EFFECT OF THE SELECTIVE REMOVAL OF NON-BASIC NITROGEN COMPOUNDS ON THE HYDROTREATMENT OF LIGHT GAS OIL

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ABSTRACT

Nitrogen compounds are strong inhibitors of catalyst activity in downstream chemical processes. Two distinct types of nitrogen compounds are present in light gas oils: basic and non-basic. Basic nitrogen compounds are generally considered to have stronger inhibitory effects on hydrotreating; however, non-basic nitrogen compounds are known to undergo inhibition reactions that can be generated during the hydrogenation process. This can cause the formation of basic nitrogen compounds, which are challenging to hydrotreat. Non-basic nitrogen compounds have also been proven to hinder further hydrodesulfurization due to competitive adsorption on the catalyst active sites during hydrotreating. With more stringent environmental laws regarding allowable sulfur limits, it is important to find ways to decrease the amount of sulfur, nitrogen and aromatics contents even further, in hydrotreating products.

In this thesis, the effect of the selective removal of non-basic nitrogen compounds on hydrotreating was studied. An absorbent material consisting of three basic components, namely, a polymer support, poly (glycidyl methacrylate-co-ethylene glycol methacrylate) (PGMA-co-EDGMA), a π-acceptor moiety (2, 4, 5, 7-tetranitroflorenone, TENF) and a linker, three-(diaminopropane, DAP (3)), was synthesized to create a PGMA-DAP(3)-TENF polymer. The polymer was used to selectively target non-basic nitrogen compounds from light gas oil through a mechanism known as charge transfer complex. The resulting light gas oil was referred to as the pretreated feed. To measure the effect of selective removal of non-basic nitrogen compounds on hydrotreating, the pretreated feed was further hydrotreated and the extent of hydrodesulfurization, hydrodenitrogenation and hydrodearomatization was measured. Hydrotreating experiments were executed in a trickle-bed reactor using a NiMo/γAl$_2$O$_3$ commercial catalyst. These measurements were compared with results from the untreated feed. Any improvement before and after the

hydrotreatment of the pretreated feed was associated with the removal of non-basic nitrogen compounds.

The first phase of this thesis involved the synthesis, adsorption and regeneration studies of the PGMA-DAP(3)-TENF polymer. Adsorption studies were carried out using a bulk mass quantity of the polymer. The effectiveness of the polymer on a bulk scale was measured and compared to a batch scale. Regeneration studies were carried out to determine if the polymer was reusable. Characterization techniques including BET and FTIR analysis were performed on each polymer, before and after adsorption and regeneration studies to determine any physical and/or chemical changes to the polymer. The second phase of this thesis focused on the hydrotreatment of the pretreated and untreated feeds to measure the effectiveness of the polymer. Statistical significance of selectively removing non-basic nitrogen compounds was also examined after hydrotreatment studies. Results from this thesis show that there was an overall improvement in nitrogen, sulfur and aromatics removal after pretreatment. The PGMA-DAP(3)-TENF polymer selectively removed 24.9% of non-basic nitrogen compounds in the untreated feed, which led to a 18.7%, 8.3% and 9.4% decrease in the total nitrogen, sulfur and aromatics content respectively, after hydrotreatment. Based on this result, pretreatment of light gas oil can serve as a useful industrial application in reducing impurities in petroleum product streams.

ACKNOWLEDGEMENT

DEDICATION

This work is dedicated in memory of my Dad

Dr. Amos Oluwafemi Olomola.

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LIST OF EQUATIONS

NOMENCLATURE

Al	Aluminum
Al_2O_3	Aluminum Oxide
BET	Brunauer-Emmett-Teller
BN	Basic Nitrogen
BT	Benzothiophenes
CoMo	Cobalt Molybdenum
DAP	Diaminopropane
DBT	Dibenzothiophene
DDS	Direct desulphurization
DMDBT	Dimethyldibenzothiophene
EDGMA	Ethylene Glycol Dimethacrylate
FTIR	Fourier Transform Infrared Spectroscopy
G/O	Gas to Oil Ratio
GMA	Glycidyl Methacrylate
HC	Hydrocarbon
HDN	Hydrodenitrogenation
HDS	Hydrodesulfurization
HDA	Hydrodearomatization
HDM	Hydrodemetallization
HOMO	Highest Occupied Molecular Orbital

HGO	Heavy Gas Oil
HYD	Hydrogenation
IBP	Initial Boiling Point
LGO	Light Gas Oil
LSHV	Liquid Hourly Space Velocity
Me	Methyl
Mo	Molybdenum
MoO_3	Molybdenum Trioxide
NBN	Non-basic Nitrogen
NiMo	Nickel Molybdenum
NiW	Nickel Tungsten
NMR	Nuclear Magnetic Resonance
N/S	Nitrogen/Sulfur
PGMA	Poly (glycidyl methacrylate)
PGMA-(DAP (3)) -TENF	Poly (Glycidyl Methacrylate) -Diaminopropane-Tetranitrofluorenone
SPSS	Statistics Package for Social Science
TENF	Tetranitrofluorenone
VDU	Vacuum Distillation Unit
VGO	Vacuum Gas Oil

CHAPTER 1

INTRODUCTION

1.1 Research Background

Over the years, there has been a steady increase in demand for alternative oil exploration and production. This is due to a variety of reasons, including a steady decline in conventional oil reserves and more stringent environmental laws and regulations (Environment Canada, 2006). Conventional oil is usually in liquid form and can flow freely without heat or further chemical dilution. Unconventional oil, on the other hand, often requires further chemical processes to make it flow (Mai et al., 2006). Unconventional oil products such as bitumen-derived light and heavy gas oils have higher levels of sulfur and nitrogen compounds in comparison to conventional oil. This is shown in Table 1.1. Nitrogen compounds have been proven to act as major inhibitors in the hydrotreating process because when high levels of hydrodesulfurization (HDS) are achieved, nitrogen compounds progressively inhibit the HDS process by competitive adsorption (Macaud et al., 2004).

Table 1.1: Nitrogen and sulfur content in conventional crude oil, heavy and light gas oil (Martinez, 1995, Rizwan et al., 2013, Chitanda et al., 2015, and Beychok, 2011).

	Typical Conventional oil	Light Gas oil	Heavy Gas oil
Boiling range (°C)	300-440	200-450	480-900
Density (g/cm^3)	0.75	0.90	0.99
Sulfur (ppm)	5000	28500	40370
Nitrogen (ppm)	900	1500	3000

There are two distinct kinds of nitrogen compounds found in bitumen-derived gas oil feeds: basic nitrogen (0.11 wt. %) and non-basic nitrogen (0.22 wt. %). Basic nitrogen (BN) compounds are distinguished from non-basic nitrogen (NBN) compounds by the location of the nitrogen atoms

and the lone pair of electrons. For basic nitrogen compounds, the lone pair of electrons is not delocalized in the structure of the ring, making it electron deficient. This renders the nitrogen atom to be an electron acceptor. On the other hand, non-basic nitrogen compounds contain a lone pair that is delocalized in the ring (Bej et al., 2001). Figure 1.1 shows examples of basic and non-basic nitrogen compounds found in petroleum products (Girgis and Gates, 1991).

<u>Basic Nitrogen Compounds</u>
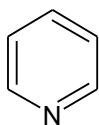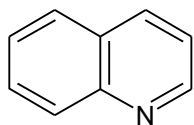
Pyridine   Quinoline   Acridine
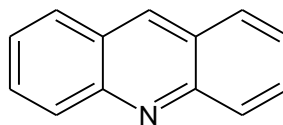
<u>Non-basic Nitrogen Compounds</u>
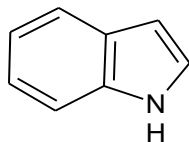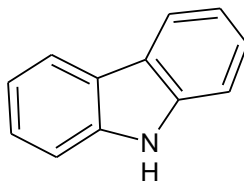
Indole   Carbazole

Figure 1.1: Basic and non-basic nitrogen compounds found in petroleum distillates (Girgis and Gates, 1991).

Basic nitrogen compounds have been established to be stronger HDS inhibitors than non-basic nitrogen compounds (Gutberlet and Bertolacini, 1983), however, non-basic compounds also pose a major threat to the HDS process because they possess inhibition reactions that can be generated during hydrotreating, which causes the formation of BN compounds (Laredo et al., 2003). A study by Sano et al. (2004) also proves that the inhibiting effect of NBN compounds on the hydrodenitrogenation (HDN) and HDS process is comparable to that of the BN compounds

because during hydrotreating, the nitrogen compounds competitively adsorb on catalyst active sites, causing loss of catalyst activity. Studies by Laredo et al. (2003) also further demonstrated that the adsorption of nitrogen in the catalyst active sites is established early in the process and does not change throughout the process. This indicates that the inhibiting performance of nitrogen is as a result of the initial strong adsorption that is experienced due to the presence of nitrogen compounds, occurring at the onset of hydrotreatment. Hence, prior removal of NBN compounds would greatly reduce the initial strong adsorption encountered on the active catalyst sites as well as limit the decline in HDS that is observed due to the formation of BN compounds during hydrotreating reactions (Laredo et al., 2003).

The pretreatment process involves the use of a synthesized polymer, which is based on a selective charge transfer complex (CTC) formation mechanism (Milenkovic et al., 1999). CTC is a chemistry-based mechanism which selectively targets and removes NBN compounds in light gas oils. Prior research by Chitanda et al. (2015) studied the effect of linker length on the selective removal of non-basic nitrogen compounds. Amongst the polymers studied, PGMA-DAP(3)-TENF polymer was found to have the highest nitrogen adsorption compared to the other polymers (Chitanda et al., 2015). To study the effects of selectively removing NBN compounds on hydrotreating, light gas oil was adsorbed with bulk polymer mass of PGMA-DAP(3)-TENF polymer. Adsorption studies was carried out in two sections: a batch scale and a pilot scale. The batch scale adsorption study was performed using a smaller ratio of polymer (1g) with light gas oil (4g). For the pilot scale, the adsorption study was scaled up using a larger polymer mass with light gas oil. For both studies, a polymer to light gas oil ratio of 1:4 was maintained. After adsorption, the polymer was separated from the light gas oil and regenerated. The polymer was

regenerated three times to account for the large quantity of light gas oil needed for the hydrotreatment study.

Hydrotreating is a major industrial application in oil and gas processing, as it is a crucial process required to reduce high concentrations of nitrogen, sulfur and aromatics compounds in feedstock, in order to meet quality and environmental specifications. Hydrotreating was therefore utilized in this study to determine catalyst activity through hydrodenitrogenation (HDN), hydrodesulfurization (HDS), and hydrodearomatization (HDA). To create a baseline for the purpose of monitoring any changes attributed to the selective removal of non-basic nitrogen compounds, the following four feeds were used to compare HDN, HDS and HDA activity before and after pretreatment:

1. Untreated feed, i.e. untreated light gas oil feed

2. Pretreated feed, i.e. feed that has been treated with PGMA-DAP(3)-TENF polymer to selectively remove non-basic nitrogen compounds.

To monitor the effects of the selective removal of NBN compounds on hydrotreating, the untreated and pretreated feeds were hydrotreated to create two hydrotreated feeds namely:

3. Hydrotreated feed, i.e. hydrotreated light gas oil feed

4. Hydrotreated-pretreated feed, i.e. feed that has been treated with PGMA-DAP(3)-TENF polymer to selectively remove non-basic nitrogen compounds and then hydrotreated.

Measuring the nitrogen, sulfur and aromatics content of both the hydrotreated feed and hydrotreated-pretreated feed would determine the effects of the selective removal of non-basic nitrogen compounds on the hydrotreatment of light gas oil.

The main purpose of this research was to study the effects of the selective removal of NBN compounds on the hydrotreatment of light gas oils. The untreated and pretreated feed were

hydrotreated in a trickle-bed reactor and the nitrogen, sulfur and aromatics contents were measured before and after pretreatment. Regeneration studies were carried out on the used polymer to determine polymer reusability. For the purpose of comparison, the untreated and pretreated feeds were hydrotreated at similar process conditions. It is expected that prior removal of non-basic nitrogen compounds would aid HDN, HDS and HDA.

1.2 Knowledge Gaps

Non-basic nitrogen compounds have been proven to inhibit catalyst activity; however, there are no known studies on the influence of the selective removal of non-basic nitrogen compounds on the hydrotreatment of light gas oil. Although several pretreatment methods have been used in the literature to selectively remove NBN compounds, there are no studies on the effects of using a PGMA-DAP(3)-TENF functionalized polymer to selectively remove non-basic nitrogen compounds before hydrotreatment. Based on the literature, the knowledge gaps associated with my research are as follows:

1) There are no known studies on the reusability and influence of bulk polymer mass on nitrogen, sulfur and aromatics adsorption on light gas oil. Although there have been adsorption and regeneration studies on PGMA-DAP(3)-TENF polymer, these studies have been performed on a batch scale.

2) There are no known studies showing the effects of the selective removal of non-basic nitrogen compounds on the hydrotreatment of light gas oil, particularly the extent of sulfur removal, while varying process conditions.

1.3 Hypothesis

The following hypotheses are made based on the above knowledge gaps.

1) Since non-basic nitrogen compounds have been reported to hinder further HDS during hydrotreating, the prior selective removal of non-basic nitrogen compounds with the use of a functionalized polymer would promote HDS. It is also hypothesized that an increase in HDS would lead to an increase in HDN and HDA as well.

2) It is expected that bulk polymer mass is reusable and would positively influence adsorption studies, provided similar conditions are followed from a batch scale to a pilot scale.

1.4 Research Objective

The primary focus of this research was to examine the effects of the selective removal of non-basic nitrogen compounds on the hydrotreatment of Athabasca-derived light gas oil. To be able to keep track of my progress, my research was divided into the following phases:

- **Phase 1**: *Synthesis, adsorption and regeneration studies on PGMA-DAP(3)-TENF polymer*

This phase of the project involved the synthesis, adsorption and regeneration of the PGMA-DAP(3)-TENF polymer. Adsorption studies had to be carried out on a pilot scale to account for the necessary amount needed for hydrotreating. The polymer was adsorbed with light gas oil over a period of time and separated by suction. The treated oil was referred to as the pretreated feed. The pretreated feed served as a baseline for monitoring the amount of sulfur, nitrogen and aromatic contents before hydrotreating. To be able to account for the large amount of light gas oil needed for hydrotreating, the polymer had to be regenerated three times. To achieve this, after the initial adsorption, the reusable polymer material was separated and dried at room temperature for 48 hours. The dried polymer was regenerated using a soxhlet extractor apparatus. The regenerated

particles were then dried at room temperature for 48 hours to have them ready to be re-used for adsorption studies.

- **Phase 2**: *Study on the effect of the selective removal of non-basic nitrogen compounds on the hydrotreatment of light gas oil while varying process conditions*

Hydrotreatment studies were carried out both on the untreated feed and pretreated feed to determine nitrogen, sulfur and aromatics removal. Hydrotreating experiments were performed at a temperature range of 350 to 370 °C, pressure range of 8.27 to 9.65 MPa and LHSV range of 1 to 2 hr^{-1} using commercially available NiMo/γ-Al$_2$O$_3$ tri lobe catalyst. Temperature, pressure and LHSV were varied to demonstrate the effect of changing process parameters before and after pretreatment. Hydrogen flow rate was sustained at 100 mL/min. The samples were run over 72 hours and samples were collected over a 12-hour interval. The sample products were then stripped with low-pressure nitrogen to remove any remaining traces of dissolved ammonia and hydrogen sulfide before being sent to the lab for analysis. The statistical significance of the pretreatment of light gas oil by selectively removing NBN compounds on hydrotreating was investigated by comparing results between the untreated and pretreated feeds at similar process conditions. The Statistics Package for Social Science (SPSS) software was used to provide comparative analysis before and after pretreatment.

CHAPTER 2

LITERATURE REVIEW

In this chapter, overview of the hydrotreating process will be discussed as well as common chemical reactions associated with the hydrotreating process such as HDN, HDS and HDA. The different types of nitrogen compounds and their effects on hydrotreatment activity will also be discussed. General selective removal methods of non-basic nitrogen compounds will be discussed as well as details of the mechanism of the nitrogen removal process.

2.1 Energy Consumption in the World

The U.S. Energy Information Administration (EIA) reported that in 2015 alone, the world consumed over 1.9 billion barrels of oil per day. Consumption of petroleum and other forms of liquid fuels is anticipated to increase by 1.4 million barrels per day in 2016 and by 1.5 million barrels per day in 2017. The United States alone consumes at total of 7.8 billion barrels of petroleum products which amounts to an average of 19.4 million barrels per day (US Energy Information Administration, 2015). In order to supplement the ever-growing global demand for oil, alternative sources have been explored. Among these alternative sources of energy are bitumen-derived oil. Unlike conventional oil, which flows through a well without further dilution or stimulation, unconventional oil such as oil sands, is thick and consists of a mixture of bitumen hydrocarbons, which usually requires more process techniques for it to be upgraded and converted into usable products (Yui, 2008). As Figure 2.1 shows, Canada currently plays a significant part in the global oil economy as it is currently the sixth largest producer of oil, and it is recognized as having the world's third largest proven oil reserves, which mostly consists of unconventional oil

such as oil sands (US Energy Information Administration, 2016). To be able to meet the growing demand for energy, it is important to shift gears into exploring the use of non-conventional oil.

Worlds Largest Proven Oil Reserves
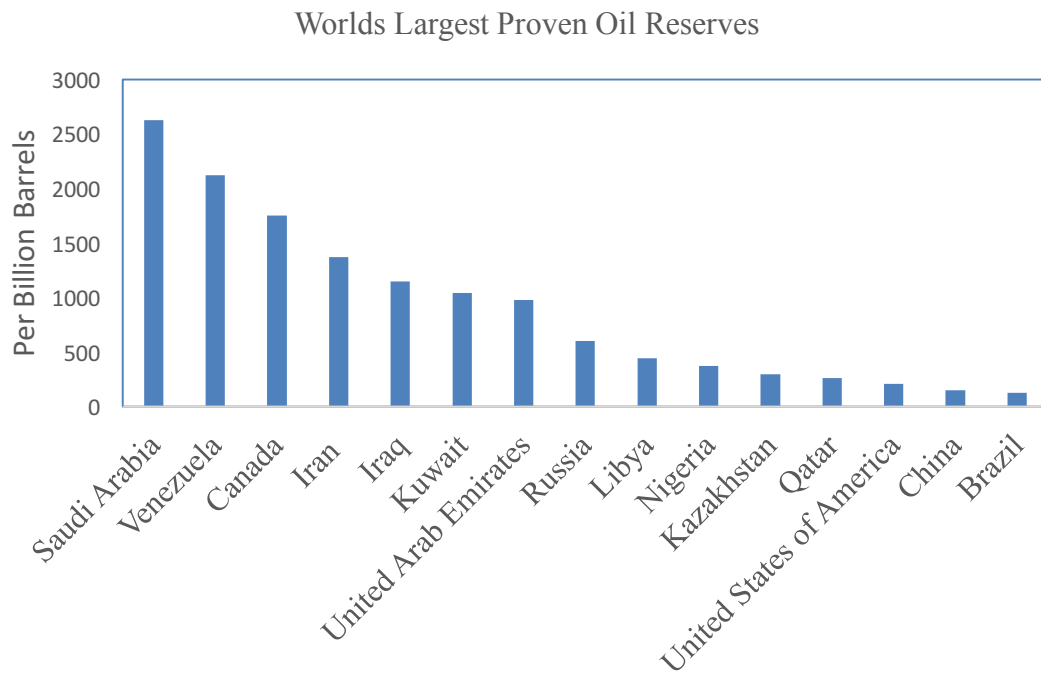
Figure 2.1: Total global oil reserves (US Energy Information Administration, 2016).

2.2 Bitumen Upgrading

Getting the oil from the ground is a complex process. There have been technological advancements over time that has enabled safe, cost effective ways to recover oil for end use. The major steps involved in oil processing are oil exploration, transportation, refining and then its availability as usable products to the market. For oil exploration, sound waves are sent into the earth and observed for changes, which are interpreted by geologists to determine the possible locations of the oil deposit (Sato et al., 1992). The use of seismic imaging has been used for over twenty years and is still the primary technology used for exploring oil. Extracting the oil uses a drilling mechanism, which enables the hydrocarbons to be pumped into various wellheads, which is then transported to the refinery for further processing.

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Oil sands are dense and very viscous sandstones consisting mostly of a mixture of sand, clay, and water, saturated with bitumen. Bitumen, which is a form of petroleum, is a solid, semi-solid or viscous hydrocarbon obtained as a residue in crude oil distillation (Gray, 1994). For oil sands and bitumen to be converted to usable products, upgrading processes has to be performed. Currently, Syncrude Limited, upgrades bitumen into a refined quality, light, low sulfur crude oil by first removing the naturally occurring light gas oil component of the bitumen before it is sent to further processing units such as the vacuum distillation unit (VDU), which removes any remaining light and heavy gas oil streams (Syncrude Canada, 2016). The light gas oil stream product is what is used throughout the course of this thesis.

Light gas oil products contain higher levels of impurities than the typical conventional oil. These impurities include sulfur, nitrogen, asphaltenes, resins and metals with particularly high sulfur and nitrogen compounds. Due to these higher levels of sulfur and nitrogen compounds, there are stringent environmental laws in place to minimize emissions (Stringham, 2006). Environmental laws over the years has become more stringent hence a need for more efficient hydrotreating processing methods. Table 2.1 shows the allowable sulfur limit by locations around the world. North America has one of the most stringent limits and laws on allowable sulfur content. According to the Environmental Protection Agency (EPA), the current allowable sulfur limit in Canada is 15 ppm.

To be in accordance with environmental rules and regulations, chemical processes such as hydrotreating is used to decrease the nitrogen, sulfur and impurities in light gas oil making it usable and environmentally safe.

Table 2.1: National diesel sulfur limits in ppm (International Council on Clean Transportation, 2014).

Year / Country	2005	2006-2009	2010	2011	2012	2013	2014	2015	2016 - 2020
Brazil	3500	2000	1800				500		
China	2000				350			50	10
European Union	50	10							
India	500		350						
Japan	50	10							
Russia	500					350		50	10
Thailand	150				50				
USA	500	15							
South Africa	3000	500							10

2.3 Hydrotreating and Hydrotreating Reactions

Hydrotreating is a chemical process that involves the elimination of contaminants, mainly sulfur, nitrogen, aromatics and metals from light gas oils, to produce a cleaner and more environmentally friendly product. The primary process involves hydrogenation in a fixed catalyst bed to improve the hydrogen/carbon (H/C) ratios while removing nitrogen, sulfur and metals. The process involves mixing hydrogen gas with the feed light gas oil which is passed in a catalyst filled reactor, at relatively high temperatures and pressures. This mixture then enters a high pressure separator for separation of the product liquid hydrocarbon from the gases, mainly hydrogen,

hydrogen sulfur and ammonia gas (Speight and Ozum, 2002). Since these impurities are detrimental to the catalyst active sites and slows down efficient hydrotreating processes, there is a need to eliminate as much nitrogen through hydrodenitrogenation i.e. the elimination of nitrogen compounds, hydrodesulfurization i.e. the elimination of sulfur compounds and hydrodearomatization i.e. the removal of aromatic compounds. Figure 2.2 shows the structures of sulfur compounds commonly found in petroleum products (Topsoe et al., 1996). Sections 2.3.1 to 2.3.3 highlights more details into the HDS, HDN and HDA reactions.

2.3.1 Hydrodenitrogenation (HDN)

Hydrodenitrogenation is a chemical industrial process used to eliminate nitrogen compounds from petroleum fractions. Nitrogen compounds are present at relatively low levels compared to sulfur compounds, yet they are unfavorable because they slow down the hydrotreating process by poisoning the active sites of catalysts during hydrotreating. Additionally, upon combustion, nitrogen compounds generate NOx, which is a pollutant and is not favorable environmentally (Topsoe et al., 1996).

During hydrotreating, the nitrogen compounds present in the light gas oil feeds are treated at high temperatures in the presence of hydrogen and a catalyst. This process replaces the nitrogen atom and leads to the emission of ammonia gas as a byproduct. This chemical reaction is shown in Equation 2.1 (Prins et al., 1997).

