved by sequential use of fresh Raney nickel. However, the latter, even though highly effective, is not recommended as the extra amounts of Raney nickel required will most likely make the process prohibitively expensive. All these processes cause an apparent increase in the olefin volume, and we have no plausible explanation for this. This may affect the end products or gasoline requirements so further research is needed.

The experiments to determine if the nickel can be recovered from the spent Raney nickel were successful. Both the method using hydrochloric acid and the roasting method removed the sulfur from the spent Raney nickel producing either H_2S or SO_2, respectively.

Therefore, these are both viable options for the recovery of nickel, which would then need to be further processed into Ni-Al.

Future studies could be performed on a larger scale with a detailed economic analysis to determine if the method is indeed feasible for larger scale operations. The tests involving the recovery of nickel showed that Raney nickel may not be saturated at this point. Perhaps further research into the amount of gasoline, which can cause 1.0 gram of Raney nickel to be saturated with sulfur, may be useful for economic determinations. Finally, the full impact of using Raney nickel on the chemical changes it imparts on FCC gasoline should be further investigated to determine, for example, if the octane value of the fuel is changed and whether other regulations and requirements are still being met.

4.6 Literature Cited

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Chapter 5: Conclusion

The objectives of this research project were to first find a solvent or compound that would specifically target sulfur compounds within FCC gasoline, second to reduce sulfur concentrations as much as possible with a goal of 30 (ppmw), third to reduce the sulfur concentrations without making any major changes to the composition of the FCC gasoline and fourth to determine if the reactants could be recycled.

The first objective was investigated through an experimental approach in chapters 2 and 3. Chapter 2 identified a variety of solvents, acids, bases and metals that were unsuccessful at causing a reduction in the sulfur concentration of the FCC gasoline. Through these experiments it was determined that a strong molecular interaction or reaction was necessary to remove the less reactive sulfur compounds, such as dibenzothiophenes. There is room for more research involving the use of solvents. Future research could involve investigating the use of secondary solvents or other extraction methods.

Chapter 3 investigated Raney nickel, which is commonly used as a hydrogenation catalyst and has been shown to remove sulfur in a variety of analytical methods. These experiments showed that Raney nickel was effective at removing sulfur-containing compounds from FCC gasoline. The effectiveness of Raney nickel was determined to be dependent on the activation temperature, sodium hydroxide concentration and the amount of Ni-Al alloy. Therefore, the most effective form of Raney nickel was determined to result from an activation method using an 80 ^{0}C activation temperature, 3.0 grams of Ni-Al alloy, and a 60 mL 20 % sodium hydroxide solution.

The second objective to reduce the sulfur concentration was investigated in chapter 4. The experiments within chapter 4 involved using the activated Raney nickel at a variety of reaction times and temperatures to determine the maximum reduction of sulfur-containing compounds. These experiments showed that the sulfur concentration in FCC gasoline could be reduced to 40 ppmw simply by allowing the reaction to proceed for 90 minutes. Whereas sulfur concentrations can be reduced to less than 20 ppmw if the reaction mixture is heated to temperatures above 40 ^{0}C as shown in Figure 4.2. Therefore, a goal of less than 30 ppmw of sulfur in FCC gasoline is possible using Raney nickel. In fact, concentrations below 10 ppmw can be achieved if the reaction is heated to 50 ^{0}C.

The third objective was also briefly investigated in chapter 4. It was determined through hydrocarbon analysis that there was a higher olefin concentration as seen in Table 4.1 and Table 4.2 after treatment with Raney nickel. This higher olefin concentration may have an effect on the end products, as olefins are regulated in fossil fuels. The decrease in aromatics found will cause a decrease in the octane number. The significance of this increase is not known and further research is necessary to determine exactly why only the C_5 olefins appeared to increase.

The fourth objective was investigated in chapter 4, determining that it is possible to recover the nickel from the spent Raney nickel. Several potential methods for the recover of nickel are possible. Spent Raney nickel can be reacted with hydrochloric acid to produce H_2S and a nickel chloride solution. This nickel chloride solution can then be further separated through an electroplating process. In addition, a nickel roasting method could also be used to recover the nickel in the form of nickel oxide. This process involves heating the spent Raney nickel to temperatures of approximately 800 ^{0}C in order to produce SO_2. Therefore, either one of these options could be a feasible method for retrieving the nickel from the spent Raney nickel.

Although this thesis gives a good starting point there is still much research needed on Raney nickel to determine if it is a viable alternative to hydrotreating. Although the nickel can be recovered from the spent Raney nickel, it will still need to be converted back into Ni-Al alloy in order to be reused. Therefore, further research is needed into the exact process for recovery and the cost of this process. Future research is also necessary on a larger scale to determine the economic feasibility of using Raney nickel in sulfur removal on refinery scales. In addition, extensive research will be needed to determine the exact chemical impacts on the FCC gasoline through the reaction with Raney nickel. This should include the effects on the octane number, density, and olefin concentrations.

This research will contribute to finding a possible alternative to hydrotreating that is more cost effective and potentially more environmentally friendly. The lower levels of sulfur resulting from the new method will reduce the health problems associated with sulfur dioxide and the environmental problems associated with acid rain. The alternative method will also give the oil and gas sector another way to meet Canada's stricter regulations by reducing sulfur levels in FCC gasoline.