Hydrodenitrogenation

$$\text{"[R–N]"} + H_2 \xrightarrow[\text{300 – 450°C}]{\text{catalyst}} \text{"[R–H]"} + NH_3$$

…………….……Equation (2.1)
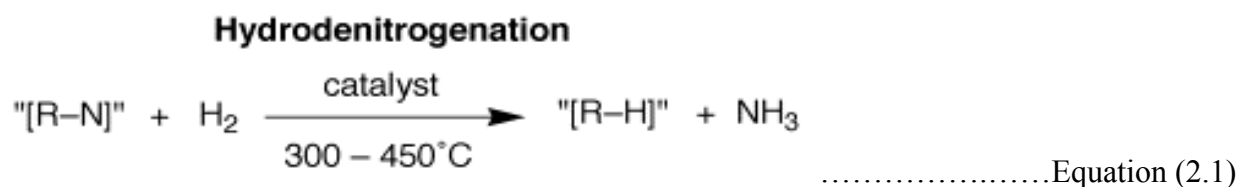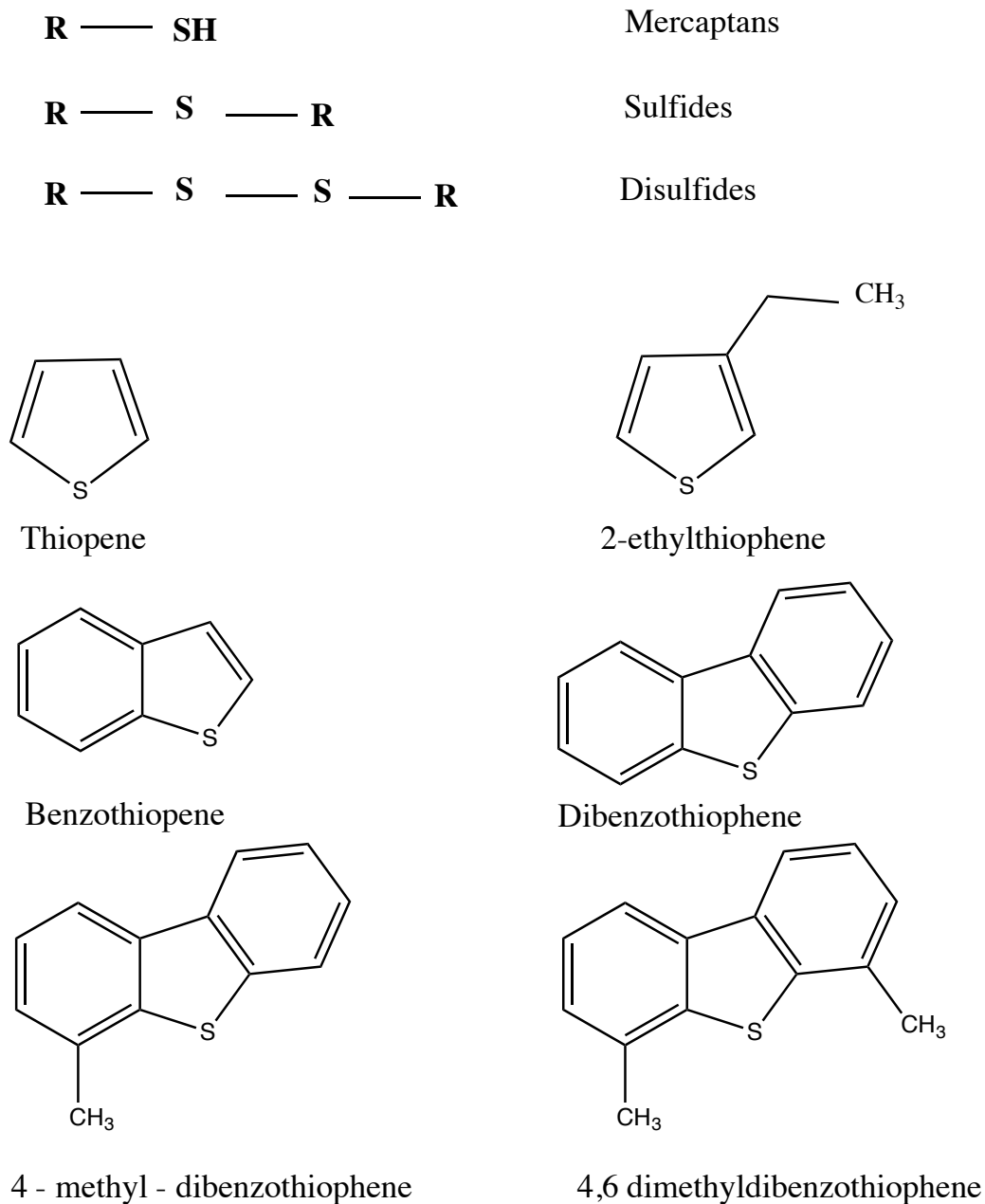
Figure 2.2: Common sulfur and nitrogen compounds found in petroleum (Topsoe et al., 1996).

Favorable hydrodenitrogenation reaction is necessary to attain a high conversion of other hydroprocessing reactions such as hydrodesulfurization and hydrodearomatization. One of the reasons for this is because nitrogen-containing compounds form a strong adsorption to catalytic active sites, which limits the hydrogenation process. This obstructs the adsorption of other process

reactants, thereby slowing the hydrotreating process (Prins et al., 1997). Hydrodenitrogenation is considered more difficult to hydrotreat than hydrodesulphurization due to the presence of the heterocyclic ring, which must be hydrogenated before the breakage of any carbon-nitrogen bond to form ammonia as a byproduct (Lu et al., 2007). Quinoline has always been a suitable model compound to use when trying to represent basic nitrogen compounds since it possesses very similar HDN reactions experienced in feedstock, making it a suitable representation of the HDN process (Prins et al., 1997). Figure 2.3 represents the reaction network of quinoline, which is an actual representation of the HDN process in feedstock.
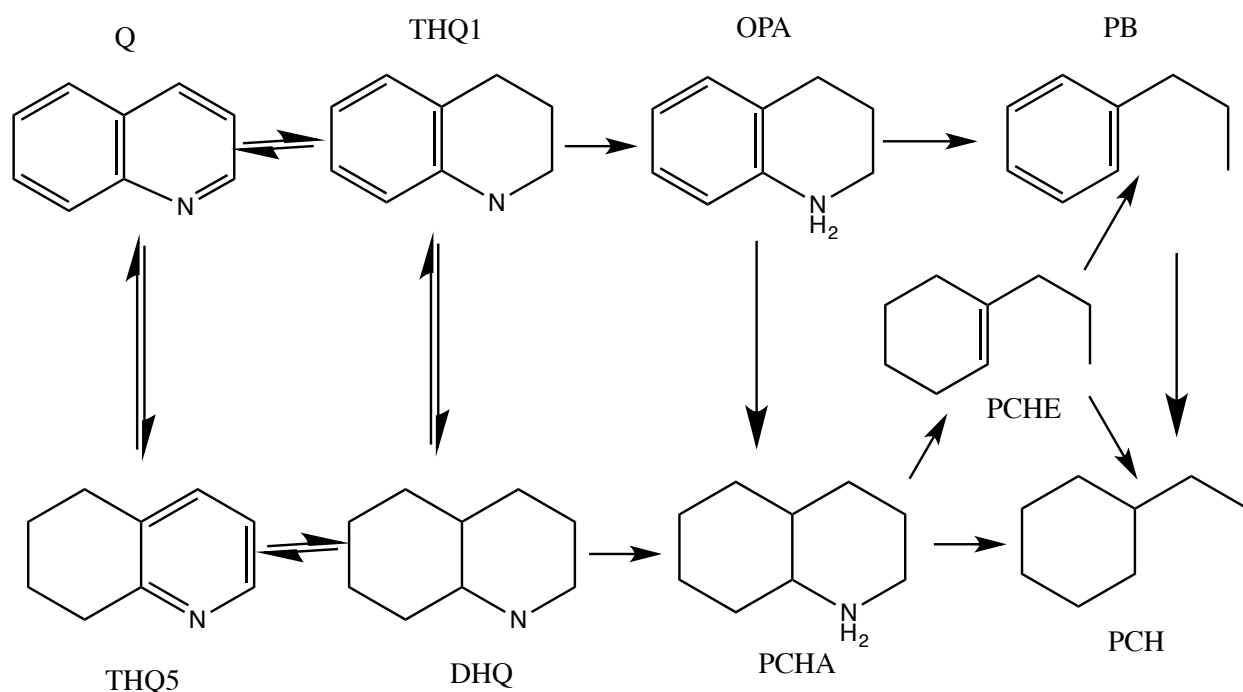
Figure 2.3: Reaction network of quinoline. Where Q = Quinoline; THQ1 = 1, 2, 3, 4-Tetrahydroquinoline; OPA = *Ortho*- propylaniline; PB = Propylbenzene; THQ5 = 5,6,7,8 Tetrahydroquinoline; DHQ = Decahydroquinoline; PCHA = 2-Propylcyclohexylamine; PCHE = Propylcyclohexene; PCH = Propylcyclohexane; (Prins et al., 1997).

As Figure 2.3 shows, there are two distinct ways of removing nitrogen compounds from quinoline. The first path requires that quinoline (Q) is hydrogenated to form 1, 2, 3, 4-

tetrahydroquinoline (THQ1), which leads to the opening of the ring to form ortho- propylaniline (OPA). The final step is the hydrogenation of OPA to form 2-propylcyclohexylamine (PCHA). It is during this final step that the nitrogen compounds are removed through the process of elimination. The second path follows a different HDN process path where quinoline is completely hydrogenated to decahydroquinoline (DHQ) that reacts with (2-Propylcyclohexylamine) to form hydrocarbons where nitrogen compounds can be separated (Prins et al., 1997). Since the goal of this research is to study the detrimental effects of non-basic nitrogen, the focus would be to understand the reaction process of non-basic nitrogen compounds in the HDN process. Figure 2.4 shows the reaction process of indole which is a common non-basic nitrogen compound.
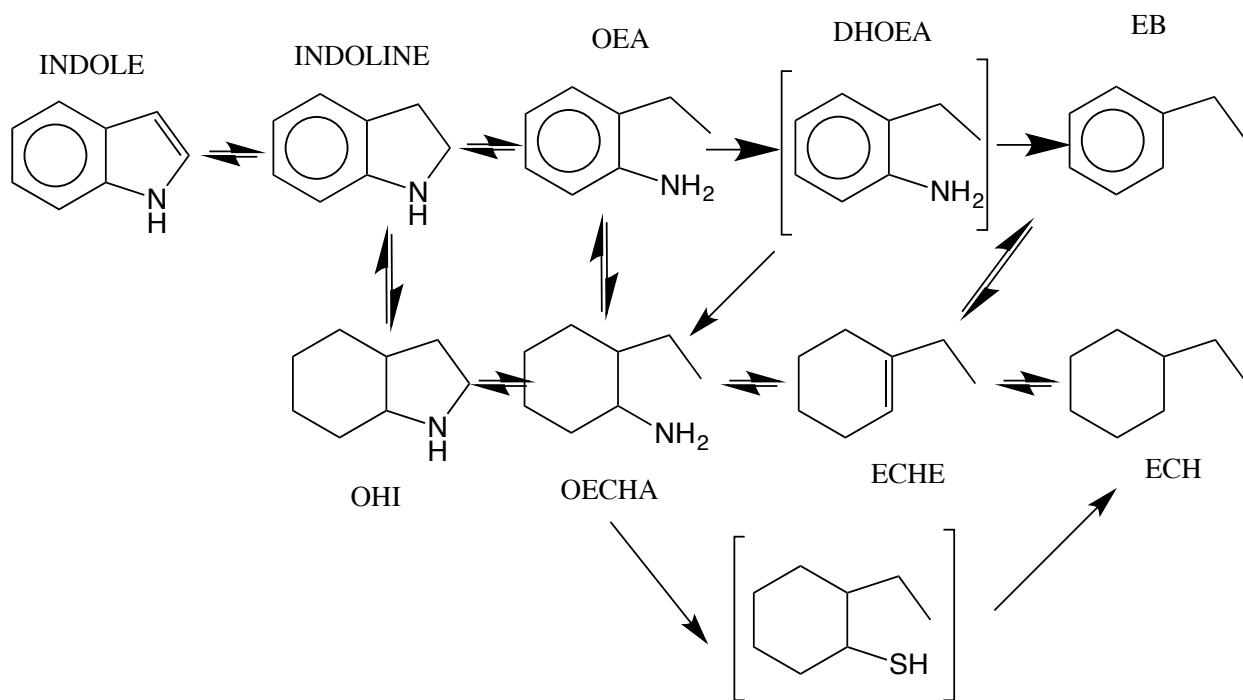
Figure 2.4: Reaction network of indole(I), where OEA = O-ethylaniline; DHOEA = Dihydro-o-ethylaniline; EB = Ethylbenzene; OHI = Octahydro-indole; OECHA = O- ethylcyclohexylamine; ECHE = Ethylcyclohexene; ECH = Ethylcyclohexane (Bunch et al., 2000).

As shown in Figure 2.4, indole is converted to indoline by a reversible hydrogenation process of the heterocyclic ring (Bunch et al., 2000). There are lots of different paths proposed for

the reaction path of indole. A study by Callant et al. (1995), projected that the reactivity of O-ethylaniline (OEA) is insignificant when combined with indole. Denitrogenation of indoline was achieved through octahydroindole (OHI), which is a transitional product of the hydrogenation of the benzene ring. Comparing the reaction pathways for both the basic (Figure 2.3) and non-basic nitrogen (Figure 2.4) pathways shows that although the reaction paths are different, both paths share a common mechanism which first involves the saturation of the ring structure containing nitrogen, then by ring opening and lastly by the elimination of nitrogen.

2.3.2 Hydrodesulfurization (HDS)

Hydrodesulfurization is a catalytic chemical process that is used to eliminate sulfur compounds from petroleum feeds. As explained in Section 2.2, there are strict environmental rules regarding sulfur limits hence a necessity for limiting sulfur compounds in petroleum products. Hydrodesulfurization helps limit by-products such as sulfur dioxide (SO_2), which is an emission released during fuel combustion (Gary, 2004). Sulfur, at low concentrations has also been proven to poison catalysts during the hydrotreatment process. The hydrodesulfurization process involves removal of sulfur by adsorption of the sulfur compounds through the structure of their aromatic rings (Girgis and Gates, 1991). Sulfur removal can occur either by direct desulfurization (DDS) of carbon-sulfur bonds or by the hydrogenation of aromatic rings. Hydrodesulfurization is a hydrogenolysis reaction which is a category of the hydrogenation reaction, which results in the breakage of the carbon - sulfur chemical bond and produces the formation of carbon-hydrogen bond. Hydrogen sulfide is emitted as a by-product as shown in Equation 2.2 (Gruia et al., 2006).

The most common sulfur compounds found in petroleum products can be divided into six types namely benzothiophenes, di-sulfides, mercaptans, sulfides, thiophenes and di-

benzothiophenes (Gruia et al., 2006). Figure 2.5 shows characteristic reaction mechanisms for organosulphur molecules during hydrotreating.

Hydrodesulfurization

$$\text{"[R–S]"} + H_2 \xrightarrow[300-450°C]{\text{catalyst}} \text{"[R–H]"} + H_2S$$

...........................Equation (2.2)

Since sulfur removal is a key application in the hydrotreating process, it is vital to comprehend the pathways by which sulfur compounds are removed. Sulfur compounds can be removed using a variety of pathways, however, the pathway of choice depends on the particular structure of the sulfur compound (Mochida and Choi, 2004). There are two likely reaction pathways for sulfur removal namely: the hydrogenation route and the hydrodesulphurization route. In the hydrodesulphurization route, the sulfur atom is eliminated from the chemical structure and directly substituted with a hydrogen atom. However, in the hydrogenation route, an aromatic ring is hydrogenated first, prior to the removal of the sulfur atom which is then replaced by a hydrogen atom. For this reason, the later mechanism weakens the aromatic ring causing weak sulfur-carbon bonds (Mochida and Choi, 2004). It is also important to note that with larger aromatics structures, desulphurization becomes even more difficult due to the increased stability of the aromatics compounds (Mochida and Choi, 2004). Since dibenzothiophenes and 4, 6-dimethyldibenzothiophene are major sulfur contributors in gas oil feedstock, both compounds can serve as good examples to show the reaction pathways of HDS. Figure 2.6 shows the HDS reaction pathway for dibenzothiophene.

Mercaptans

$$R - SH + H_2 \longrightarrow R - H + H_2S$$

Sulfides

$$R1 - S - R2 + 2H_2 \longrightarrow R1 - H + R2 - H + H_2S$$

Disulfides

$$R1 - S - S - R2 \longrightarrow R1 - H + R2 - H + 2H_2S$$

Thiophenes

$$+ 4H_2 \longrightarrow R - CH(CH3) - CH2 - CH3 + H_2S$$

Benzo-thiophenes

$$+ 3H_2 \longrightarrow \qquad + H_2S$$

Benzo-thiophenes

$$+ 2H_2 \longrightarrow \qquad + H_2S$$

Figure 2.5: Typical reactions mechanisms for organosulphur molecules in petroleum crude (Gruia et al., 2006).

For the dibenzothiophene reaction pathway, HDS occurs directly through direct desulfurization (DDS) and hydrogenation (HYD) reactions. To achieve this, biphenyl (BP) compounds were produced through the DDS pathway. Cyclohexylbenzene (CHB) and dicyclohexyl (DCH) were created through the HYD reactions after DBT was partly hydrogenated to the intermediates (Liu and Ng, 2010). For the 4, 6-dimethyldibenzothiophene reaction pathway, HDS also occurred by direct desulfurization (DDS) and hydrogenation (HYD). However, in the direct desulfurization (DDS) step, 3, 3'-dimethylbiphenyl was made.
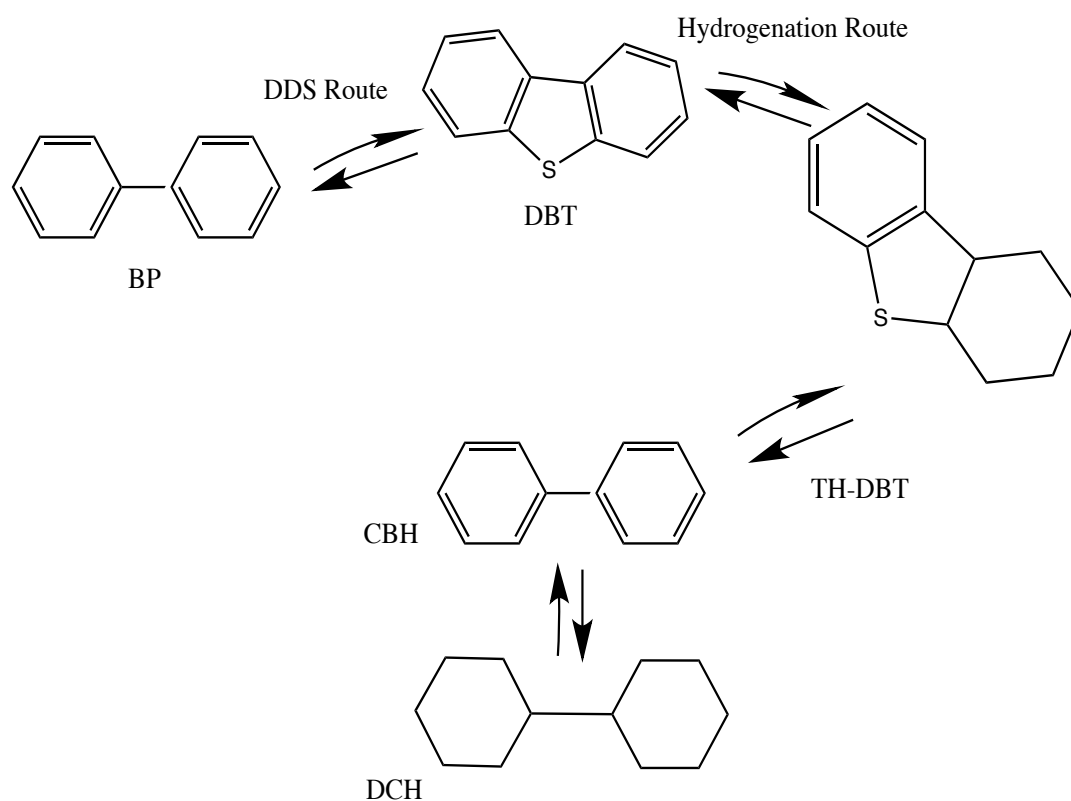
Figure 2.6: Hydrodesulfurization pathways of dibenzothiophene (Liu and Ng, 2010).
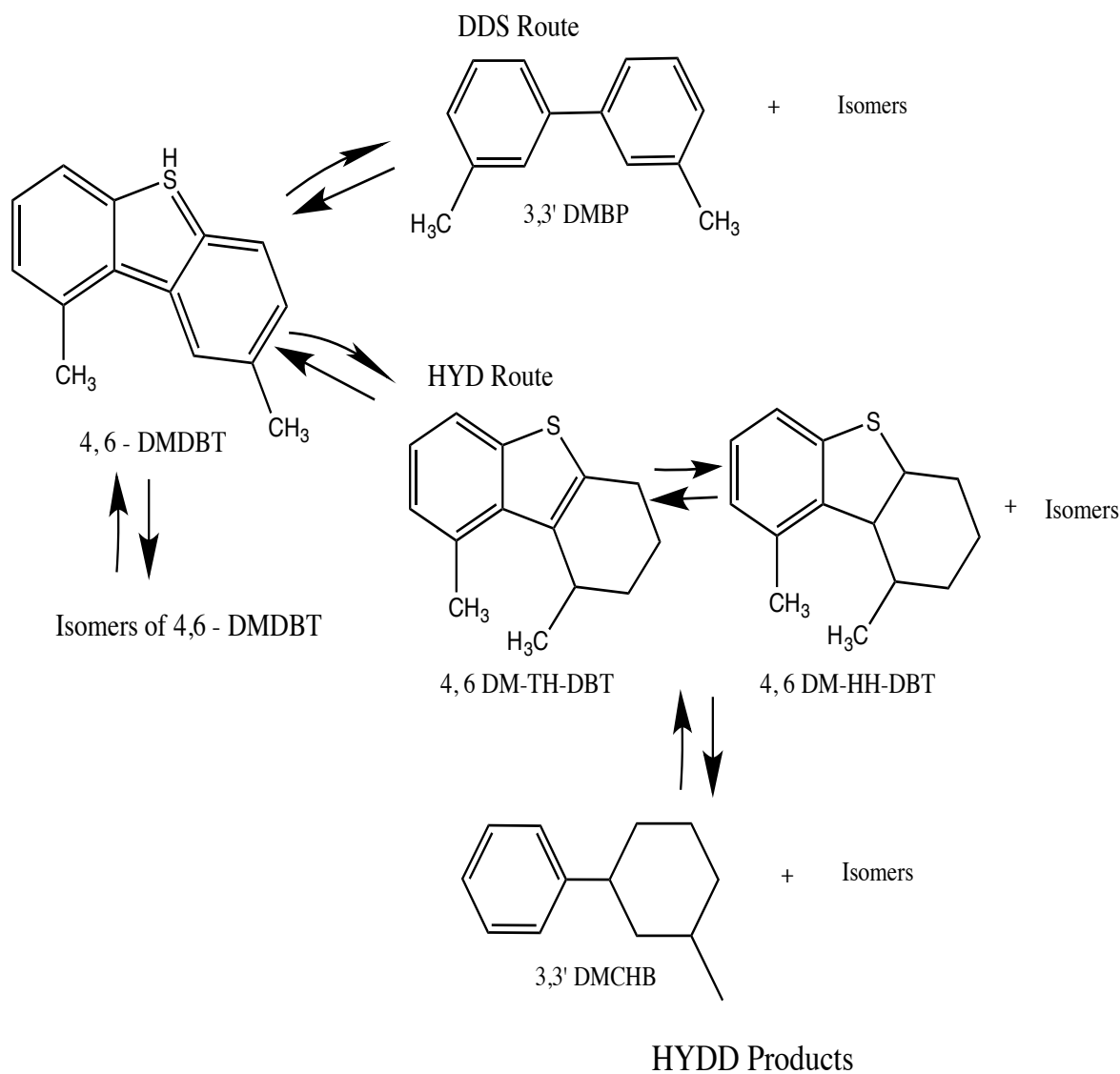
Figure 2.7: Hydrodesulfurization pathways of 4, 6-Dimethyldibenzothiophene (Liu and Ng, 2010).
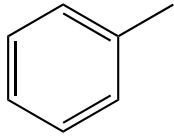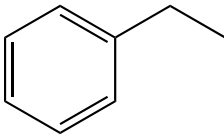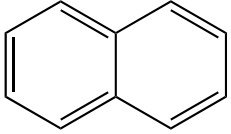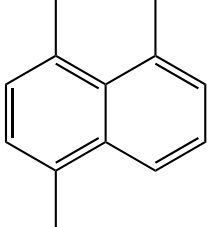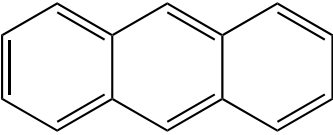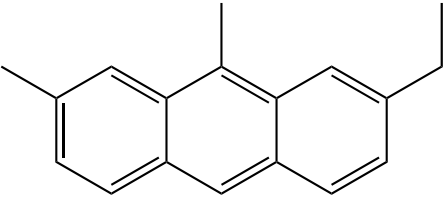
The HYD reaction pathway occurred in multiple steps. The first HYD stage yielded 4,6-dimethyl-hexahydro-DBT (4,6-DMHH-DBT) and 4,6-dimethyl-tetrahydro-DBT (4,6-DM-TH-DBT), with the desulfurization process yielding 3,3'-dimethylcyclohexylbenzene (3,3'-DMCHB) (Speight, 1999). Figure 2.7 shows the HDS reaction pathway for 4, 6-Dimethyldibenzothiophene. Although both paths are different, they both share a common mechanism for sulfur elimination.

2.3.3 Hydrodearomatization (HDA)

Compounds whose molecular configuration contains planar rings (one or more) are considered as aromatics compounds. Aromatics ring comprises of single or double bonded carbon-carbon bonds. These bonds typically share equal number of atoms around the ring to form an electron cloud. Hydrodearomatization also known as the saturation of aromatic compounds is a process where the aromatics are converted to naphthenes which is a favorable property in petroleum products. The aromatics found in gas oils are mostly present in one, two, or three ring aromatics (Wilson et al., 1985). Table 2.2 shows some of the typical aromatic species present in petroleum fractions. During the process of hydrotreating, a hydrogenation reaction occurs which convert aromatic compounds to hydroaromatics and naphthenes. The more saturated a hydrocarbon is, the more favorable the hydrogenation reaction. Figure 2.8 shows the aromatic saturation reactions among common aromatic compounds found in petroleum feeds. Reactivity of aromatics generally decrease with stability. For example, monoaromatics, which are generally very high in stability due to the placement of the benzene ring structure, are considered very unreactive (Gray, 1994). On the other hand, poly-aromatics which can contain more than 2 or 3 aromatic rings combined can undergo hydrogenation much easier than the monochromatic.

The reaction path for aromatics species containing more than one ring generally follows a hydrogenation process which is a reversible step that requires higher temperatures and pressures to maintain saturation of the aromatic rings (Stanislaus and Cooper, 1994). Naphthalene possesses very similar HDA reactions to that found in petroleum feedstock, hence making it a suitable representation of the HDA process. Figure 2.9 shows the reaction pathway for hydrogenation of naphthalene at high pressure (Albertazzi et al., 2004).

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Table 2.2: Typical structure of some aromatic compounds in petroleum distillates (Owusu-Boakye, 2005).

Monochromatics e.g alkyl benzene		
Diaromatics e.g napthalene		
Triaromatics e.g anthracene		

It is important to note that a reverse order of reactivity is used in the hydrogenation of hydrocarbons on sulfide catalysts such as the one used in the course of this thesis which is a NiMo on alumina support. However, adding an alkyl group to the present aromatic ring speeds up the hydrogenation reaction (Moreau and Geneste, 1990). Hydrodearomatization is a favorable hydrotreating process since it goes hand in hand with hydrodenitrogenation and hydrodesulfurization, as it promotes deep hydrodesulfurization and helps in ensuring diesel requirements are met.

2.4 Importance of Hydrotreating

The main reason for hydrotreating is to enable oil products with higher impurities meet the required environmental and product specifications to make them usable (Speight and Ozum, 2002).
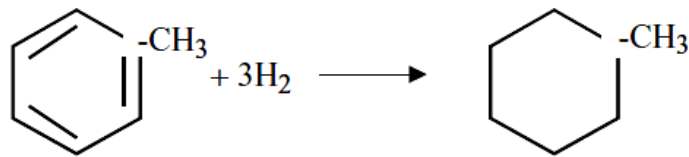
(i)   One ring - Toluene
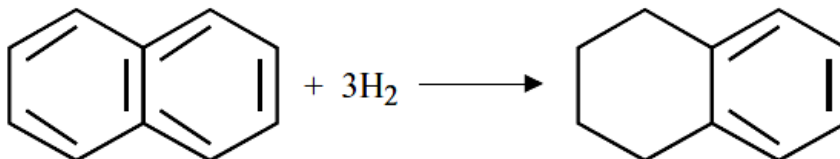
(ii)   Two ring - Naphthalene
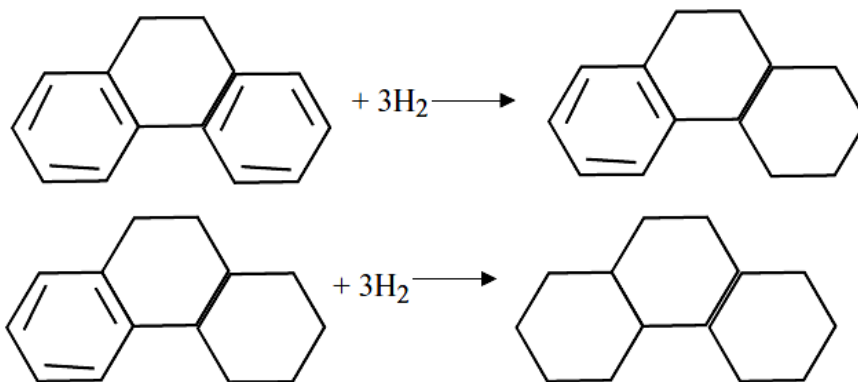
(iii)   Three ring – Phenanthrene

Figure 2.8: Aromatic Saturation of common mono and poly aromatics (Owusu-Boakye, 2005).

The hydrotreating of gas oil feedstocks such as light and heavy gas oil can contribute greatly to the decrease of coke yield which thereby leads to an increase in liquid product yield, improved feed quality, and increase in product cost due to achieved lower sulfur and metal content. Hydrotreating leads to the production of better quality fuel oil which is usable and environmentally friendly (Bhattacharyya and Talukdar, 2005).
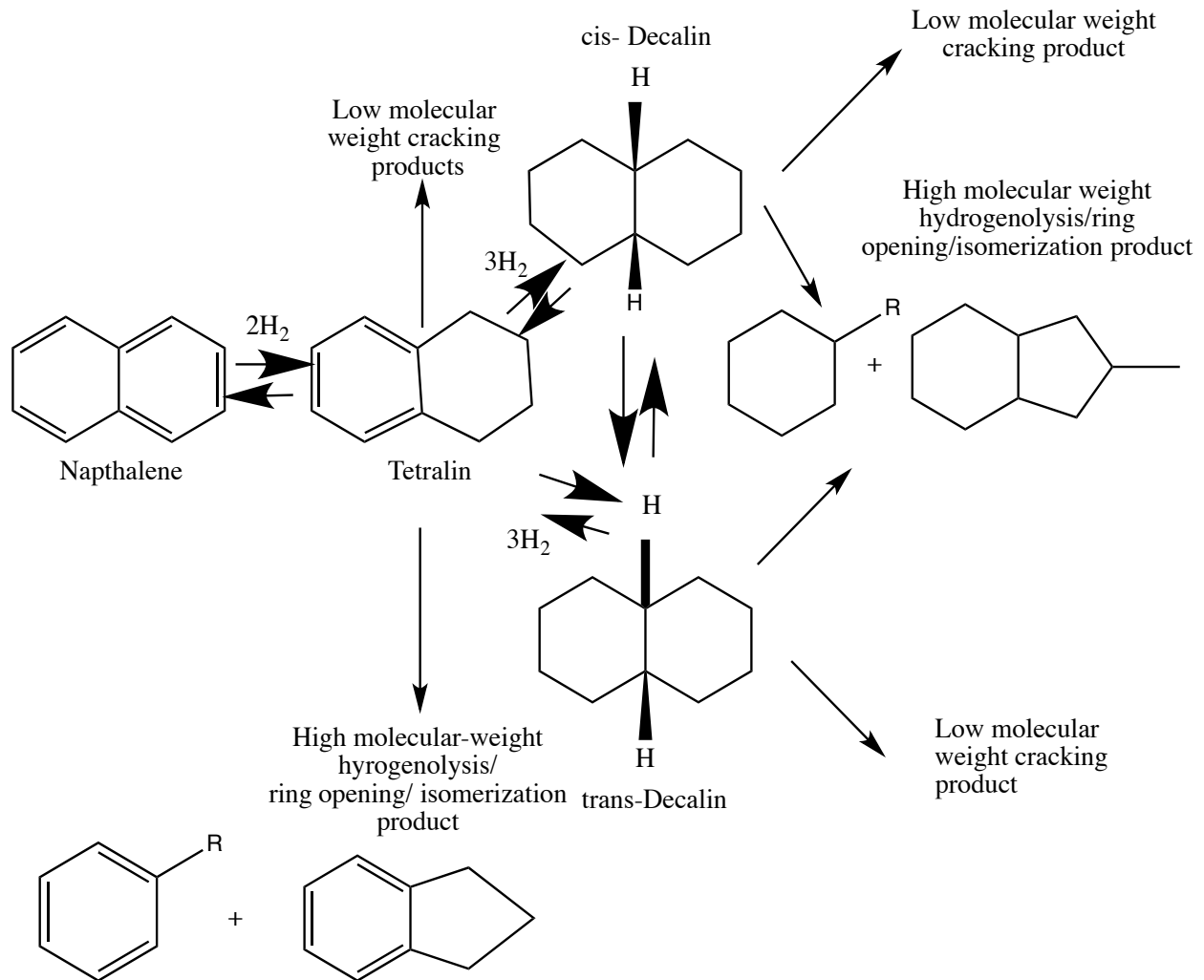
Figure 2.9: Proposed reaction pathway for hydrogenation of naphthalene at high pressures (Albertazzi et.al, 2004).

2.4.1 Effects of Process Conditions on Hydrotreating

There are different parameters that affect the hydrotreating process. Variation of these parameters can determine product quality of the petroleum product after hydrotreating. Figure 2.10 shows the common process parameters used during hydrotreating.
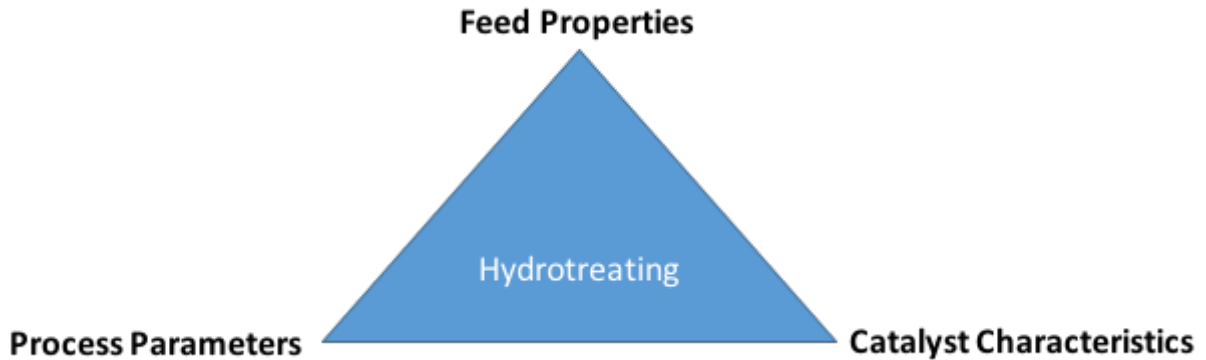
Figure 2.10: Different factors affecting hydrotreating process (Speight, 1999).

The following factors have been proven to affect the hydrotreating process:

i) Feed Properties: The process parameters used for hydrotreating greatly depends on the physical and chemical characteristics of the petroleum feed. This includes properties such as density, hydrogen carbon ratio, carbon number, boiling point and the presence of any heteroatoms or metals (Speight, 1999). Generally, an increase in carbon bonds of petroleum fractions increases the boiling points thereby making it more difficult to hydrotreat.

ii) Catalyst Characteristics: Physical and chemical characteristics of catalysts such as surface morphology, surface area and type of catalyst support affects the hydrotreating process. The type of catalyst is a major contributor to the hydrotreating process, as different catalysts are used for different hydrotreating results. Catalyst selection is based on the product specification of the petroleum product. The most common catalyst used in hydrotreating aim to achieve relatively high levels of sulfur and nitrogen conversions.

iii) Process Parameters: Process parameters for hydrotreating includes reactor specifications such as reactor kinetics and configuration, and operating process conditions variables such as temperature, pressure, hydrogen partial pressure and liquid hourly space velocity (LHSV) (Speight, 1999). These conditions are also varied based on the desired quality of the

petroleum product. The type of petroleum feed determines the kind of reactor that would be used. There are different kind of reactors used in petroleum industries such as fixed bed reactors and moving bed reactors (Ancheyta and Speight, 2007). In general, the fixed bed reactor is easier to operate, hence is the reactor of choice in the industry. In a typical fixed bed reactor, the petroleum feed is fed from the top of the reactor and travels down through the catalyst bed, where it is conditioned at certain temperature and pressure before it is collected at the bottom of the reactor. To ensure the desired product quality, operating conditions such as temperature, pressure and LHSV have to be monitored. Ensuring a stable reactor temperature is critical in ensuring product quality as having a temperature too high can be detrimental to the reactor and product quality since it can lead to coke formation and shorten the life of the catalyst (Ancheyta and Speight, 2007). Other factors such as feed rate and quality also determines the appropriate temperature that should be used during hydrotreating. Monitoring the feed rate is achieved by measuring the Liquid Hourly Space Velocity (LHSV). LHSV by definition is the inverse of the contact time it takes for the feed to go through the reactor before the samples are collected (Ancheyta and Speight, 2007). The unit of LHSV is usually hr^{-1}. LHSV can be represented mathematically by Equation 2.3:

LHSV = [Volumetric flow rate of feed (m^3/h)/Catalyst Volume (m^3)] ($time^{-1}$) ..… Equation (2.3)

Increasing LHSV leads to an increase in higher reactor rates. The recommended LHSV for light gas oil is between 0.5 to 2 hr^{-1}. Ensuring a consistent hydrogen partial pressure is also critical in hydrotreating. An increase in hydrogen partial pressure prevents catalyst deactivation and maintains catalyst function (Ancheyta and Speight, 2007).

2.4.2 Hydrotreating Catalysts

A catalyst is a substance that changes and accelerates the rate of a reaction. The key feature of a catalyst is that it is not used up in the chemical process. A catalyst can undergo one or more chemical reactions and its efficiency or effect may be influenced by the use of inhibitors or promoters which slows down or hasten the catalysis process respectively (Mapiour, 2009). The use of catalyst in hydrotreating is to remove unwanted contaminants such as nitrogen, sulfur, aromatics and metals. A catalyst generally consists of an active component and promoters (Topsoe et al., 1996). Common catalyst used in hydrotreating consists of a mix of nickel/molybdenum (NiMo), cobalt/molybdenum (CoMo) or nickel/Tungsten (NiW) usually with supports. Different catalysts are used to achieve different results. For example, if nitrogen is the one of the key major contaminants that needs to be eliminated, a NiMo sulfide catalyst would be appropriate for use with a support (Topsoe et al., 1996). For HDS reactions, CoMo catalysts are found to be preferred choice of catalyst but lacks hydrogenation abilities (Jones and Pujado, 2006).

2.4.3 Catalyst Composition

The most common hydrotreating catalysts consist of a Ni/Co-promoted Mo/W sulphides supported on γ-alumina (γ-Al_2O_3). Typically, depending on the desired products, Co-Mo- and Ni-Mo-P catalysts are generally used for application requiring higher yields in HDS and HDN. SiO_2-Al_2O_3 catalysts are generally used to achieve higher yields in hydrocracking applications (Jong, 2009). The catalyst of choice also depends on certain physical properties such as pore diameter, pore size and pore area in relation to the choice of feedstock used as these properties would ensure large catalyst beds do not collapse causing deviations in pressure drop in the reactor (Jong, 2009). Molybdenum (Mo) and Tungsten (W) are popularly used active components for hydrotreating of different types of petroleum feeds. These active components are promoted with either cobalt or

nickel and dispersed with a support that has a quality of high surface area (Lauritsen et al., 2007). There has been numerous research focused on providing insights into sulphided Co-Mo or Ni-Mo phases. The functionality of Ni or Co for hydrotreating is commonly researched using different model techniques. For example, the rim-edge model takes on the fact that the selectivity of the sulfur reaction pathways are generally affected by the morphology of the sulfur compounds attached to Mo or W structure - MoS_2 or WS_2 (Daage and Chianelli, 1994). For the Co-Mo-S Model, it is assumed that the Co-Mo-S phase contains the MoS_2 structure with the promoters generally placed on the outer edge planes of MoS_2 (Topsoe and Clausen, 1984). For the monolayer model, it is assumed that the molybdenum species are attached to the outer surface of the alumina (Schuit and Gates, 1973). For the intercalation model, it is assumed that the MoS_2 compound contains a layer of Mo(W) atoms packed amidst two hexagonal pack of sulfur atoms (Voorhoeve, 1971). Both the "Co-Mo-S model" and the "Rim-Edge model" are regarded as the most commonly used and generally accepted model used in hydrotreating catalysts (Topsoe and Clausen, 1984).

Promoters are used to increase active catalyst components, as well as HDN and HDS activity. The most common promoters used in hydrotreating are cobalt and nickel. These promoters are sometimes combined with other compounds like molybdenum or tungsten to produce a bimetallic catalyst (Gates et al., 1979). The catalyst support mostly used for hydrotreating is γ–Al_2O_3. One of the major reasons why this support is used is because of its high surface area and its well-structured pore size which provides easier diffusion (Boahene, 2011).

2.4.4 Inhibition and Deactivation of Catalysts

Often, there is a loss in catalytic activity or selectivity that generally happens over time which leads to a decline in product quality. This loss in catalyst activity is due to a variety of reasons. An effective way that has been proven to limit loss of catalyst activity is either by

increasing the temperature of the reactor or by reducing the LHSV (Gruia et al., 2006). Other reasons for decline in catalyst activity can be as a result of the presence of nitrogen compounds particularly the non-basic nitrogen compounds. In comparison to basic nitrogen compounds, there are minimal publications highlighting the threat of non-basic nitrogen compounds in inhibiting catalyst activity. Catalyst deactivation could also be achieved through other means such as catalyst poisoning due to impurities in the petroleum feedstock and the formation of intermediate reactions that hinders catalyst activity (Boahene, 2011). The decline in HDS activity that is experienced due to catalyst deactivation can be categorized into three steps, first fouling due to the formation of coke, followed by fouling due to the deposition of metal, and thirdly, extreme fouling due to plugging of the pore mouth (Boahene, 2011). Other factors that can contribute to extended periods of catalyst deactivation include active site poisoning by nitrogen species, and also active site coverage or blockage by deposition of active metals such as coke, nickel and vanadium (Furimsky and Massoth, 1999). Catalyst Poisoning is mostly due to nitrogen atoms strongly adsorbed to the unsaturated catalyst active sites (Sigurdson, 2009). Based on feedstock and operating conditions, the catalyst poisoning may be irreversible (permanent) or reversible (temporary). In the case of irreversible poisoning, the nitrogen atom is adsorbed on the catalyst active sites causing permanent deactivation. Generally, Athabasca derived bitumen gas oils are known to have very high organonitrogen contents which leads to catalyst poisoning during HDS and HDN reactions (Boahene, 2011). Section 2.4.5 focuses on the effects of nitrogen compounds on catalyst activity in details.

2.4.5 Effects of Nitrogen Compounds on Hydrotreating

The nitrogen content in petroleum fractions vary from 0.1 to 1 wt. % depending on the amount of heterocyclic nitrogen compounds present (Speight, 1999). Nitrogen compounds found

in petroleum fractions are divided into two different types namely: basic and non-basic nitrogen.

As showed in Figure 1.1 of this thesis, the key difference between the basic and non-basic chemical structure is that the basic nitrogen compounds contain six-membered pyridine groups. Non-basic nitrogen compounds on the other hand contains five-membered pyrrole groups (Topsoe et al., 1996). Non-basic nitrogen compounds process a lone pair that is delocalized in the ring and is at least a five-membered ringed family (Topsoe et al., 1996). Basic nitrogen compounds are assumed to be more reactive than NBN compounds. This is due to basic nitrogen compounds having stronger adsorption characteristics on catalyst active sites (Girgis and Gates, 1991 and Zeuthen et al., 2001). Although basic nitrogen compounds generally have significant detrimental effects on catalyst activity, non-basic nitrogen compounds also have been proven to have significant effects in inhibiting catalyst activity. Research by Kanda et al. (2004) concluded that decreasing trends in hydrodenitrogenation was as a result of the presence of nitrogen compounds particularly non-basic nitrogen compounds like alkyl-carbazoles and tetrahydrobenzocarbazoles in lighter boiling fractions (Kanda et al., 2004). Nitrogen compounds act as major inhibitors in the hydrotreating process because when high levels of HDS are achieved, nitrogen compounds progressively inhibit the HDS process by competitive adsorption (Macaud et al., 2004). Extensive research has been achieved in exploring the detrimental effects of BN compounds on the process of hydrotreating, however, non-basic nitrogen also poses a threat because they possess inhibition reactions that can be generated during the hydrogenation process of hydrotreating, thereby causing the formation of basic nitrogen compounds (Laredo et al., 2003).

2.5 Selective Removal of Non-Basic Nitrogen Compounds

Since it has been established that non-basic nitrogen compounds have a detrimental effect on hydrotreating activity by inhibiting catalyst active sites. It was important to look into ways to

reduce or eliminate the presence of non-basic nitrogen compounds. Section 2.5 focuses on the different selective removal methods generally used to remove non-basic nitrogen compounds as well as more details into the charge transfer mechanism.

2.5.1 Selective Removal Methods

There are a variety of methods that have been used to selectively remove non basic nitrogen compounds. Jewell and Snyder. (2001), used complexation with ferric chloride method to seperate basic and non-basic nitrogen compounds. This was achieved by forming isolable complexes with ferric chloride and then further seperation of the non-basic nitrogen compounds, either by total removal of the nitrogen compounds or selectively seperating the basic from the non-basic nitrogen compounds. The basic compounds were then eliminated with a mineral acid using a strong anion exhange resin.

Transition metals has also been used as a means to selectively extract nitrogen compounds by complex formation (Janchig and Yoshikazu, 2008). Another method for selectively removing nitrogen compounds was through the use of polymer supported by ionic liquid moieties. Chloride based ionic liquids has been used to extract nitrogen compounds from diesel feeds (Kulkarn and Afonsoac., 2010). The methods listed above tend to be a partially effective methods to selectively remove nitrogen compounds, however, majority of these processes have not been proven to selectively remove non-basic nitrogen compounds primarily.

2.5.2 Charge Transfer Complex (CTC) Mechanism

There are numerous literatures highlighting the different removal methods of basic nitrogen compounds by non-catalytic processes such as the use of volatile carboxylic acids (Qi et al., 1998a), ion-exchange resins (Prudich et al., 1986; Cronauer et al., 1986), metal complexation (Qi et al., 1998b), activated carbon (Almarri et al., 2009), amongt others. These aforemnetioned

removal methods are not effective in selectively removing non basic nitrigen compounds. Hence, it was important to explore processes that selectively removed non-basic nitrogen compounds alone without having effects on other compounds found in petroleum fractions. The use of a polymer poly(glycidyl methacrylate) combined with tetranitrofluorenone (TENF) organic compound has been explored for selectively targeting and removing the non-basic nitrogen compounds through the charge transfer complex mechanism without affecting other compounds such as sulfur or basic nitrogen compounds.

The charge transfer complex mechanism involves electron charge transfer between two or more molecules which gives way to electrostatic attraction providing a strong and stable base for a new molecular complex (Milenkovic et al., 1999). The charge transfer complex mechanism uses the principle of electron donors i.e. the charge molecule that does the transferring and electron acceptor i.e. the charge molecules that accept the charge. Related research using CTC mechanism has been in used by Milenkovic et al. (1999) for selective removal of alkyl-dibenzothiophene (DBT) from gas oils. Lemaire et al. (2002) also successfully used the CTC mechanism in the selective removal of dibenzothiophene from diesel feeds using an immobilized π acceptor molecule.

A strong covalent bond is created by attaching the π acceptor molecule to a hydrophilic support. More charge transfer complex interaction mechanism is enhanced by using a hydrophilic polymer in contact with a π acceptor molecule (Lemaire et al., 2002). The non-basic molecules in gas oils can be selectively removed by creating a charge transfer complex with a π acceptor and a hydrophilic polymer support. Recent studies show that there has been success in the selectively removing sulfur and nitrogen compounds from light gas oils by the use of an hydrophilic polyglycidyl methacrylate (PGMA) polymer support and 2,4,5,7-tetranitro-9-fluorenone (TENF)

as a π acceptor (Lemaire et al., 2002). Athabasca derived light gas oil contains the presence of aromatic compounds which can form CTC's with the π-acceptor molecules which makes them capable of competing with the DBT derivatives. A general rule is that the higher the HOMO (highest occupied molecular orbital), which is an approximate estimate of the oxidation potential of a compound, the lower the oxidation potential which leads to stronger connection and bonding with the π-acceptor molecules (Milenkovic et al., 1999). Table 2.3 shows the HOMO and oxidation potential of some sulfur species.

Table 2.3: Oxidation potential and HOMO values of DBT derivatives (Milenkovic et al., 1999).

	AROMATIC COMPOUND	E^{ox} (V/SCE)	HOMO (eV)
	2,8-DMDBT	1.44	-8.44
	4,6-DMDBT	1.53	-8.51
	4-MDBT	1.57	-8.55
	DBT	1.60	-8.60
	MN	1.63	-8.71
	Benzothiophene	1.70	-8.80
	Fluorene	1.79	-8.84

There has been lots of research with the use of different π-acceptor molecules to determine which has the highest selective removal towards 4,6-DMDBT compared to other aromatics containing heteroatoms. Figure 2.11 shows a list of the potential π-acceptor molecules used for charge transfer complexation reactions. TENF has been found to have better and higher selectively

towards 4, 6-DMDBT hence is a preferred choice for π-acceptor molecules (Milenkovic et al., 1999).
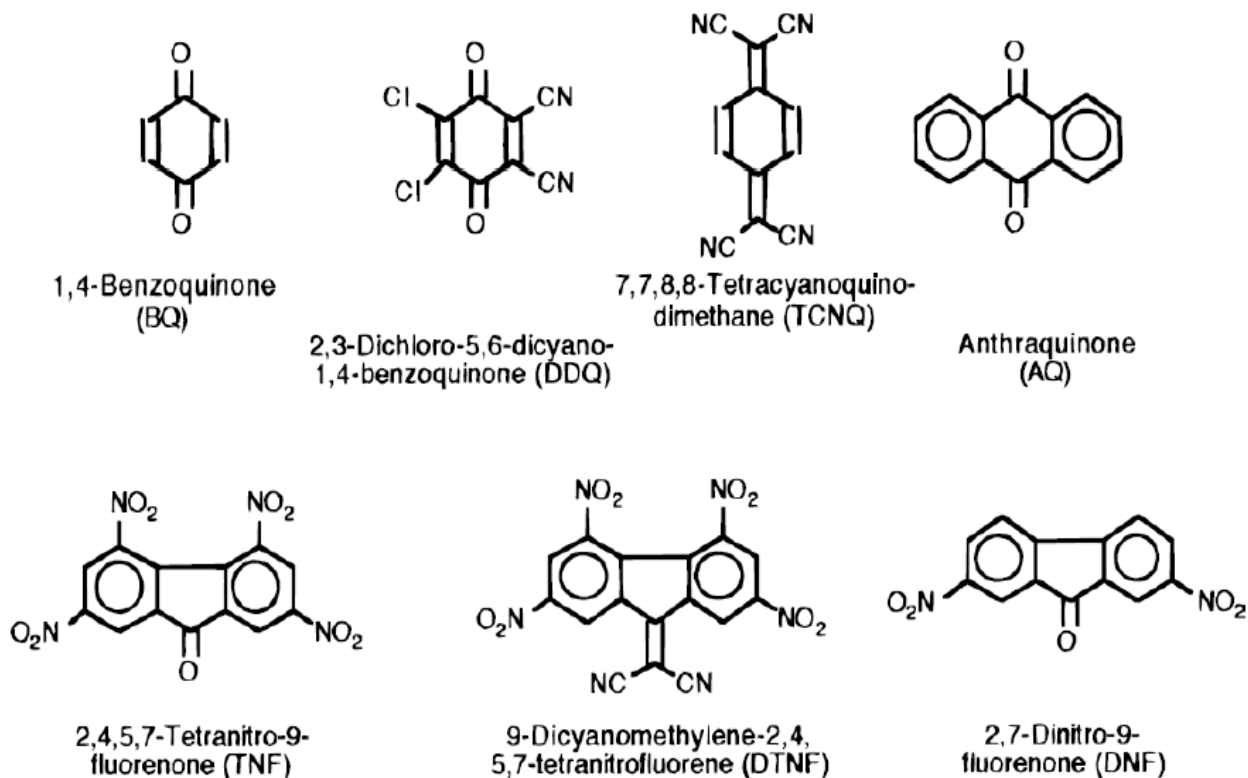
Figure 2.11: Structure of potential π-acceptor molecules for charge transfer complexation (Milenkovic et al., 1999).

2.5.3 Use of Functionalized Polymer for Selective Removal of Non-basic Nitrogen Compounds

Literature by Macaud et al. (2004) indicated that because of the electron rich nature of non-basic nitrogen compounds, it was believed that they would be suitable in forming charge transfer complexes with π-acceptor molecules such as tetranitrofluorenone (TENF). Based on this mechanism , it was speculated that the interactions between the π-acceptor molecules and hydrophilic polymer would lead to improved selectivity of the charge transfer complex formation towards non-basic nitrogen compounds (Macaud et al., 2004). Figure 2.12 shows the structure of

an hydrophilic polymer attached with π- acceptor molecule.
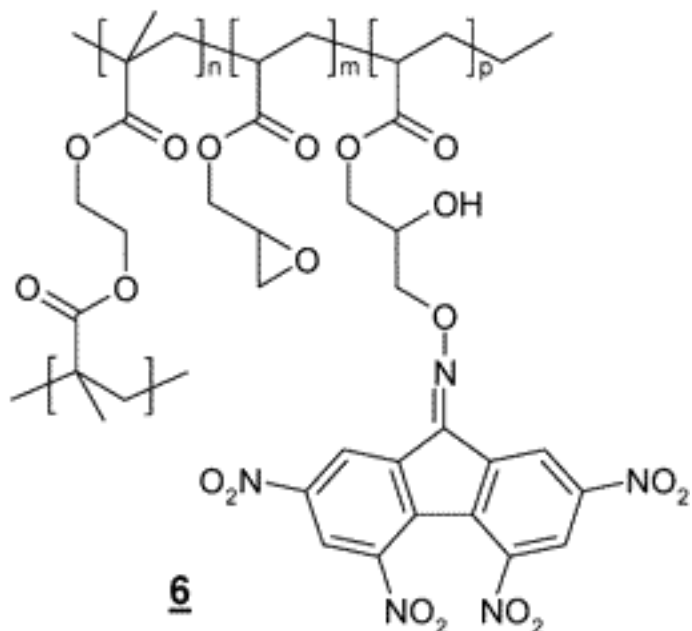
Figure 2.12: Structure of hydrophilic polymer (6) with π-acceptor molecule (TENF) attachment (Macaud et al., 2004).

After experimental analysis , it was discovered that the hydrophilic polymer used showed improved selectivity towards the non-basic nitrogen compounds such as carbazole and indole and also possesed qualities that made it have low selectivity to sulfur and basic nitrogen compounds (Macaud et al., 2004). This application has been modified and used to selectively remove non-basic nitrogen compounds in feedstocks. Figure 2.13 shows the experimental results by Macaud et al. (2004) when Polymer 6 which is an hydrophilic polmer was used for sulfur and nitrogen removal using straight run Iranian oil feedstock. Polymer 6 (an hydrophilic polymer) had the highest nitrogen removal via a single contact with the feedstock compared to Polymer 7 (not an hydrophilic polymer). For the sulfur levels, although they were insignificant, polymer 6 had comparable results as polymer 7, proving that Polymer 6 being an hydrophillic polymer had a huge impact on the selectivity of non-basic nitrogen molecules during the adsorption studies (Macaud

et al., 2004). Based on these results, it is importnmat to note that the synthesis of an hydrophilic polymer with a suitable π-acceptor molecule such as TENF, is a promising method for selectively removing non-basic nitrogen compounds from petroleum fractions.
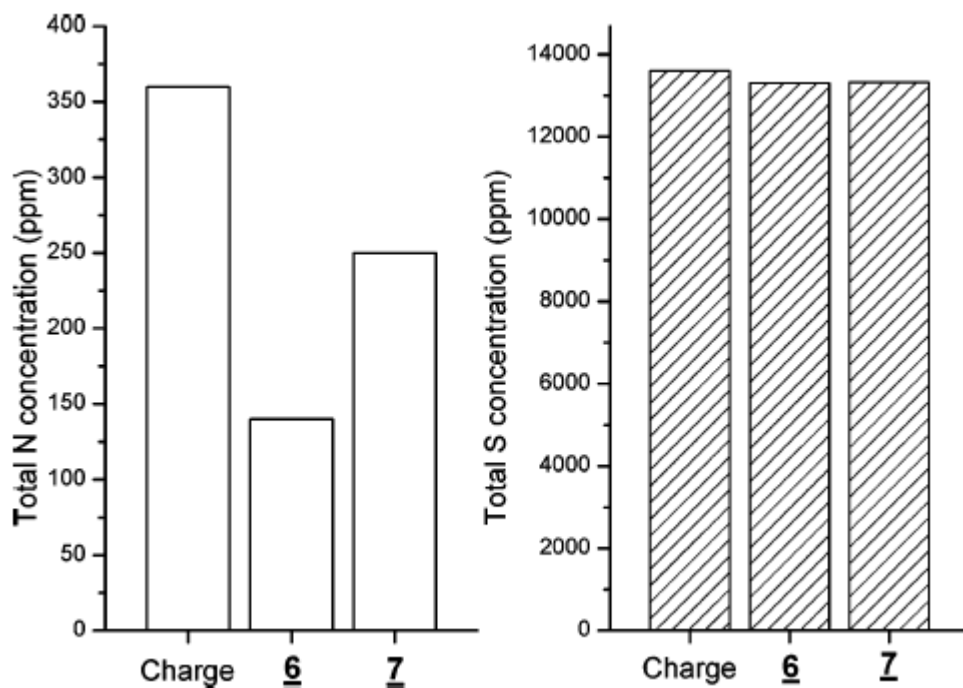
Figure 2.13: Total nitrogen and sulfur content before and after contact with polymers (Macaud et al., 2004).

Based on promising results obtained from the selective removal of non-basic nitrogen compounds using an hydrophilic polymer, there has been numerous literature using variations of hydrophilic polymer support and π-acceptor molecule to increase selectivity of non-basic nitrogen compounds. For example, Rizwan (2012) synthesized an electron deficient polymer, which was designed to selectively remove non-basic nitrogen species from heavy gas oil. This was done to study the impact of non-basic nitrogen compounds on catalyst inhibition and deactivation. The polymer support used was a synthesized poly(glycidyl methacrylate) polymer bead. Tetranitrofluorenone (TENF) was the choice of π-acceptor molecule used. Both the polymer support and π-acceptor was attached producing a PGMA-TENF polar polymer (Rizwan, 2012).

Similarly, a contact study was done to determine the selectively of the polymer to primarily target non-basic nitrogen compounds in heavy gas oil. Seven different polymers were synthesized with different variations of TENF coupling unto oxime functionality and it was discovered that although, all the synthesized polymers were able to target and selectively remove non-basic nitrogen compounds, the sample T polymer (which had the highest TENF coupling) was found to have the highest removal of nitrogen at 6.7 %. There was no significant increase or decrease in sulfur or aromatic contents in the heavy gas oil feed stock. Proving that the polymer selectively targeted non- basic nitrogen compounds alone. An analysis of the basic and non-basic nitrogen content also showed minimal basic nitrogen compounds, again, signifiying that non-basic nitrogen compounds were selectively removed.

Rizwan (2012), went a step further to determine the reusability of the polymer to see if the selective removal of non-basic nitrogen compounds for Sample T increased or decreased after the initial contact as shown in Figure 2.14. Figure 2.14 shows that the polymer was reusable and selectivity was maintained, provided that the polymer was restored to its original state by washing multiple times with toluene. Nitrogen removal remained relatively the same (6.7 to 7%) after the first and second contact , however, it was interesting to note that sulfur removal improved after each contact. Rizwan (2012) attributed this to inadequate washing of the polymer after adsorption studies.

Another application of the use of a functionalized polymer for the selective removal of non-basic nitrogen was researched by Chitanda et al. (2015) where different hydrophilic functionalized polymeric materials were used as polymer supports with a π-acceptor moiety and attached to a linker. Since linker attachment had not be studied before, the effect of linker length on the selectivity of non-basic nitrogen compounds was explored. It was expected that an

attachment of a linker per polymer bead would lead to an increase in the amount of π-acceptor on the surface of the particles, hence increase selectivity (Chitanda et al., 2015).
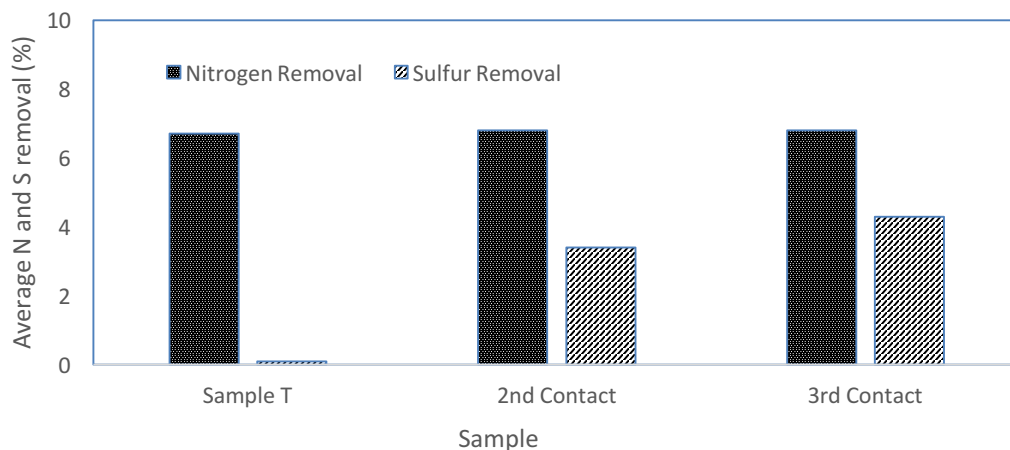
Figure 2.14: Contact study performed using sample T to determine reusability of the polymer (Rizwan, 2012).

All the polymer used in this study consisted of a common polymer support (PGMA-co-EDGMA, referred to as PGMA) and π-acceptor moiety (2, 4, 5, 7-tetranitroflorenone, TENF), while the linkers (linear diamines) were varied from a two- (diaminoethane, DAE (2)), a three- (diaminopropane, DAP (3)) to a four-carbon (diaminobutane, DAB (4)) containing compounds. Each polymer was represented by the notations PGMA-DAE (2)-TENF, PGMA-DAP (3)-TENF and PGMA-DAB (4)-TENF, respectively (Chitanda et al., 2015). It was important to note all the polymer particles, irrespective of linker length selectively removed non-basic nitrogen compounds. The results showed that diaminopropane (DAP (3)) linker length gave the highest nitrogen adsorption of 19% compared to the other polymers as shown in Figure 2.15.
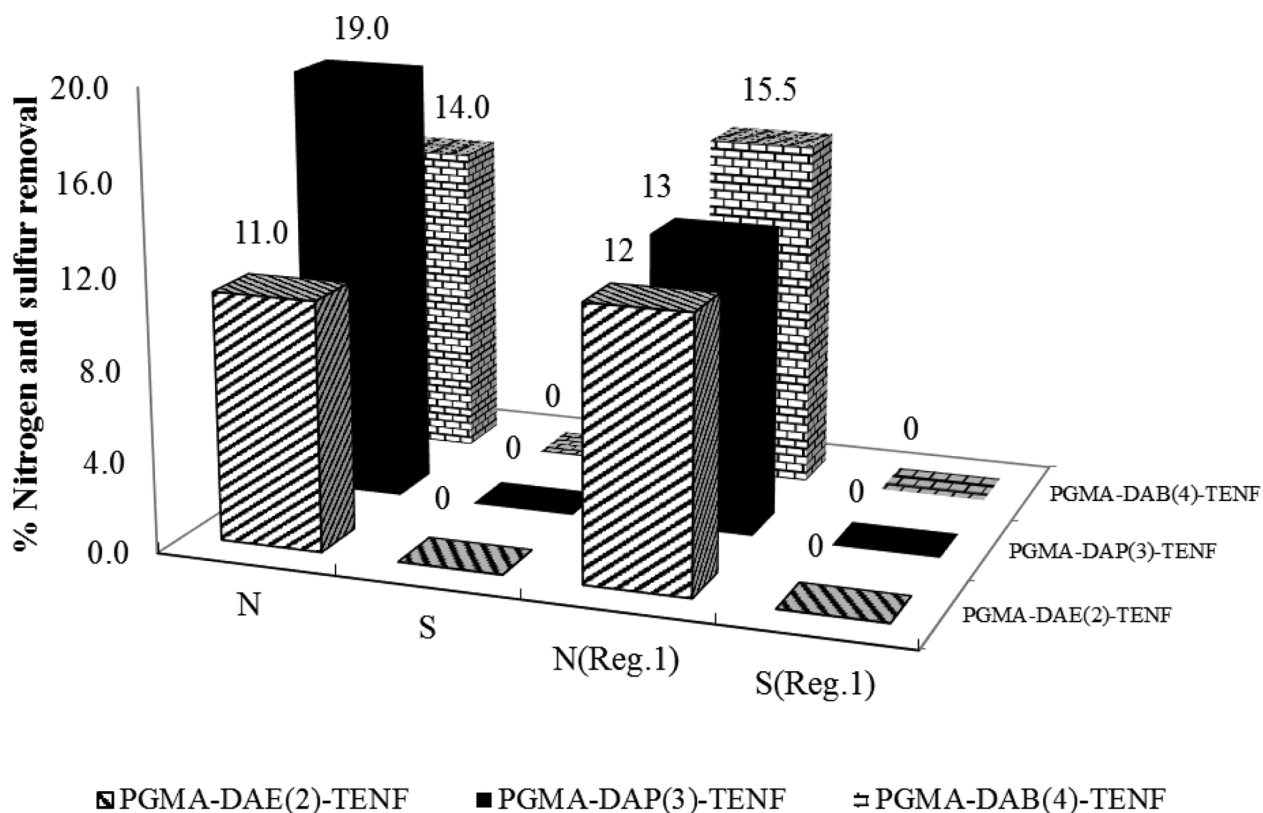
Figure 2.15 : Nitrogen and sulfur adsorption results using fresh and regenerated polymer particles (Chitanda et al., 2015).

Similar to Rizwan (2012), regeneration studies were also performed to monitor any increase or decrease in the selectivity of the non-basic nitrogen compounds. The results from the study by Chitanda et al. (2015) showed that most of the synthesized polymer was restored back to their original states, displaying similar nitrogen adsorptions after the first contact. However, it was noted that the PGMA-DAP (3)-TENF polymer which had the highest nitrogen adsorption initially, decresed in selectivity after regeneration. Based on these results from literature, it is believed that the use of an hydrophilic polymer attached to a π-acceptor is a promising application for selectively removing non-basic nitrogen compounds.

2.5.4 Polymer Support, Linker and π Acceptor

Svec et al. (1975) concluded that poly (glycidyl methacrylate) (PGMA) is a good choice of polymer support due to the placement and reactivity of the functional groups such as the epoxy

group, which enables reactive substitution of molecules such as carboxylic acids and amines. (PGMA) is generally prepared by polymerization of glycidyl methacrylate (GMA) and ethylene dimethacrylate (EDMA) which are reactive monomers:. 2, 4, 5, 7-tetranitroflorenone (TENF) also is a good choice for a π-acceptor moiety due to its high selectivity capabilities and reactivity with the polymer support. Since the effect of adding a linker has been researched by Chitanda et al. (2015), results showed that adding a linker positively aided selectivity of non-basic nitrogen compounds. Based on these literatures, the synthesized polymer used in this thesis was a particle consisting of a polymer support (PGMA-co-EDGMA), a π-acceptor moiety (2, 4, 5, 7-tetranitroflorenone, TENF) and a three- (diaminopropane, DAP (3)) linker to create a PGMA-DAP (3) –TENF polymer.

CHAPTER 3

EXPERIMENTAL METHODOLOGY

This chapter focuses on the experimental method that was used in the synthesis of the PGMA-DAP (3) –TENF polymer as well as the adsorption and regeneration methods used. The synthesis process is classified into three different steps with each stage involving modified experimental set up. Figure 3.1 shows the three-step process involved in the synthesis of PGMA-DAP (3)-TENF. First the absorption of poly (glycidyl methacrylate) with tetranitroflorenone which is the π-acceptor, and eventually with the diaminopropane, DAP (3) linker. Hydrotreating conditions, set up and process are also discussed in this section.

3.1 Synthesis of the Polymer Support (Poly (glycidyl methacrylate) (PGMA))

The synthesis of a support polymer was achieved by using the proposed method by Svec et al. (1975) with some adjustments. This process involved the use of a 2 L three-neck flask which was fitted with a mechanical stirrer, and valve. The valve was used to purge nitrogen. The active phase reactants were sequentially mixed in three sections, first with 85.5 g of glycidyl methacrylate and 36.75 g of ethylene glycol dimethacrylate which was eventually mixed with 1.2 g azobis (isobutyronitrile) which served as a radical initiator. Independently, the inert phase of the experiment was achieved by mixing 147.9 g of cyclohexanol and 14.7 g of dodecanol. In a separate set up, a solution consisting of 9.0 g of polyvinylpyrrolidone in 900 mL of distilled water was made. The three solutions were mixed and stirred at a rate of 400 rpm in the 3-neck flask. It was important to ensure that all the solutions were mixed in an inert nitrogen environment. Initially, the reaction was done at a temperature of 70 °C for 2 hours and subsequently at 80 °C for the following 6 hours. After the reaction, the heater was turned off while the stirrer was still

maintained. This lasted for approximately 2 hours, to let the reaction and system cool down.
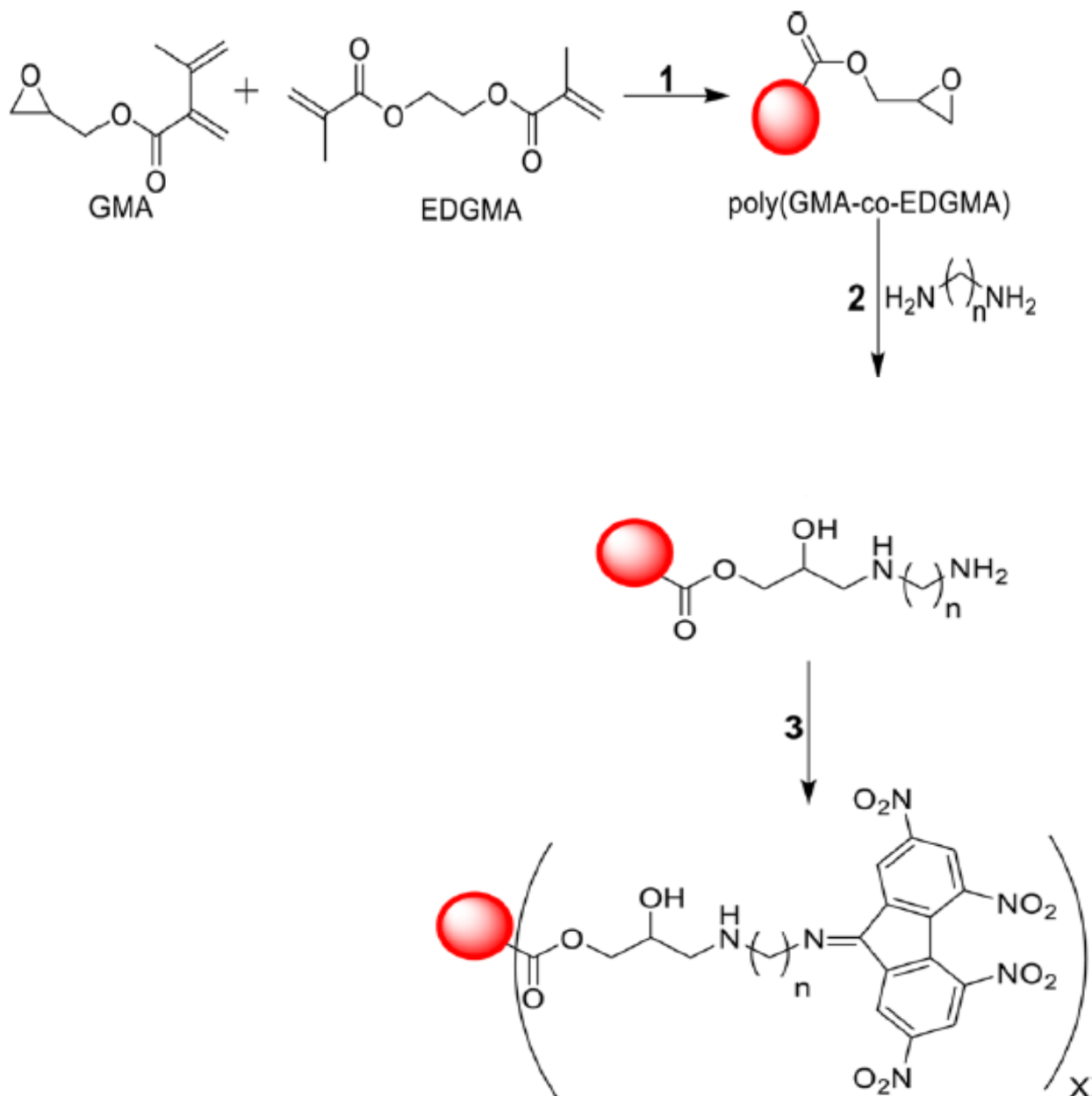
Figure 3.1: Synthesis of particles of PGMA-co-EDGMA functionalized with a π-acceptor (Chitanda et al., 2015).

The synthesized polymer was then washed initially several times with distilled water, after which it was further washed with ethanol to eliminate any other impurities or soluble components

distilled water could not get rid of. To ensure proper drying, the PGMA beads were kept in a vacuum oven at 90°C for approximately 24 hours (Chitanda et al., 2015).

3.2 Attachment of Polyglycidyl Methacrylate (PGMA) with the Diaminopropane (3) Linker

To synthesize a PGMA-DAP (3) compound, the epoxy ring had to be substituted with a linker. This was achieved by using a modified experimental setup by Nastasovic et al. (2004). To achieve this, a mechanical stirrer was placed in a 500 mL two-necked flask and placed in a 100 °C preheated oil bath. When the temperature was stabilized, 150 mL of diaminopropane was added to the flask slowly ensuring total dissolution. After this, approximately 61.5 g of PGMA beads were slowly added till dissolution and stirred for 24 h at 400 rpm. After 24 hours, the PGMA beads were washed on multiple occasions first with distilled water, and subsequently, with ethanol to eliminate any undisolved solvent. Further washing was done using isopropyl in a soxhlet apparatus for approximately 48 hours to remove any impurities present. After thorough washing of PGMA beads, the particles were collected and left to dry for 24 hours in a vacuum oven at 90 °C (Chitanda et al., 2015).

3.3 Attachment of Polyglycidyl Methacrylate (PGMA) - Diaminopropane, DAP (3) to the π-Acceptor (2, 4, 5, 7-tetranitroflorenone (TENF))

The next and final stage after the attachment of the polymer support to the linker, involved the synthesis of the π- acceptor compound. For this to be achieved, approximately 150 ml of toluene and 10 ml of acetic acid were added to a 500 ml two-necked flask in the presence of a mechanical stirrer. This was placed on a 100 °C preheated oil bath and stirred at 400 rpm. When the temperature was stable, approximately 2.45 g of TENF was carefully added to the flask ensuring complete dissolution. Approximately 6.20 g of the PGMA beads was added slowly to the mixture and was left to stir for approximately 3 days. After this process, it was observed that the PGMA beads changed color from white to light brown. It was also observed that the texture of the PGMA beads

was finer and more "powdery" after this process. After completing the reaction, the separated polymer was filtered and washed with toluene to remove any impurities. The compound was then left to dry at 90°C in the vacuum oven for approximately 24 hours (Chitanda et al., 2015). Figure 3.2 shows the chemical structure of the PGMA-DAP (3) –TENF polymer. Due to the large mass of polymer that was needed for hydrotreating, this three step procedure was repeated as needed.
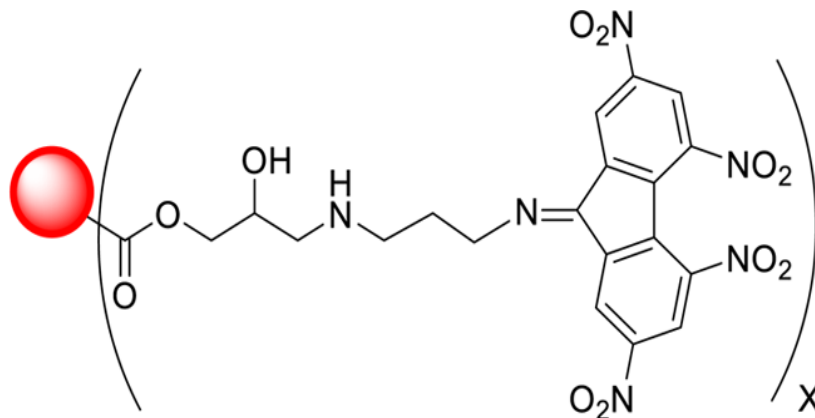
Figure 3.2: Chemical structure of synthesized PGMA-DAP (3) –TENF polymer (Chitanda et al., 2015).

3.4 Adsorption of PGMA –DAP (3) – TENF Polymer with Light Gas Oil

Adsorption studies on the PGMA –DAP (3) – TENF polymer was carried out at room temperature of 23°C. The polymer was added to light gas oil in a 1:4 (wt/wt) ratio. Prior research on adsorption of polymers with light gas oils was performed on a batch scale using 1 g of polymer with 4g of oil. In this adsorption study, large amounts of light gas oil were needed for hydrotreating. Hence, adsorption studies had to be carried out on a larger scale using 290 g of bulk mass of PGMA-DAP (3) –TENF polymer with 1160 g of light gas oil. The mixture was stirred at 400 rpm using an overhead stirrer for 24 hours. The mixture was separated by vacuum suction separating the polymer from the treated oil. The treated oil is referred to as pretreated feed. The

pretreated feed served as a baseline for monitoring the amount of sulfur, nitrogen and aromatics contents in the light gas oil before hydrotreating.

3.5 Regeneration of PGMA-DAP (3) –TENF Polymer

To be able to account for the large amount of light gas oil needed for hydrotreating, the polymer had to be regenerated three times. To achieve this, the reusable polymer material after the initial adsorption was separated and dried at room temperature for approximately 48 hours to ensure proper drying of the polymer. The polymer was then regenerated with toluene using a soxhlet extractor apparatus. The polymer was washed multiple times using toluene at 110°C for approximately a week. The regenerated particles were then dried at room temperature for 48 hours ready to be re-used for adsorption studies.

3.6 Characterization of the PGMA –DAP (3) - TENF Polymer

It was important to characterize the original polymer as well as the regenerated polymer to monitor any physical or chemical changes in the polymer such as the presence of absence or chemical groups.

3.6.1 Fourier Transform Infrared Spectroscopy (FTIR)

The PerkinElmer Spectrum GX system (PerkinElmer, Waltham, MA, USA) Fourier transform infrared spectroscopy (FTIR) is a technique which works by monitoring the emittance of infrared radiation through a product sample. The dry powder sample was carefully placed on the hydraulic press to take the shape of a discs spectroscopy plate. The samples were ran at room conditions. An average of 32 scans spectrum was used with a nominal resolution of 4 cm^{-1}. The samples were then exposed to radiation which was either absorbed or transmitted. The transmitted radiation provides unique peaks which is specific to certain molecular structure, adsorption and functional groups.

3.6.2 Nitrogen Adsorption/Desorption (BET)

The Brunauer−Emmett−Teller (BET) device was used to measure pore size, surface area, and pore volume of the polymer samples through the use of a Micromeritics ASAP 2000 analyzer. The BET mechanism works by predicting the physical components of a sample by calculating the size of the adsorbtion monolayer associated with the sample (Gregg and Sing., 1967). About 0.20 g of the polymer sample was used for each sample analysis. To ensure the sample was free of any moisture, it was degassed for 2 hours at 200°C in a vacuum at 550 Torr. Depending on the amount of N_2 that was adsorbed by the sample polymer materials, the average pore diameter (nm), specific surface area (m^2/g), and pore volume (cm^3/g) of the cylindrical arrays of pores were estimated.

3.7 Hydrotreating Experimental

This section focuses on the details of the experimental setup of the trickle bed reactor that was used for hydrotreatment studies using light gas oil derived from Athabasca bitumen. This section focuses on the analysis of the product samples. The characteristics of light gas oil were listed previously in Table 1.1.

3.7.1 Reactor and Process Conditions

The hydrotreating reactor consists of three main sections – the feeding section, where the light gas oil is introduced to the reactor, a reactor section where catalytic activity takes place and a high pressure gas/liquid separation section where the sample products are separated for analysis. Figure 3.3 shows a schematic of the reactor setup used in the lab. It includes a gas supply, which is used to introduce hydrogen or helium to the reactor system through the use of a mass flow controller. Helium gas was used to pressurize the system. The light gas oil feed was introduced to the system through the use of a feed tank and a pump that maintains a desired flow rate to the reactor. To ensure constant flow of liquid from the feed tank, 1.48 to 2.17 MPa of low-pressure

helium was used to provide a positive pressure to push the liquid LGO through the feed tank. Once the LGO exited the feed, it was combined with hydrogen gas before it entered the reactor section. A temperature controller was used to control temperature. After catalytic activity in the reactor, the reactor exit stream, which contained residue of ammonia and hydrogen sulfide, was then passed through a scrubber to dissolve trace residue of hydrogen sulfide. The liquid and gas products were then sent to a high-pressure separator that separated the liquid from the gas products. The liquid product was analyzed for nitrogen, sulfur and aromatics content while the gas product was vented off safely. The back pressure valve served as a regulator to maintain the system pressure of the reactor unit and vented excess gas to the scrubbers if needed. As a safety measure, the reactor was equipped with multiple pressure safety and check valves. Details of catalyst loading is provided in Appendix A. Figure A.1 shows a general representation of the catalyst loading used in the lab.

After loading the reactor, it was tightened with caps to ensure it was air tight and had no leaks. After this, the reactor was placed into the insulator pocket where it was also free of leaks. After loading, the whole system was pressurized to 10.0 MPa with helium gas. This was important to be able detect any leaks. In the case of leaks, the system was depressurized and any loose valves were tightened. In the absence of leaks, the reactor was reduced to the operating pressure needed for hydrotreating, and observed for stabilization before introduction of any liquid stream.

After the reactor system reached and maintained a constant pressure, the next step was to begin sulfidation. Sulfidation is a required active phase of hydrotreating as it is necessary in the conversion of the oxide catalysts into sulfides before hydrotreating reaction takes place (Mochida and Choi, 2004). To achieve this, the feed tank was filled with a mixture of cleaning oil and 2.9% volume of butanethiol to produce a gas oil blend. The first stage of the sulfidation process required 100 ml of the sulfiding solution to be used to wet the catalyst at a reactor temperature of 193°C for

24 hrs. After pre-wetting the catalyst, hydrogen flow was introduced to the system to begin the next stage of the sulfidation process. This was achieved by raising the temperature to 343 °C for 24 hours. The sulfidation process was carried out in two stages to ensure thorough completion of the sulfidation of MoO_3 active compounds in the catalyst (Ferdous, 2003). After sulfidation, the solution was replaced with actual feed which was the light gas oil feed derived from Athabasca bitumen. The catalyst was then precoked with the LGO feed for 3 consecutive days at a temperature, pressure and LHSV of 370°C, 8.8MPa and 1 hr^{-1}, respectively. Hydrogen flow was ensured at 100 ml/min. Precoking was carried out for three days in order to monitor and obtain a stable catalyst activity. After precoking, the temperature and pressures were varied to suit experimental process conditions for the untreated and pretreated feeds after which hydrotreatment catalytic activities was measured. The sample products were collected for analysis every 12 hours. The time on stream (TOS) chart is included in Appendix B. Figure B.1 and B.2 show the TOS for the untreated and pretreated feed respectively. Samples within 12 hours of a process change were discarded at the end of the stabilization period to ensure equilibrium. Each sample was then collected and stripped for 2 hours with nitrogen to get rid of any residual NH_3 and H_2S products in the stream. Samples were then taken for analysis of nitrogen, sulfur and aromatics content.

3.8 Product Analysis

This section highlights the instruments used to measure nitrogen (including non-basic), sulfur and aromatics content in the product gas oil stream. Nitrogen and sulfur contents were measured by using an Antek 9000 NS analyzer. Aromatics content was measured by using a Nuclear Magnetic Resonance device and non-basic nitrogen compounds were measured by using a HI-902 Potentiometric titrator.

3.8.1 Analysis of Nitrogen Content

Nitrogen content was measured by using ASTM D4629 Method. This was achieved by premeasuring quantities (0.05g) of the sample gas oil product diluted with xylene, and thoroughly mixed to ensure homogeneity of both liquids. After mixing, approximately 5 µL of the prepared sample was inserted into the sample boat. The sample was brushed with argon and oxygen. The gaseous byproducts were then passed dried through a membrane to eliminate any moisture before it went into the detector chamber. Nitrogen detection was achieved by converting nitrogen to nitric oxide gas, which was then contacted with ozone to produce excited NO_2 atoms. The decay of the excited NO_2 atoms resulted in the emissions of photons at different specific wavelengths through the chemiluminescence, which is then detected by the photomultiplier tube. The chemiluminescence is designed to target, measure and detect a response for known nitrogen concentrations. This detection represents the nitrogen content in the product sample.

3.8.2 Analysis of Non-basic Nitrogen Content

HI-902 Potentiometric titrator was used to measure basic nitrogen compounds using the ASTM D4739 method. The necessary equipment used in the titrator involved the use of pH electrode for detecting the basic nitrogen compounds and an analytical balance. A blank solvent was prepared by mixing Isopropyl alcohol, toluene, and chloroform and deionized water in a ratio of 3:3:3:1 respectively. The blank solvent was ran through the titrator to create a baseline. To run the actual gas oil samples, the auto sample titrator was used in the following sequence, the first three beakers served as rinse beakers, the forth beaker served as a storage beaker after titration was complete and beakers five through sixteen had the actual gas oil samples measured and diluted with exactly 100ml of the titrant solvent along with a stir bar. At the end of each titration samples, the full tray report highlighted the amount of basic nitrogen compounds in mg/g KOH which was

then converted to ppm. The total number of nitrogen compounds was subtracted from the number of basic nitrogen compounds to get the amount of non-basic nitrogen compounds present in each product sample.
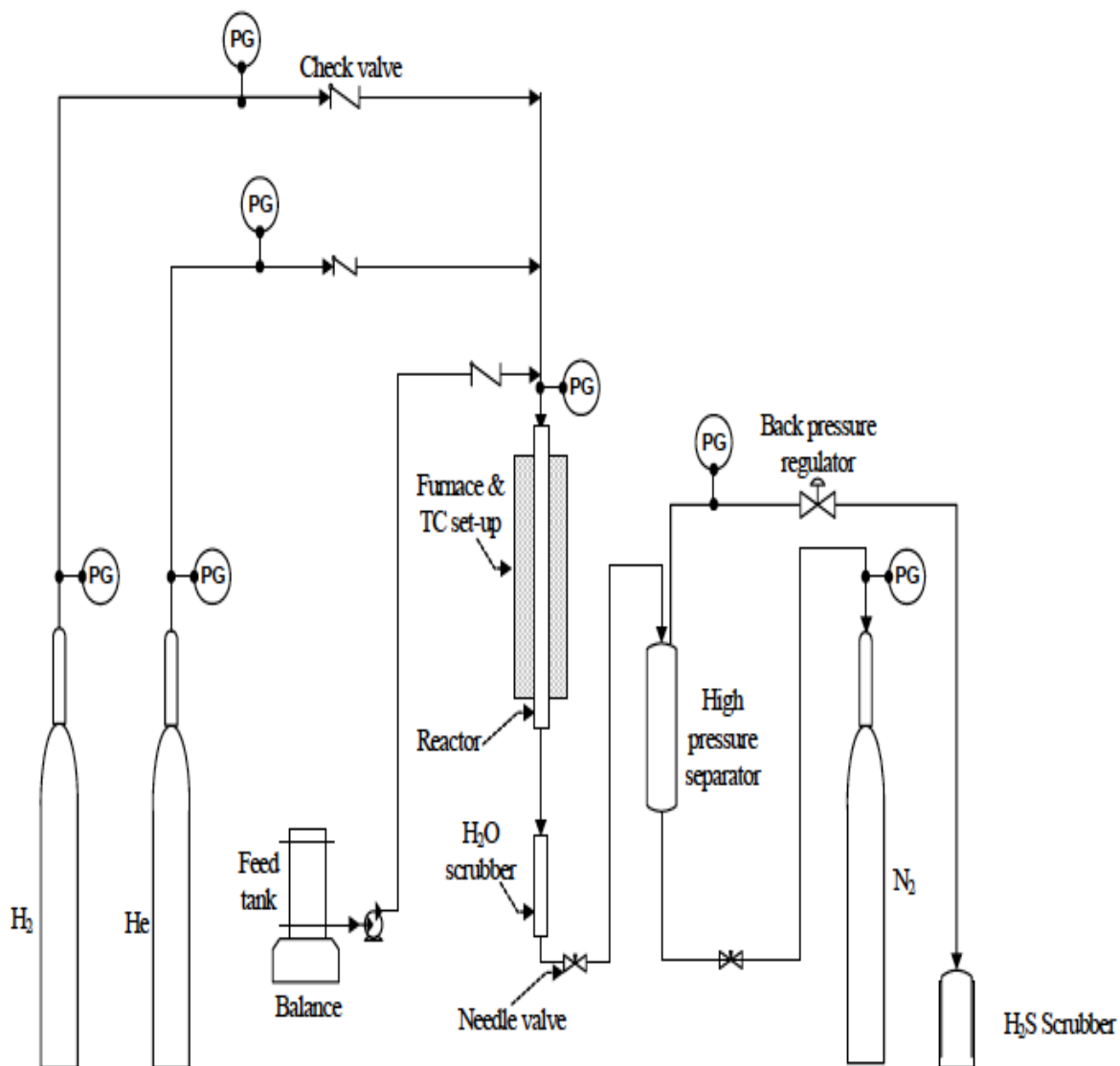
Figure 3.3: Schematic of the trickle- bed reactor set-up for hydrotreatment studies

3.8.3. Analysis of Sulfur Content

Similar to nitrogen content, sulfur content was measured using the ASTM 5453-06 method. Sulfur in the sample was converted into sulfur-dioxide (SO_2). After moisture removal, the SO_2 gas was visible to the ultra violet radiation which converted it to excited sulfur SO_2 compounds which can be identified by a photomultiplier tube with a fluorescence signal which is specific to sulfur atoms. This was used to target, measure and detect a response for known sulfur concentrations. This detection represents the sulfur content in the product sample.

3.8.4. Analysis of Aromatics Content

Nuclear magnetic resonance data were obtained using a Bruker 500 MHz NMR (Bruker BioSpin Corporation, Billerica, MA, USA). This was obtained by dissolving light gas oil samples in $CDCl_3$ in a 1:1 ratio. To measure total percent aromatic carbon content, the feed/product was dissolved in deuterated chloroform ($CDCl_3$) under the conditions outlined in ASTM D5292-99 (2014) using a - 4 s pulse delay, 28 kHz and inverse gated H_2 decoupling and 2500 scans. Percent aromatic carbon content (% CAr) was calculated using % CAr = [A/(A + B)] × 100, where A was the integral value of the aromatic portion of the spectrum (100 to 110 ppm) and B is the one for aliphatic carbons (0 to 50 ppm).

3.8.5. Stability of NiMo/γAl$_2$O$_3$ catalyst

In order to determine the stability of the catalyst over the course of the hydrotreatment experiments carried over a time on-stream of 21.5 days, a performance test was performed on the effectiveness of the catalyst by repeating the hydrotreatment studies at similar temperature and pressure at the beginning of the run and at the end of the run. Product samples were collected over 12 hour intervals, at the following reaction conditions: 370°C temperature, 8.96 MPa pressure and

1.0 h^{-1} LHSV, 600mL/mL H$_2$/LGO ratio, and 1.5 g NiMo/γAl$_2$O$_3$ catalyst loading. Similar test was performed under identical conditions after the hydrotreatment of the pretreated LGO feed.

3.9 Statistical Analysis using SPSS software

The statistical package for the social science (SPSS) software is a comprehensive tool used for data analysis by using factor analysis to describe variability among correlated parameters. The SPSS tool was used to compare nitrogen, sulfur and aromatic conversions before and after the selective removal of non-basic nitrogen compounds. This was done to determine the statistical significance of selectively removing non-basic nitrogen compounds in the hydrotreatment of light gas oil provided all process conditions such as temperature, pressure and LHSV were identical during hydrotreatment for both the untreated and pre-treated feeds. This was analyzed using a two-sample t-test for dependent samples. Normality was tested for each variable (nitrogen, sulfur and aromatics conversions) and based on the normality test results, the hypothesis was created for each variable. Based on the level of significance, the evidence was either accepted or rejected validating statistical significance or not between the hydrotreated and hydrotreated-pretreated feeds. The interrelationships between the independent and dependent variables is used to provide descriptive statistical data for HDN, HDS and HDA. Inter-relationships between the dependent and independent variables are based on the multicollinearity between the dependent variables: nitrogen and sulfur and aromatics conversions and the independent variables: temperature, pressure and LHSV.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Total Nitrogen, Sulfur and Aromatics Contents in Untreated Feeds

The nitrogen, sulfur and aromatics contents of Athabasca-derived light gas oil feeds vary by composition due to reasons such as type of feed, boiling point range, volatility, length of time the feed has been exposed and so on (Speight, 1999). Due to these reasons, it was important to measure the nitrogen, sulfur and aromatics contents of the LGO feed that was used in this research. The nitrogen, sulfur and aromatics contents were measured for the untreated feed to create a baseline reference for monitoring catalyst activity after pretreatment. Figure 4.1 and 4.2 show the nitrogen (including non-basic nitrogen compounds), sulfur and aromatic contents for the untreated light gas oil feed in ppm.

As shown in Figure 4.1, the untreated feed has relatively high nitrogen, sulfur and aromatics contents. Hence, it is necessary to reduce it to make it usable and environmentally friendly. The high content of non-basic nitrogen compounds (1009 ppm) also shows a need to reduce nitrogen content since non-basic nitrogen has been known to inhibit catalyst performance by reducing nitrogen, sulfur and aromatics conversion.

4.2. Total Nitrogen, Sulfur and Aromatic Contents in the Pretreated Feed

The PGMA-DAP(3)-TENF polymer was adsorbed with LGO to selectively remove the non-basic nitrogen compounds. To monitor its effectiveness, it was necessary to measure the nitrogen, sulfur and aromatics content after pretreatment. Figure 4.2 shows the sulfur and aromatics contents in the untreated and pretreated light gas oil feed. The selective removal of non-basic nitrogen compounds led to a decrease in total nitrogen (including non-basic) and aromatics content.

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Total nitrogen content (including non basic) in the untreated and pretreated feeds
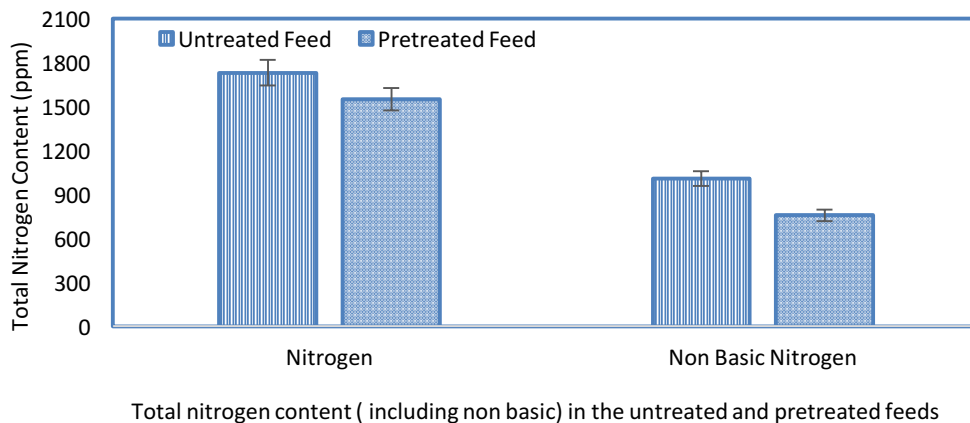
Figure 4.1: Nitrogen content (including non-basic nitrogen) between the untreated and pretreated.

Sulfur and aromatics content in untreated and pretreated feed in ppm
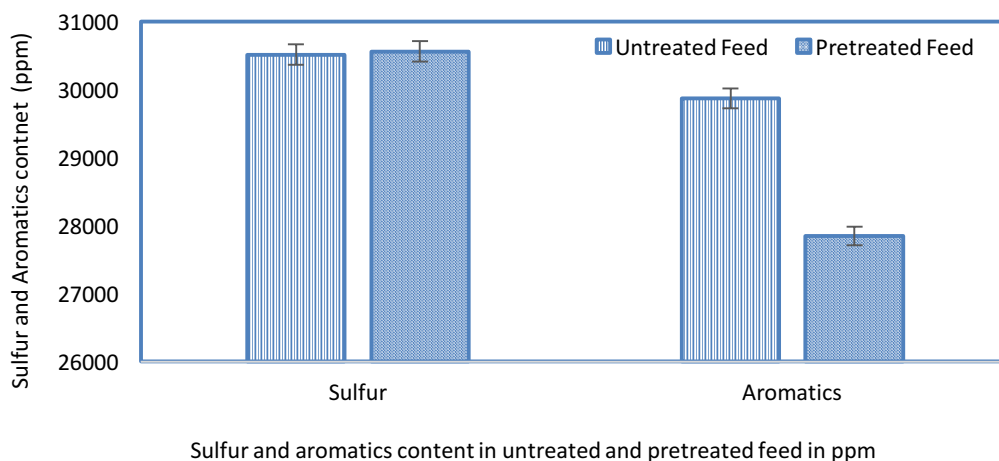
Figure 4.2: Sulfur and aromatics contents in ppm of the untreated and pretreated light gas oil feed.

Decrease in total nitrogen content was expected, as the polymer was designed to selectively target and remove NBN compounds in light gas oils. Pretreatment of the light gas oil led to a 24.9% decrease in non-basic nitrogen compounds and a 10.5% decrease in total nitrogen compounds. Since total nitrogen content is a combination of basic and non-basic nitrogen content, it was expected that a reduction in non-basic nitrogen content would lead to a reduction in total

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nitrogen content.

The selective removal of non-basic nitrogen compounds had no effect on sulfur content. Again, since the polymer targets only non-basic nitrogen compounds by forming charge transfer complexes between the π-acceptor polymer and heterocyclic non-basic nitrogen species, it was not expected that it would have an effect on sulfur removal. Selective removal of the non-basic nitrogen compounds led to a 6.8% decrease in total aromatics content.

4.3 Nitrogen, Sulfur and Aromatic Contents in the Regenerated Pretreated Feeds

To determine polymer reusability as well as to measure the effectiveness of a polymer on a larger scale, it was important to regenerate the polymer. Polymer regeneration was attained by washing the polymer with toluene after the adsorption experiments. Characterization techniques including BET and FTIR were used to monitor physical and chemical changes of the polymer over time. Total nitrogen, sulfur and aromatic content was also measured after each adsorption experiment to determine the activity of the regenerated polymers. The polymer was regenerated three times to account for the mass of LGO needed for hydrotreatment. Each polymer activity is represented by the number of times it was regenerated, specifically, pretreated regeneration feeds 1, 2 and 3, respectively. Table 4.1 shows the total nitrogen, sulfur and aromatic contents in ppm of the pretreated regenerated feeds.

Table 4.1: Total nitrogen, sulfur and aromatics content in regenerated pretreated feeds in ppm.

	Total N (ppm)	Total S (ppm)	Aromatics (ppm)
Pretreated Original	1537	30555	27867
Pretreated Regenerated 1	1618	30530	27775
Pretreated Regenerated 2	1649	30518	27967
Pretreated Regenerated 3	1701	30584	27919

As the results show in Table 4.1, the pretreated original feed (without regeneration) had the lowest nitrogen content. This was expected, since it was a fresh polymer that had not undergone any regeneration. However, with further regeneration, it was observed that the total nitrogen content increased for subsequent regenerated feeds 1, 2 and 3. This indicated a reduction in nitrogen adsorption compared to the pretreated original feed as shown in Table 4.1. Although it is expected that after regeneration, the polymer is restored to its original state, these results indicate otherwise, as regeneration reduced nitrogen adsorptions. It was important to perform FTIR analysis on both the fresh and regenerated polymers to monitor any changes in the presence of functional groups, as this may shed some light on why the regenerated polymer had lower nitrogen adsorptions. Figure 4.3 shows FTIR results between the fresh polymer and the regenerated polymers. As the results show, there is a decrease in the percent transmission between the fresh and regenerated polymers. It was apparent that the desired functionalized polymer was synthesized successfully since both the fresh and regenerated polymers showed the expected functional groups producing signals within the range at 1282 and 1504cm^{-1}, indicating the presence of the nitro groups. However, comparing the results between the fresh and regenerated polymers signified lower transmittance in the regenerated polymer. This can be attributed to the decrease in polymer activity, particularly nitrogen adsorption which was experienced between the fresh and regenerated polymer. An increase in the nitrogen content was observed after each regeneration of the polymer. The nitrogen content for the pretreated regeneration feeds 1, 2 and 3 increased by 5.2, 7.2 and 10.7%, respectively thereby indicating a decrease in nitrogen adsorption.
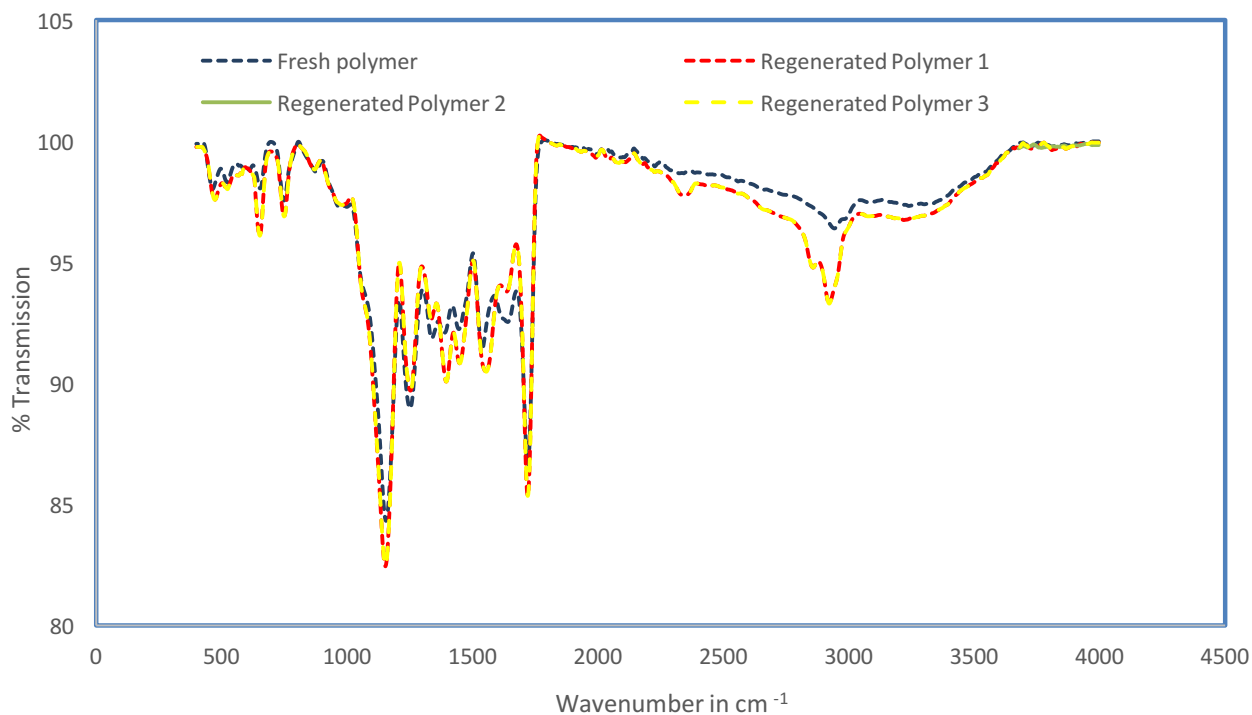
Figure 4.3: FT-IR spectra for fresh and regenerated PGMA-DAP (3)-TENF polymers

Another possible reason for the difference in nitrogen adsorption between the fresh and regenerated polymer might be due to its physical properties, including surface area, pore size and pore volume. BET techniques were used to achieve this, and the results are shown in Table 4.2.

Table 4.2: BET surface area (m^2/g), Pore Volume (m^3/g) and Pore Diameter (nm) of the fresh and regenerated polymers.

Sample	BET Analysis		
	Surface Area (m^2/g) ±4	Pore Volume (m^3/g) ±0.1	Pore Diameter (nm) ±2
Fresh Polymer	36	0.15	16
Regeneration Polymer 1	33	0.14	13
Regeneration Polymer 2	31	0.14	12
Regenerated Polymer 3	31	0.13	12

As the results in Table 4.2 show, there were overall minimal difference in surface area, pore volume and pore diameter between the fresh polymer and the regenerated polymers. It is

important to note that the biggest difference in change was observed between the fresh polymer and the first regenerated polymer. This shows that although the chemical properties such as the presence of the functional group remained the same, it is evident that the physical properties of the polymer after regeneration slightly changed and might be the reason behind the decline in nitrogen adsorption between the fresh and regenerated polymer. Although increase in surface area of synthesized particles is generally expected to promotes polymer activity (Chitanda et al., 2015), it is evident in these results that the initial decreases in surface area, pore size and volume of the PGMA-DAP (3)-TENF polymer could have contributed be attributed to the decrease in nitrogen adsorption observed in the regenerated polymers.

Similar literature by Chitanda et al. (2015) also follows this trend. When the PGMA-DAP(3)-TENF polymer was produced on a small scale, nitrogen adsorption decreased by 6% (from 19% to 13%) after only one regeneration. Further regeneration studies were not carried out on a small scale. However, comparing the nitrogen adsorption on the small and large scales showed that the small scaled polymer had better nitrogen adsorption of 19% compared to that of the large scale at 10.5%. Although nitrogen adsorption was higher in the small scale after just one regeneration, there was a lower decrease of 4% (from 10.5% to 6.5%) in the large scale compared to a 6% decrease in the small scale.

For the larger scaled polymer, it was notable that the nitrogen adsorption decreased even further after the second and third regenerations. There was a 1.8% (from 6.5% to 4.7%) decrease in nitrogen adsorption after the second regeneration and a 3% (from 4.7% to 1.7%) decrease after the third regeneration. This steady decline in nitrogen adsorption can be attributed to insufficient washing of the polymer after adsorption studies.

It was also notable that regeneration had no effect on sulfur and aromatics content. For

sulfur compounds, this was expected, since prior removal of non-basic nitrogen compounds, even with a fresh polymer, showed no effects on sulfur content. It was imperative that since polymer activity decreased with regeneration, there would be no change in sulfur content for the regenerated feeds. Although the fresh polymer removed 6.8% of aromatics contents initially, it was observed that there was no further decrease in aromatics content after each regeneration.

4.4 Bulk Polymer Activity and Reusability

As the results in Section 4.3 of this thesis show, it can be concluded that bulk polymer mass had an effect on polymer activity with regards to nitrogen adsorptions. Higher nitrogen adsorptions were experienced in the small scale compared to the large scale. However, for sulfur, there was no difference between the small and large scale, indicating that bulk polymer mass had no effect on sulfur removal. Since aromatics content removal was not studied on the small scale, there was no means of comparing the result to a large scale; however, bulk polymer mass led to a 6.8% decrease in aromatics content after pretreatment. Based on these results, it can be concluded that the use of bulk polymer mass led to nitrogen and aromatics removal but had no effect on sulfur removal.

Results in section 4.3 also signify that the PGMA-DAP(3)-TENF polymer is reusable on a large scale, although it has been established that the effectiveness of the polymer in the removal of nitrogen contents reduced with each regeneration.

4.5 Hydrotreatment Study Using Untreated and Pretreated Light Gas Oil

After adsorption studies were performed using bulk mass of the PGMA-DAP(3)-TENF polymer with LGO, the next step was to hydrotreat both the untreated (hydrotreated feed) and pretreated (hydrotreated-pretreated) feeds using a commercial NiMo/γAl$_2$O$_3$ to determine the effect on hydrotreating of prior selective removal of non- basic nitrogen compounds on

hydrotreating. To monitor these changes before and after hydrotreatment, it was important to measure the nitrogen, sulfur and aromatics contents of the hydrotreated feed and compare those results with the hydrotreated-pretreated feed. Hydrotreatment studies were performed at a temperature, pressure and LHSV range of 350 to 370°C, 8.27 to 9.65 MPa and 1 hr^{-1} to 2 hr^{-1}, respectively. Since the maximum nitrogen, sulfur and aromatics conversions for both the hydrotreated and the hydrotreated-pretreated feeds were observed at temperature, pressure and LHSV conditions of 370°C, 8.96 MPa and 1 hr^{-1} respectively, these results were used in this section to compare hydrotreatment activity between the hydrotreated and hydrotreated-pretreated feed. Section 4.5 focuses on the effect of changing process parameters on the pretreatment of oil using the full range of temperature, pressure and LHSV for the hydrotreated and hydrotreated-pretreated feeds. Table 4.3 shows the nitrogen, sulfur and aromatics contents in the hydrotreated and hydrotreated-pretreated feeds.

Laredo et al. (2003) recognized non-basic nitrogen compounds as the main cause of the decline in HDS that is observed during hydrotreating due to the formation of basic nitrogen compounds during the hydrogenation reaction. Based on this literature, it is expected that selectively removing non-basic nitrogen compounds prior to hydrotreating would increase HDS. Similarly, since reduction in the number of non-basic nitrogen compounds also translates to a decrease in total nitrogen, it is expected that selective removal of non-basic nitrogen compounds would have a positive effect on HDN. As HDA goes hand in hand with HDS and HDN, it is expected that selective removal of non-basic nitrogen compounds would also positively impact HDA as well.

Table 4.3: Nitrogen, sulfur and aromatics contents (in ppm) of the hydrotreated and hydrotreated-pretreated feed at 370°C, 8.96 MPa and 1 hr^{-1}.

Feed	Total N (ppm)	Total S (ppm)	Total A (ppm)
Hydrotreated LGO	321	1497	20845
Hydrotreated-pretreated LGO	261	1373	18885

Hydrotreating alone without prior removal of non-basic nitrogen compounds is a major industrial application used to reduce nitrogen contents in light gas oils. It can, on its own reduce the total nitrogen content by 83.7%. In the same hydrotreating conditions, with prior removal of non-basic nitrogen compounds, the nitrogen conversion increased to 86.9%. The percentage change in conversion does not represent the actual changes in ppm observed between the hydrotreated and hydrotreated-pretreated feed. As Table 4.3 shows, selective removal of non-basic nitrogen compounds led to an 18.7% (from 321 ppm to 261 ppm) decrease in total nitrogen compounds between the hydrotreated and hydrotreated-pretreated feeds. Similarly, at optimized sulfur conditions of temperature, pressure and LHSV of 370°C, 8.96 MPa and 1 hr^{-1}, respectively, hydrotreating alone without prior removal of non-basic nitrogen compounds reduced the total sulfur content by 95.1%. With prior removal of non-basic nitrogen compounds before hydrotreatment, the sulfur conversion increased to 95.5%. Again, in terms of actual changes in ppm, there was an 8.3% (from 1497 ppm to 1373 ppm) decrease in total sulfur compounds between the hydrotreated and hydrotreated-pretreated feeds. For aromatics contents, a conversion of 21.1% was measured at optimized conditions of temperature, pressure and LHSV of 370°C, 8.96 MPa and 1 hr^{-1}, respectively, without prior removal of non-basic nitrogen compounds. After prior removal, the aromatics conversion increased to 23.4%. In terms of changes in ppm, there was a 9.4% (from 20845 ppm to 18885 ppm) decrease in aromatics content between the hydrotreated and hydrotreated-pretreated feeds. To ensure nitrogen removal was due to the characteristic

performance of the polymer alone, blank tests samples were performed by mixing light gas oil with 90 mesh silicon carbide in similar ratio of 1 g of light gas oil to 4 g of silicon carbide. Silicon carbide was used because it has a comparable texture to the PGMA-DAP(3)-TENF polymer. After mixing with light gas oil for approximately 24 hours, the silicon carbide was separated from the light gas oil in similar conditions used when separating the polymer from light gas oil. This was performed in a fume hood at room temperature using a vacuum. After separation of the silicon carbide from light gas oil, nitrogen and sulfur content was measured for the separated light gas oil feed to ensure that nitrogen adsorption was solely due to the polymer beads. The nitrogen and sulfur contents before (1728 ppm and 30535 ppm respectively) and after (1721ppm and 30529 ppm respectively) the blank test showed that there was no difference in nitrogen and sulfur adsorption. This demonstrated that any difference in nitrogen and sulfur adsorption was due to the polymer beads.

These results showed that the selective removal of non-basic nitrogen compound prior to hydrotreating led to an increase in HDS, HDN and HDA. This was expected since non-basic nitrogen compounds hinder the hydrotreating process. Section 4.6 of this thesis would focuses on the effects of changing process conditions such as temperature, pressure and LHSV, on the hydrotreatment of light gas oils between the hydrotreated and hydrotreated-pretreated feeds.

4.6 Effect of Changing Process Conditions on Hydrotreating

The following sections focuses on the effects of changing process conditions of the untreated and pretreated light gas oil feed during hydrotreatment. HDS, HDN and HDA activities were measured for both feeds at similar process conditions. This was done to determine if selective removal of non-basic nitrogen compounds had an effect on changing process conditions between the hydrotreated and hydrotreated-pretreated feeds. Hydrotreatment studies were performed using

commercial NiMo/γAl$_2$0$_3$ catalyst at a temperature, pressure and LHSV range of 350 to 370°C, 8.27 to 9.65 MPa and 1 hr^{-1} to 2 hr^{-1}, respectively.

Table 4.4 and 4.5 show the nitrogen, sulfur and aromatics conversions for the hydrotreated and the hydrotreated-pretreated feeds. These results will be analyzed and compared in the subsequent sections.

Table 4.4: Nitrogen, sulfur and aromatics conversions for hydrotreated-pretreated light gas oil using NiMo/γAl$_2$0$_3$ catalyst.

Temperature (˚C)	Pressure (MPa)	LHSV (hr^{-1})	Nitrogen Conversion (%)	Sulfur Conversion (%)	Aromatics Conversion (%)
350	8.27	1	72.5	90.8	18.7
360			76.3	91.1	20.1
370			79.1	91.2	20.8
350	8.96		82.3	91.7	21.4
360			83.9	94.1	22.6
370			86.9	95.5	23.4
350	9.65		80.9	91.2	20.9
360			82.7	92.7	21.7
370			84.3	93.9	22.3

Table 4.5: Nitrogen, sulfur and aromatics conversions for hydrotreated light gas oil (without pretreatment) using NiMo/γAl$_2$0$_3$ catalyst

Temperature (˚C)	Pressure (MPa)	LHSV (hr^{-1})	Nitrogen Conversion (%)	Sulfur Conversion (%)	Aromatics Conversion (%)
350	8.27	1	71.5	90.2	17.9
360			73.3	90.7	19.3
370			77.5	91.1	19.6
350	8.96		79.4	91.2	20.2
360			81.3	93.6	21.2
370			83.7	95.1	21.5
350	9.65		80.1	92.6	20.1
360			80.9	92.8	20.6
370			81.5	93.8	21.1
350	8.27	2	52.4	89.7	16.9
360			61.4	90.1	18.1
370			63.5	90.8	18.4
350	8.96		59.1	90.2	18.5
360			66.6	91.2	19.1
370			70.8	92.5	19.9
350	9.65		58.1	90.1	18.4
360			64.8	91.1	19.2
370			70.2	91.8	19.6

4.6.1 Effects of Temperature on the Hydrotreated and Hydrotreated-pretreated Feed

Increase in temperature is generally expected to increase stability of the catalyst, thereby playing a major role in increasing HDS, HD and HDA reactions (Gruia et al., 2006). This same trend is expected in the hydrotreated and hydrotreated-pretreated feed. Results in Tables 4.4 and 4.5 show that irrespective of prior selective removal of non-basic nitrogen compounds, increase in temperature increased the hydrotreatment activity for both feeds. The highest hydrotreatment activity for both the hydrotreated feed and hydrotreated-pretreated feed was observed at a temperature of 370°C, pressure of 8.96 MPa and LHSV of 1hr^{-1}. Figures 4.4, 4.5 and 4.6 show the nitrogen conversion between the hydrotreated and hydrotreated-pretreated feeds with respect to changing temperature. Other parameters such as pressure, hydrogen/oil ratio, and LHSV were kept constant for both feeds.

Figure 4.4: Effects of temperature on nitrogen conversion for hydrotreated and hydrotreated-pretreated LGO feeds at LHSV of 1 hr^{-1} and pressure of 8.27 MPa.

Figure 4.5: Effect of temperature on nitrogen conversion for hydrotreated and hydrotreated-pretreated LGO feeds at LHSV of 1 hr^{-1} and pressure of 8.96 MPa.

Figure 4.6: Effect of temperature on nitrogen conversion for hydrotreated and hydrotreated-pretreated LGO feeds at LHSV of 1 hr^{-1} and pressure of 9.65 MPa.

Figures 4.4, 4.5 and 4.6 show that regardless of prior selective removal of non-basic nitrogen compounds, increase in temperature led to better hydrotreatment activity for both the hydrotreated and hydrotreated-pretreated feeds. However, between both feeds, nitrogen

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conversions were consistently higher for the hydrotreated-pretreated feed. As Figure 4.4 shows, the nitrogen conversions at similar pressure and LHSV of 8.27 MPa and 1 hr^{-1}, respectively, was higher for the hydrotreated-pretreated feed compared to the hydrotreated feeds. Comparing the two feeds, the highest nitrogen conversion for the hydrotreated-pretreated feed was at 79.1% compared to 77.5% observed in the hydrotreated feed. It was interesting to note that in the hydrotreated feed, higher nitrogen conversion difference of 4.2% (77.5 to 73.3%) was experienced in the tail end of the temperature range from 360°C to 370°C; however, in the hydrotreated-pretreated feed, a higher nitrogen conversion difference of 4% (72.5 to 76.3%) was observed earlier on in the temperature range from 350°C to 360°C. Laredo et al. (2003) proposed that the inhibiting performance of nitrogen compounds is largely due to the initial strong adsorption experienced at the onset of hydrotreatment. These results show that prior removal of non-basic nitrogen compounds could be the reason for the higher conversions early on in the hydrotreatment process. Following the same trend of higher temperature yielding higher conversions, similarly, at pressure of 8.96 and 9.65 MPa and LHSV of 1 hr^{-1}, the highest nitrogen conversions for the hydrotreated-pretreated feed was higher at 86.9 and 84.3%, respectively compared to 83.7 and 81.5%, respectively observed in the hydrotreated feeds.

The sulfur conversions between the hydrotreated and hydrotreated-pretreated feeds were also studied, and are shown in Figures 4.7, 4.8 and 4.9 with respect to changes in temperature. Similarly, other parameters such as pressure, hydrogen/oil ratio, and LHSV were kept constant for both feeds.

Figure 4.7: Effect of temperature on sulfur conversion for hydrotreated and hydrotreated-pretreated LGO feeds at LHSV of 1 hr^{-1} and pressure of 8.27 MPa.

Figure 4.8: Effect of temperature on sulfur conversion for hydrotreated and hydrotreated-pretreated LGO feeds at LHSV of 1 hr^{-1} and pressure of 8.96 MPa.

Figure 4.9: Effect of temperature on sulfur conversion for hydrotreated and hydrotreated-pretreated LGO feeds at LHSV of 1 hr^{-1} and pressure of 9.65 MPa.

As shown in Figures 4.7, 4.8 and 4.9, increase in temperature led to better sulfur conversions for both the hydrotreated and hydrotreated-pretreated feeds. However, when both feeds were at similar process conditions, sulfur conversion was consistently higher for the hydrotreated-pretreated feed. For both feeds, maximum sulfur conversion were observed at a temperature, pressure and LHSV of 370°C, 8.96 MPa and 1 hr^{-1}, respectively. At a temperature of 370°C and pressure condition of 8.27 to 9.65 MPa, the highest sulfur conversion for the hydrotreated-pretreated feed was recorded at 91.2, 95.5 and 93.9%, respectively, compared to 91.1, 95.1 and 93.8 %, respectively, in the hydrotreated feeds. Although increases in sulfur conversions were not as substantial as nitrogen conversions, there was still a higher conversion observed at each temperature range from 350°C to 370°C for the hydrotreated-pretreated feeds, demonstrating that prior removal of non-basic nitrogen compounds had a positive impact on sulfur conversion.

Similarly, Figures 4.10, 4.11 and 4.12 show the aromatic conversions between the hydrotreated and hydrotreated-pretreated feeds with respect to changes in temperature while keeping other parameters such as pressure, hydrogen/oil ratio, and LHSV constant.
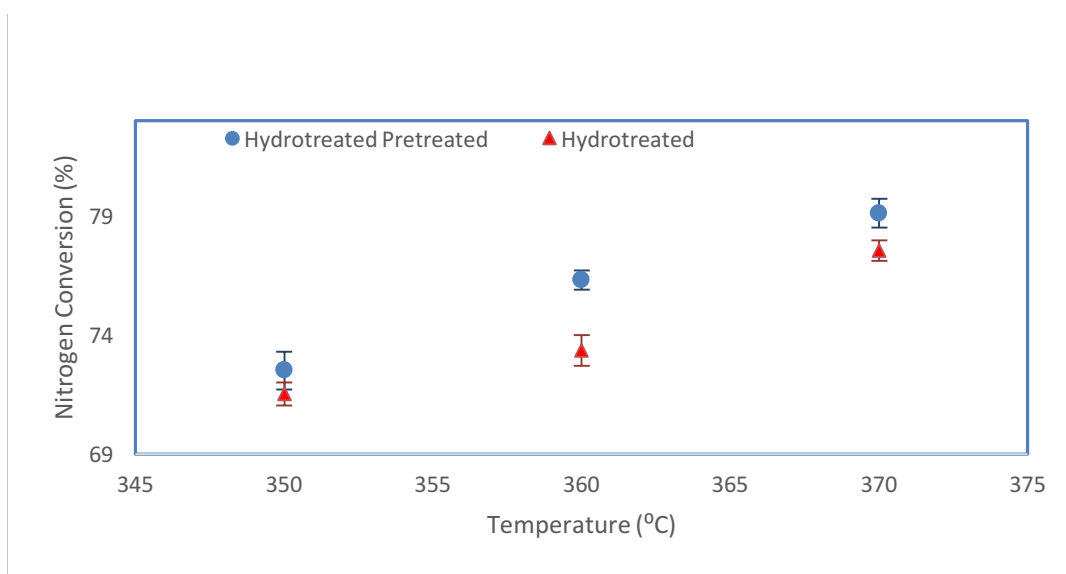
Figure 4.10: Effect of temperature on aromatics conversion for hydrotreated and hydrotreated-pretreated LGO feeds at LHSV of 1 hr⁻¹ and pressure of 8.27 MPa.

Figure 4.11: Effect of temperature on aromatics conversion for hydrotreated and hydrotreated-pretreated LGO feeds at LHSV of 1 hr^{-1} and pressure of 8.96 MPa.

Similar to nitrogen and sulfur conversions, Figures 4.10, 4.11 and 4.12 shows that an increase in temperature led to better aromatic conversions for both the hydrotreated and hydrotreated-pretreated feeds. Again, aromatics conversions were consistently higher for the hydrotreated-pretreated feed. Comparing both feeds, maximum aromatics conversion was observed at a temperature of 370°C, pressure of 8.96 MPa and 1 hr^{-1}, respectively.
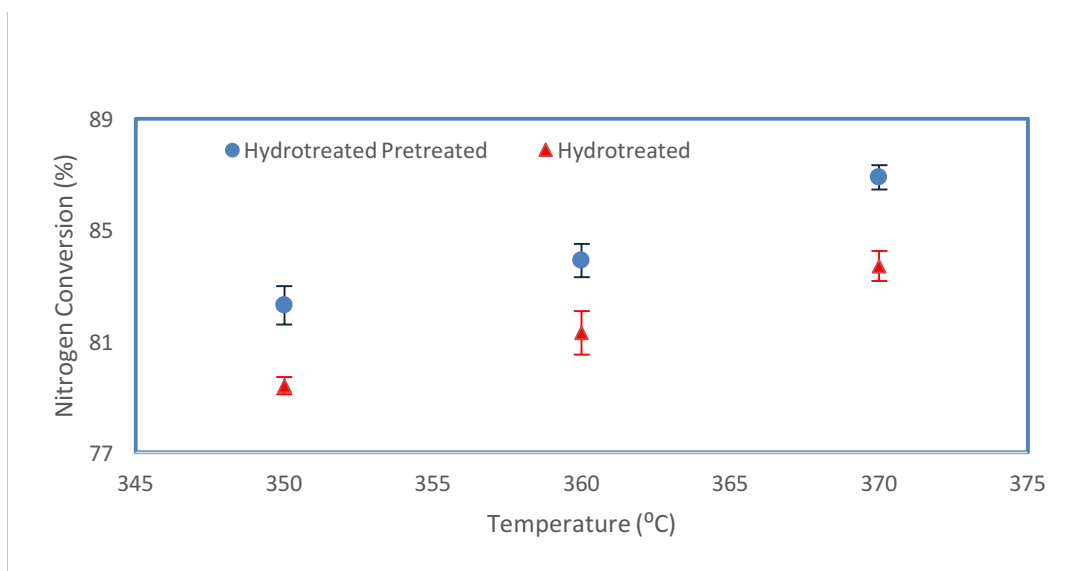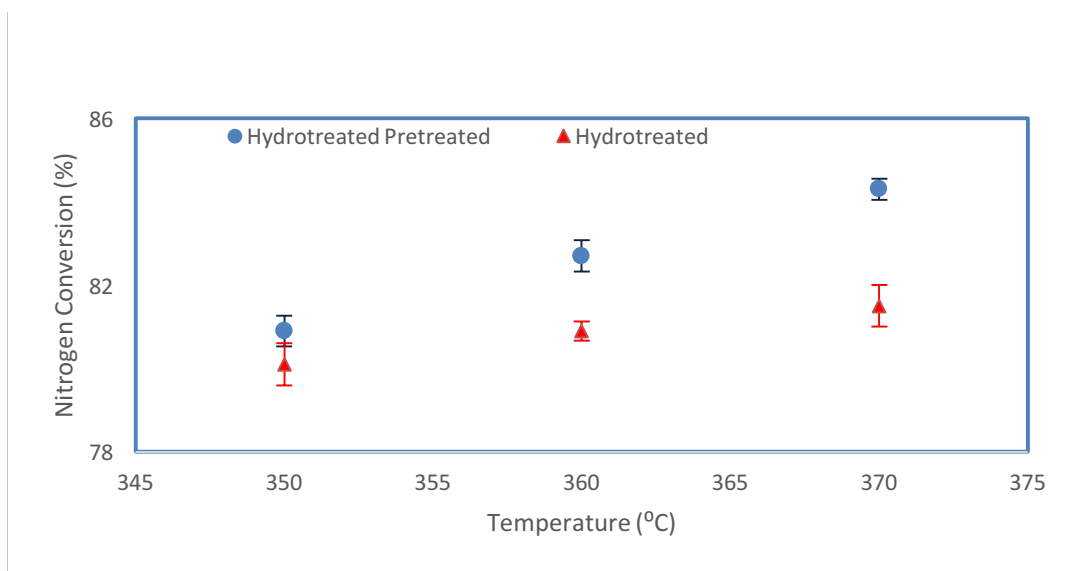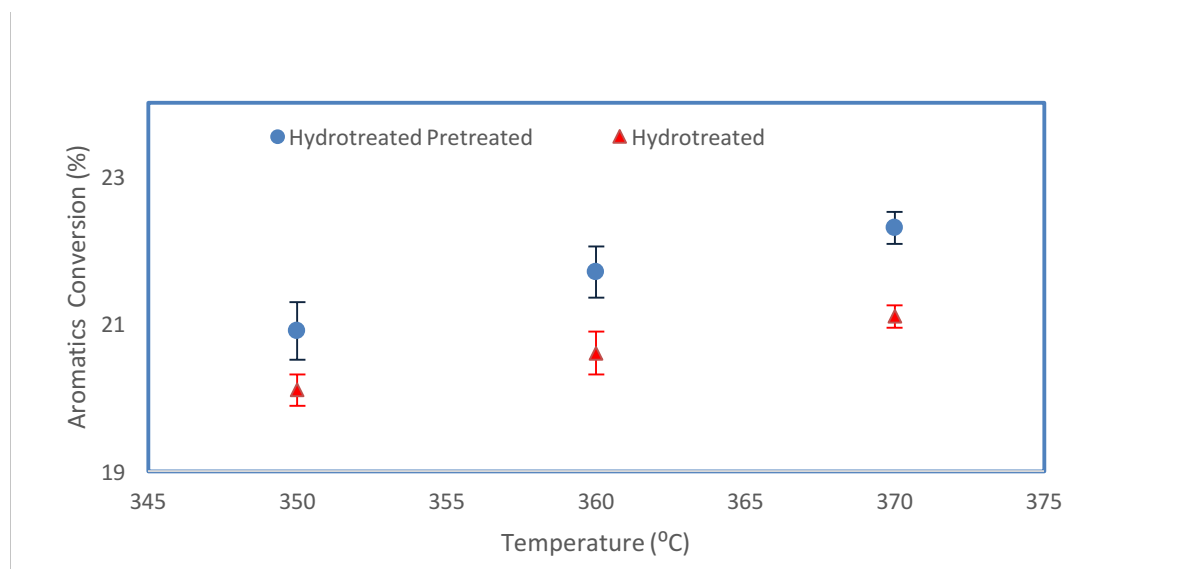
Figure 4.12: Effect of temperature on aromatics conversion for hydrotreated and hydrotreated-pretreated LGO feeds at LHSV of 1 hr^{-1} and pressure of 9.65 MPa.

At a temperature of 370°C and pressure condition of 8.27 to 9.65 MPa, the highest aromatics conversion for the hydrotreated-pretreated feed was measured at 20.8, 23.4 and 22.3%, respectively compared to 19.6, 21.5 and 21.1%, respectively in the hydrotreated feeds. This shows that at similar process conditions in both feeds with respect to increasing temperature, the selective removal of non-basic nitrogen compounds had a positive effect on aromatics conversions. It was important to note that the trends in aromatics conversions were very similar to nitrogen conversions as the highest difference in conversion for both hydrotreated feeds was experienced at the lower temperature range of 350°C to 360°C.

Figures 4.4 to 4.12 demonstrate that an increase in temperature increased nitrogen, sulfur and aromatics conversions regardless of prior selective removal of non-basic nitrogen. However, pretreatment of the light gas oil by selectively removing non-basic nitrogen compounds before hydrotreating led to even higher nitrogen, sulfur and aromatics conversion. The effect of pressure on hydrotreatment activity for the hydrotreated and hydrotreated-pretreated feeds is discussed in the Section 4.6.2.

4.6.2 Effects of Pressure on the Hydrotreated and Hydrotreated-pretreated Feed

Increase in pressure using NiMo/γAl$_2$0$_3$ commercially available catalyst has been known to increase hydrodesulfurization and hydrodenitrogenation reactions and has minimal effects on hydrodearomatization (Mann et al., 1987). Similarly, while keeping other parameters, such as temperature, and LHSV constant for both the hydrotreated and hydrotreated-pretreated feeds, the nitrogen, sulfur and aromatics conversions were determined with respect to changes in pressure and are shown in Figures 4.13, 4.14 and 4.15. Conversion at temperature of 370°C was used at all pressure conditions since that was highest conversion determined for nitrogen, sulfur and aromatics.

Figure 4.13 shows the nitrogen conversions at 370°C, 1 hr^{-1} and a pressure range of 8.27 to 9.65 MPa. It can be noted that as pressure increased up until 8.96 MPa, the nitrogen conversion also increased for both the hydrotreated and hydrotreated-pretreated feeds. However, at 9.65 MPa, the nitrogen conversion dropped slightly but was still higher than the conversions at 8.27 MPa. It was important to note that at all pressure conditions, the hydrotreated-pretreated feed had higher nitrogen conversions compared to the hydrotreated feed. For both feeds, the difference in nitrogen conversions was also higher between pressures ranges of 8.27 to 8.96 MPa compared to the conversions between 8.96 MPa to 9.65 MPa. Nitrogen conversions followed the following pressure trend, 8.27 MPa < 9.65 MPa < 8.96 MPa, with highest conversions at 8.96 MPa and lowest conversions at 8.27 MPa.

Based on these results, it is apparent that although nitrogen conversions reduced at 9.65 MPa, selective removal of non-basic nitrogen compounds still led to higher nitrogen conversions at all pressure conditions compared to the hydrotreated feed. Similarly, Figure 4.14 shows the sulfur conversions at 370°C, 1 hr^{-1} and a pressure range of 8.27 to 9.65 MPa for the hydrotreated

and hydrotreated-pretreated feed. It can be noted that sulfur conversions slightly increased with

each increase in pressure for both feeds.
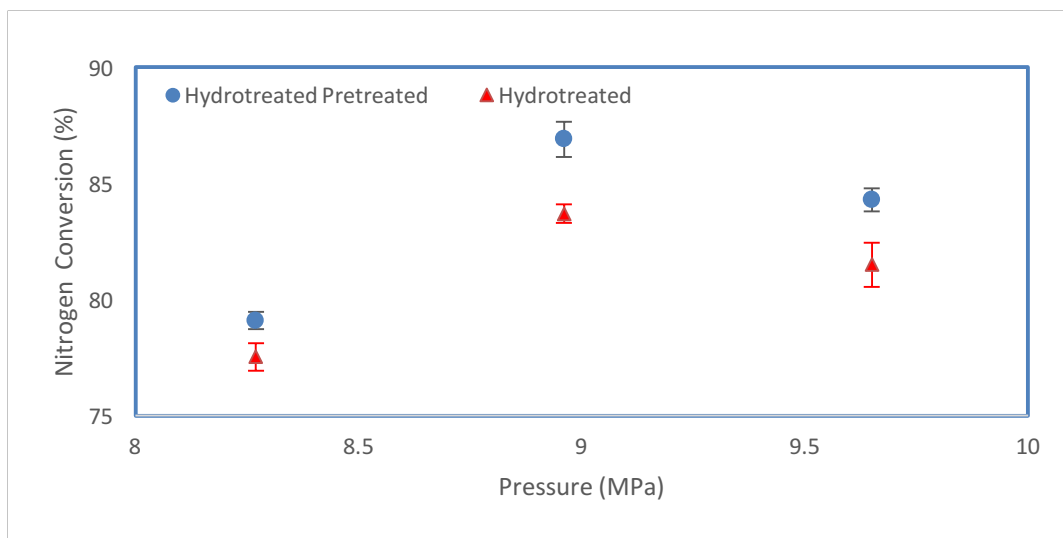
Figure 4.13: Effect of pressure on nitrogen conversion for hydrotreated and hydrotreated-pretreated LGO feeds at LHSV of 1 hr^{-1} and temperature of 370°C.
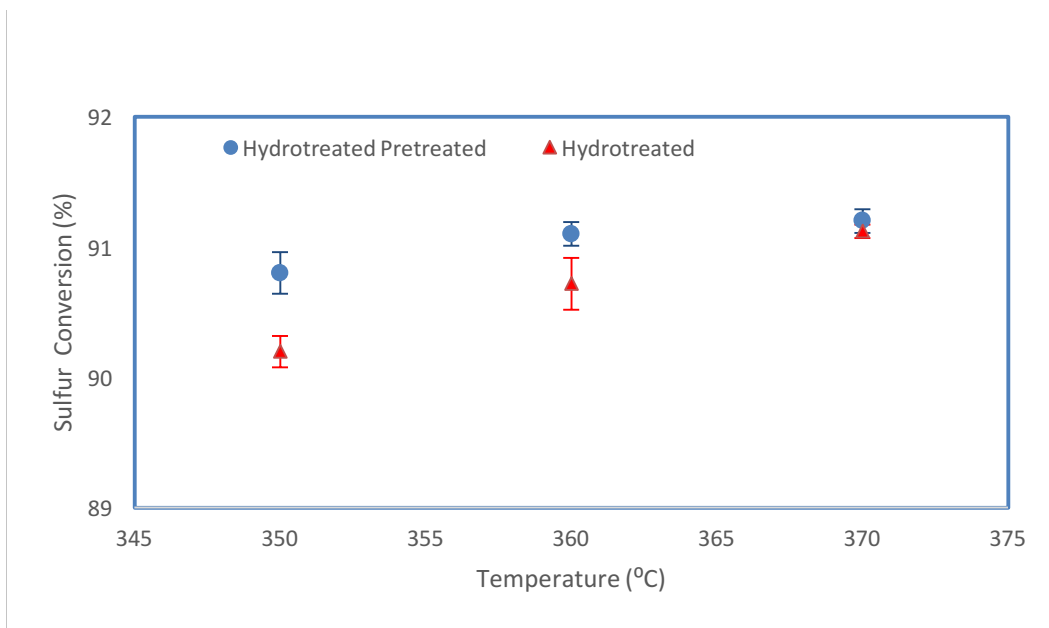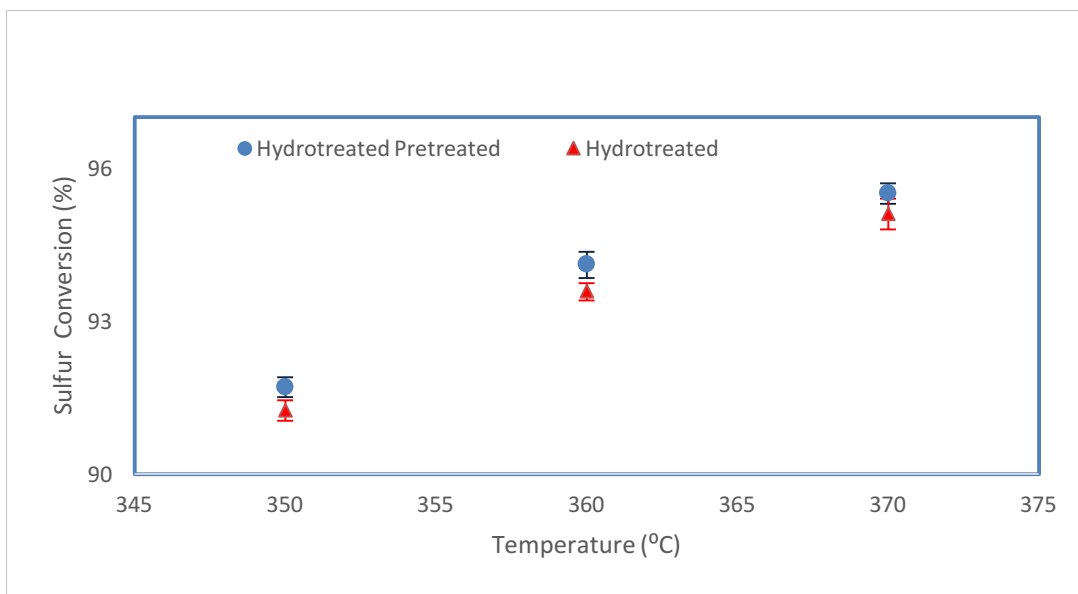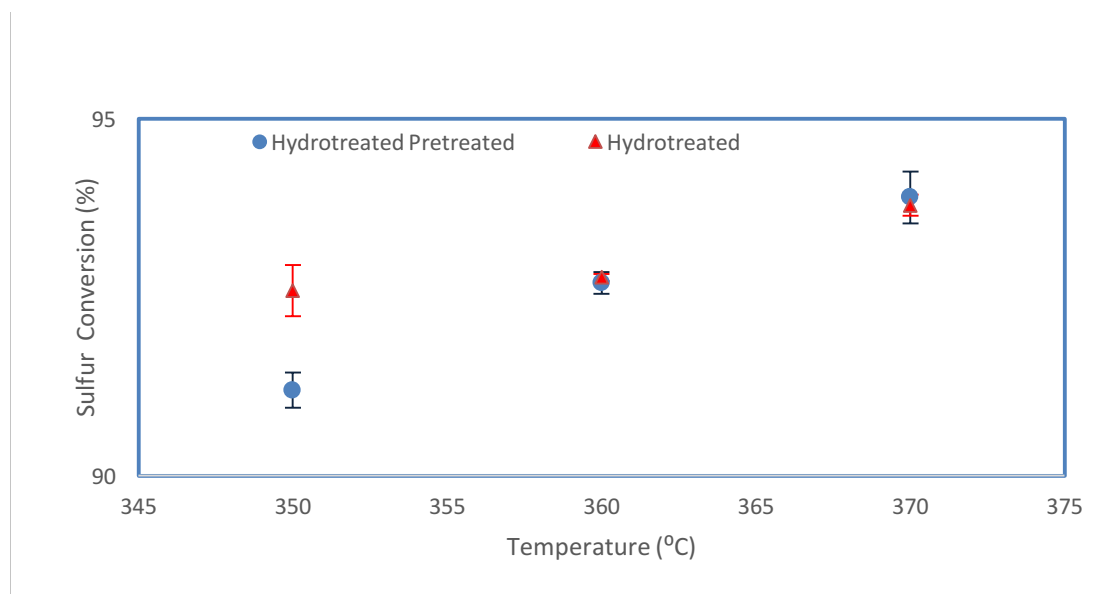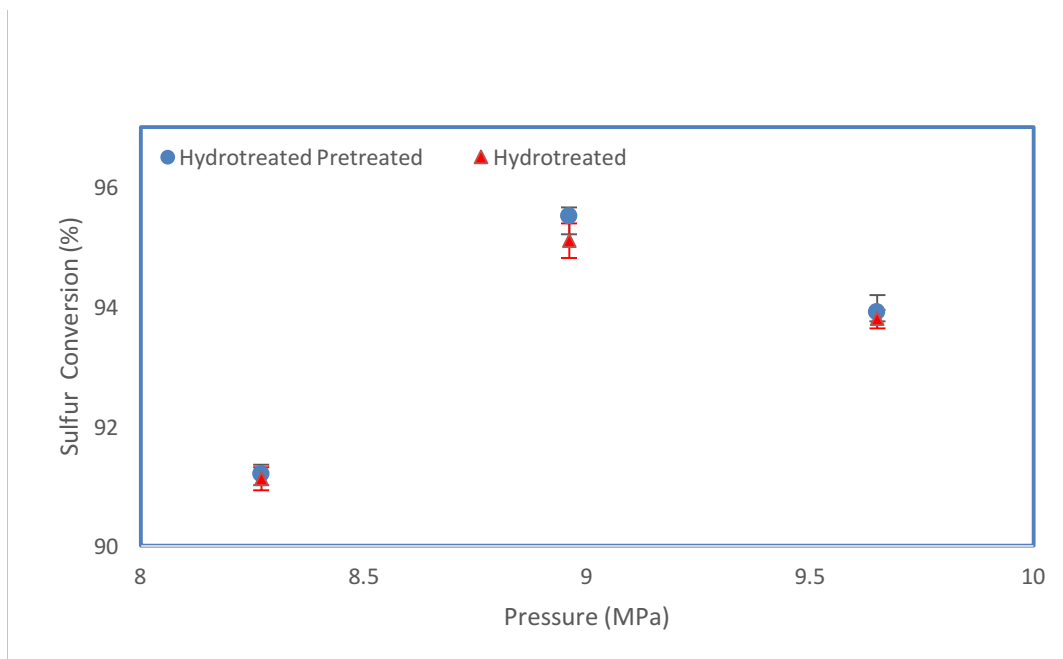

Figure 4.14: Effect of pressure on sulfur conversion for hydrotreated and hydrotreated-pretreated LGO feeds at LHSV of 1 hr^{-1} and temperature of 370°C.
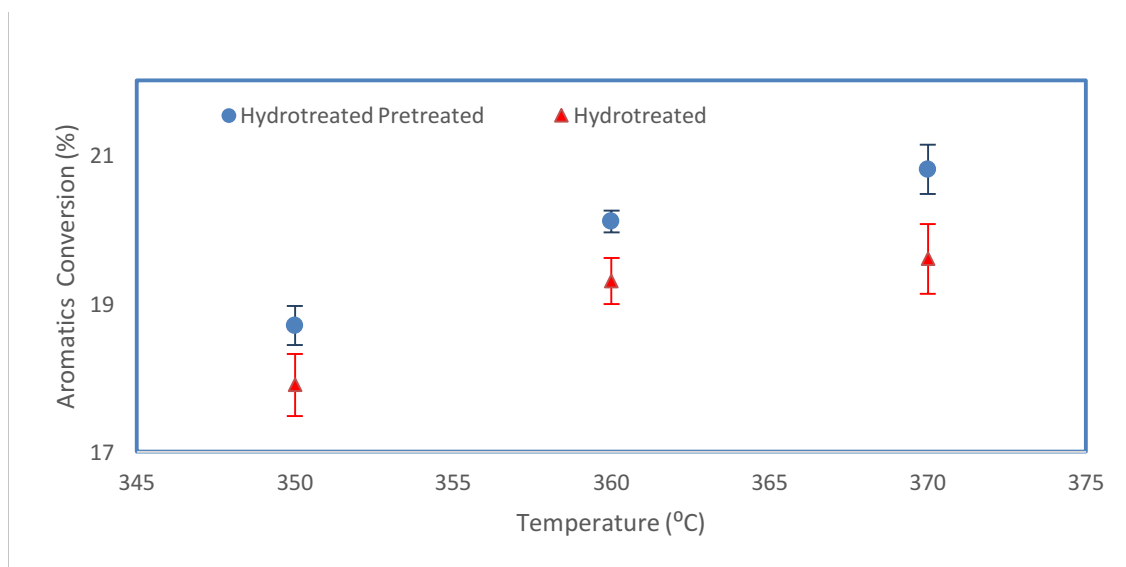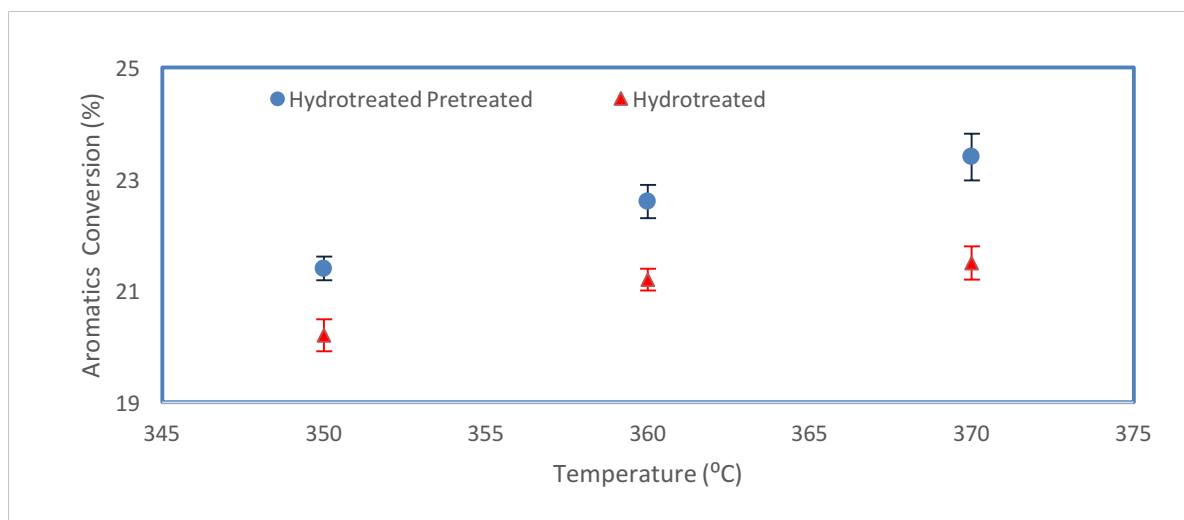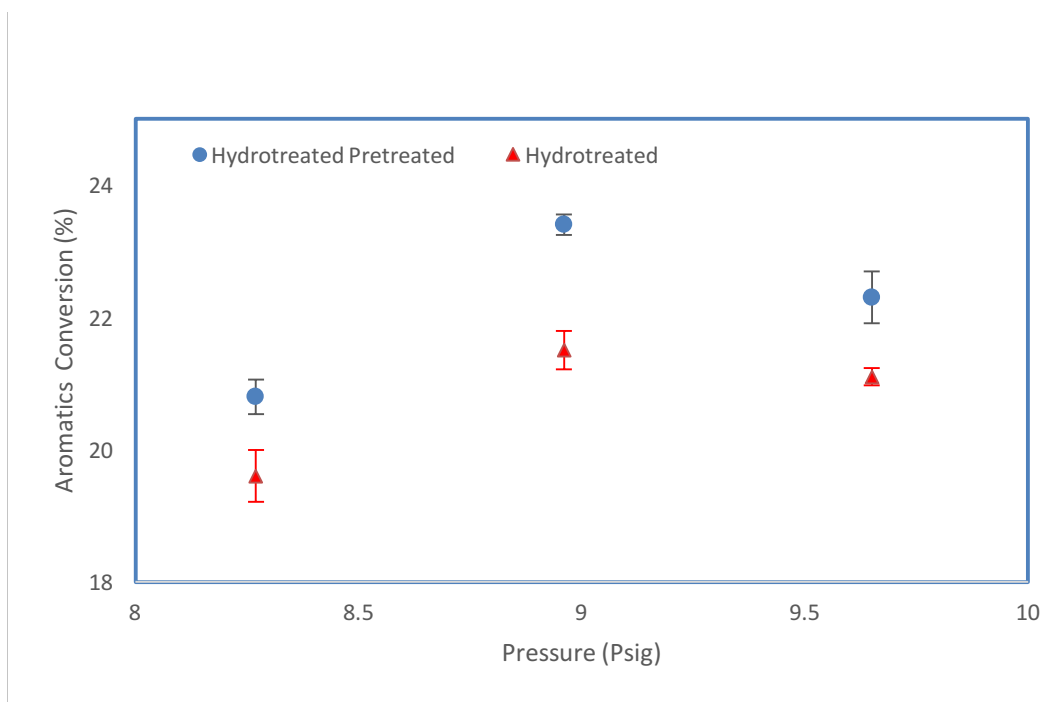
Figure 4.15: Effect of pressure on aromatics conversion for hydrotreated and hydrotreated-pretreated LGO feeds at LHSV of 1 hr^{-1} and temperature of 370°C.

However, the increase was minimal compared to the nitrogen conversion. A reason for this might lie with the catalyst been used, NiMo/γAl$_2$0$_3$, which is documented in the literature to increase both HDS and HDN with increasing pressure; however, HDN improvements were more significant than HDS, as the NiMo/γAl$_2$0$_3$ catalyst is more sensitive to pressure than temperature (Mann et al., 1987). This explains the slightly significant increase in HDS that is observed with increase in pressure. Although, change in pressure only led to a slight increase in sulfur conversion for both feeds. It was important to note that at the process conditions, the sulfur conversion for the hydrotreated-pretreated feed was higher than the hydrotreated feed. This also signifies that selective removal of non-basic nitrogen compounds has a positive effect on sulfur conversions.

Figure 4.15 shows the aromatics conversions at 370°C, 1 hr^{-1} and a pressure range of 8.27 to 9.65 MPa for the hydrotreated and hydrotreated-pretreated feed. Again, the aromatics conversion trend is very similar to the nitrogen conversion trend with respect to change in pressure.

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There was an increase in aromatics conversions up until 8.96 MPa, after which conversion dropped for both the hydrotreated and hydrotreated-pretreated feeds. Similar to the nitrogen trends, increasing pressure up to 8.96 MPa generally increased both feed conversions; however, the hydrotreated-pretreated feeds had higher conversions compared to the hydrotreated feeds at all pressure conditions. Aromatics conversions also follow similar trends as nitrogen conversions with respect to change in pressure: 8.27 MPa < 9.65 MPa < 8.96 MPa. Similar to nitrogen and sulfur conversions, selective removal of non-basic nitrogen compounds led to higher conversions in the hydrotreated-pretreated feeds compared to the hydrotreated feed. This shows that selective removal of non-basic nitrogen compounds has a positive effect on aromatic conversions.

4.6.3 Effects of LHSV on the Hydrotreated Feed

It has been demonstrated that as LHSV increases, there is a decrease in nitrogen, sulfur and aromatics conversion, due to decrease in contact time (Mann et al., 1987). LHSV studies at 1 and 2 hr^{-1} were performed on the hydrotreated feed and at temperature and pressure ranges, of 350 to 370°C and 8.27 to 8.96 MPa, respectively. It can be seen from Table 4.5 that high LHSV led to a significant decrease in nitrogen, sulfur and aromatics conversions. For the hydrotreated feeds, the highest nitrogen, sulfur and aromatics conversions observed at LHSV of 2 hr^{-1} were 70.8, 92.5 and 19.9%, respectively, which were significantly lower than the highest conversions at LHSV of 1hr^{-1} at 83.7, 95.1 and 21.5%, respectively.

4.6.4 Catalyst Stability Study on NiMo/γAl$_2$O$_3$ Catalyst

A test for the stability of the NiMo/γAl$_2$O$_3$ catalyst was performed to determine its stability over extended time periods. To achieve this, hydrotreated samples which were analyzed for sulfur and nitrogen content were collected every 12 hours, over a period of 1.5 days The time on-stream for this study is shown in Figure B.2 in the appendix of this thesis. The precoking period for three

days was used to attain a steady-state conversion for sulfur and nitrogen. Figure 4.16 shows the results of the stability study. It can be observed that the NiMo/γAl$_2$O$_3$ commercial catalyst attained steady-state conversions at 86.9% for nitrogen compounds and 95.5% for sulfur compounds respectively, with average error margins of $\pm$ 1 wt%. After the hydrotreatment study on the pretreated feed, repeat hydrotreatment studies at similar process conditions as the precoking, gave a conversion at 86.2% for nitrogen compounds and 95.1% for sulfur compounds respectively, with average error margins of $\pm$ 1 wt%. It can be determined from these results, that the commercial catalyst was stable throughout the course of the hydrotreatment study and did not undergo any significant catalyst deactivation.
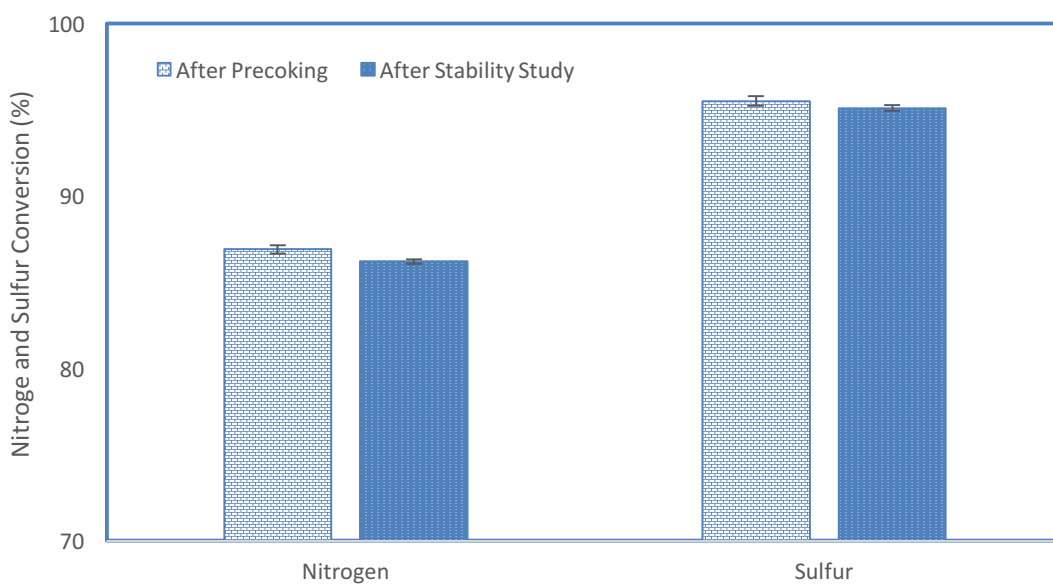
Figure 4.16: Catalyst Stability Study on the hydrotreated-pretreated LGO feed at LHSV of 1hr^{-1} Temperature of 370°C and Pressure of 8.96MPa.

4.7 Statistical Significance of the Pretreatment of Light Gas Oil

The SPSS tool was used to compare nitrogen, sulfur and aromatic conversions before and after the selective removal of non-basic nitrogen compounds. This was done to determine the effectiveness of selectively removing non-basic nitrogen compounds in the hydrotreatment of light

gas oil. The test choice for nitrogen conversions determined the effects of the pre-treatments of light gas oil on process parameters, provided all process conditions such as temperature, pressure and LHSV were identical during hydrotreatment for both the untreated and pre-treated feeds. This signified that the only difference in both feeds was the pre-treatment factor which was represented by before and after/ matched pairs sample and analyzed using a two-sample t-test for dependent samples. The basis for the two test assumptions assumed that the data was from a simple random sample and both samples (untreated and pretreated) were matched pairs which was implicit by design. Nitrogen conversions for both samples were tested for normal distribution and it was determined that at a 5% level of significance, there was insufficient evidence to reject the assumption that the distribution of the nitrogen conversions with or without pre-treatments were normal with each having a p-value of 0.746 and 0.680, respectively. The test of normality values is shown in Table 4.6. Based on the results from this test, the hypothesis to be tested between the nitrogen conversions before and after pre-treatment was defined:

H_O: There is no difference between the true mean nitrogen conversions with and without pre-treatment

H_A: The true mean pre-treated nitrogen conversion are greater than the true mean nitrogen conversion scores without treatment

Table 4.7 shows the paired sample test for nitrogen conversions with and without pretreated of light gas oils. At the 5% level of significance, the evidence stated to reject the null hypothesis ($p = 0.013$) concluding that the interrelationships between process parameters within the true mean pre-treated nitrogen conversions were greater than the true mean nitrogen conversions without treatment. Comparing these results to the actual sample results stated in 4.5 of this thesis, it is evident that nitrogen conversions before and after pretreatment were significant. The paired sample

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test for nitrogen conversions also validates that the difference in nitrogen conversion between the hydrotreated and hydrotreated-pretreated feed is statistically significant.

Similarly, a test choice for sulfur conversion determined the effects of the pre-treatments of light gas oils on process parameters provided all other conditions such as temperature, pressure and LHSV during hydrotreatment were identical for both the pre-treated and untreated feeds. This signified that the only difference in both feeds was the pre-treatment factor which was represented by before and after/ matched pairs sample and analyzed using a two-sample t-test for dependent samples. The basis for the two test assumptions assumed that the data was implicit by design since the data was from a simple random sample and both samples (untreated and pretreated) were matched pairs with the only difference in both feeds being the pre-treatment factor. Sulfur conversions for both samples were tested for normal distribution and it was determined that at a 5% level of significance, there was insufficient evidence to reject the assumption that the distribution of the sulfur conversions with or without pre-treatments were normal with each having a p-value of 0.344 and 0.603, respectively. Table 4.8 shows the test for normality for sulfur conversions with and without pretreatment of light gas oil.

Based on these results the hypothesis to be tested between the sulfur conversions before and after pre-treatment was defined:

H_O: There is no difference between the true mean sulfur conversions with and without pre-treatment

H_A: The true mean pre-treated sulfur conversion is greater than the true mean nitrogen conversion scores without treatment

Table 4.9 shows the paired sample test for sulfur conversions with and without pretreated of light gas oils. At the 5% level of significance, there was insufficient evidence to reject the null

hypothesis (p = 0.053). Suggesting that there is no evidence to conclude that the true mean pre-treated sulfur conversion is greater than the true mean sulphur conversion scores without pre-treatment. Comparing these results to the actual sample results stated in section 4.5 of this thesis, it is evident that the difference in sulfur conversions between the pretreated and untreated feed was minimal compared to the nitrogen conversions. The results from the sample t test also validates the fact that the difference in sulfur conversion between the hydrotreated and hydrotreated-pretreated feed is statistically insignificant.

Similarly, a test choice for aromatics conversion determined the effects of the pre-treatments of light gas oils on process parameters provided that all process conditions such as temperature, pressure and LHSV during hydrotreatment were identical for both the pre-treated and untreated feeds stating that the only difference in both feeds is the pre-treatment factor. Aromatics conversions for both samples were tested for normal distribution and it was determined that at a 5% level of significance, there was insufficient evidence to reject the assumption that the distribution of the aromatics conversions with or without pre-treatments were normal with each having a p-value of 0.482 and 0.772, respectively as shown in Table 4.10.

Based on the results from the test of normality, the hypothesis to be tested was defined:

H_O: There is no difference between the true mean aromatics conversions with and without pre-treatment

H_A: The true mean pre-treated aromatics conversion are greater than the true mean aromatic conversion without treatment.

Table 4.11 shows the paired sample test for aromatic conversions with and without pretreated of light gas oils. At the 5% level of significance, there was insufficient evidence to reject the null hypothesis (p = 0.155).

Table 4.6: Test for normality for nitrogen conversions with and without pretreatment of light gas oil.

Tests of Normality						
Feed	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Nitrogen Conversion with Pretreatment	0.243	3.000	.	0.972	3.000	0.680
Nitrogen Conversion without Pretreatment	0.227	3.000	.	0.982	3.000	0.746

a. Lilliefors Significance Correction

Table 4.7: Paired sample test for nitrogen conversions with and without pretreatment of light gas oil.

Paired Samples Test									
		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	**Nitrogen Conversions Without Pretreatment** **- Paired with-** **Nitrogen Conversions With Pretreatment**	-2.166	0.423	0.244	-3.218	-1.114	-8.859	2.000	0.013

Suggesting that there was no evidence to conclude that the true mean pre-treated aromatic conversion were greater than the true mean aromatic conversion without treatment. Comparing these results to the actual results of aromatics conversion between the pretreated and untreated feeds in this thesis, it was evident that although aromatics conversions were slightly higher than sulfur conversions, they were lower in comparison to the nitrogen conversions.

The results from the sample t test also validates that fact that the difference in aromatic conversions between the hydrotreated and hydrotreated-pretreated feed is statistically insignificant. It was notable that although the statistical tests for the effects of pre-treatment on conversion rate was only significant for nitrogen, results from chapter 4 of thesis shows that there was a positive difference in nitrogen, sulfur and aromatics conversions between the hydrotreated-pretreated feed compared to the hydrotreated feed alone. This signifies that the selective removal of non-basic nitrogen compounds improved hydrotreatment activity. A possibility for the lack of statistical significance for sulfur and aromatics conversion could be speculated to the small sample size and consequent reduction of statistical power might be explanatory for the failure of the difference in conversion.

Table 4.8: Test for normality for sulfur conversions with and without pretreatment of light gas oil.

Tests of Normality						
Feed	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Sulfur Conversion with Pretreatment	0.261	3.000	.	0.957	3.000	0.603
Sulfur Conversion without Pretreatment	0.318	3.000	.	0.887	3.000	0.344

a. Lilliefors Significance Correction

Table 4.9: Paired sample test for sulfur conversions with and without pretreatment of light gas oil.

Paired Samples Test									
		Paired Differences					t	df	Sig. (2 tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	**Sulfur Conversions Without Pretreatment - Paired with- Sulfur Conversions With Pretreatment**	-1.766	0.735	0.424	-3.593	.059	-4.162	2.000	0.053

Table 4.10: Test for normality for aromatics conversions with and without pretreatment of light gas oil.

Tests of Normality						
Feed	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Aromatics Conversion with Pretreatment	0.221	3.000	.	0.986	3.000	0.772
Aromatics Conversion without Pretreatment	0.288	3.000	.	0.928	3.000	0.482

a. Lilliefors Significance Correction

Table 4.11: Paired sample test for aromatics conversions with and without pretreatment of light gas oil.

Paired Samples Test									
		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Aromatics Conversions Without Pretreatment - Paired with- Aromatics Conversions With Pretreatment	-1.220	0.944	0.545	-3.566	1.126	-2.237	2.000	0.155

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The main objective of this thesis was to study the effect of the selective removal of non-basic nitrogen compounds in the hydrotreatment of light gas oil. To achieve this, PGMA-DAP(3)-TENF polymer that is capable of selectively removing non-basic nitrogen compounds was synthesized, characterized and used for adsorption studies with light gas oil. Hydrotreatment studies at varying process conditions were monitored before and after pretreatment to assess the performance of the pretreated light gas oil. In addition, bulk polymer mass reusability was studied by monitoring polymer activity before and after regeneration studies. This section focuses on the key conclusions drawn from the results obtained in this thesis as well as recommendations for future studies.

5.1 Conclusions

A polymer support poly(glycidyl methacrylate-co-ethylene glycol methacrylate) (PGMA-co-EDGMA), a π-acceptor moiety (2, 4, 5, 7-tetranitroflorenone, TENF) and a three-(diaminopropane, DAP (3)) linker was synthesized to create a PGMA-DAP(3)-TENF polymer. Characterization studies were performed on the polymer to ensure that physical and chemical properties of the bulk polymer were consistent with the batch scale. The polymer was adsorbed with light gas oil to selectively remove the non-basic nitrogen compounds before it was hydrotreated. Results from this thesis showed that the PGMA-DAP (3) –TENF polymer is indeed capable of selectively removing non-basic nitrogen compounds and led to improvements in HDN, HDS and HDA. While selectively removing non-basic nitrogen compounds was expected to have the most significant effect on HDS, results in this thesis show that nitrogen had the highest removal, followed by aromatics and then sulfur. Regeneration study showed that although the

polymer was reusable, nitrogen adsorption was consistently reduced with each regeneration, showing that, regeneration reduced polymer activity. Pilot scale production of the polymer also signified the possibility of commercial application of the polymer to selectively remove non-basic nitrogen compounds on an industrial scale. Regeneration of the polymer multiple times had no effect on sulfur and aromatics contents.

Without hydrotreatment, the polymer selectively removed 24.9% of non-basic nitrogen compounds which led to a 10.5% decrease in total nitrogen content and 6.8% decrease in total aromatics content. There was no change in the sulfur content before and after the pretreatment of light gas oil. Hydrotreatment before and after pretreatment of light gas oil showed that prior selective removal of non-basic nitrogen compounds led to 18.7, 8.3 and 9.4% decrease in total nitrogen, sulfur and aromatics contents respectively. The effect of process conditions such as temperature, pressure and LHSV on the hydrotreated-pretreated and hydrotreated feeds showed that nitrogen, sulfur and aromatic conversions of the hydrotreated-pretreated feeds was always higher than the hydrotreated feeds alone. Increase in temperature, increase in pressure (up to 8.96 MPa), and decrease in LHSV favored both the hydrotreated and hydrotreated-pretreated feeds, however, the conversions for the hydrotreated-pretreated feed were consistently always higher.

Data obtained from hydrotreatment of pretreated and untreated feeds were analyzed and compared using a paired sample t-test. The statistical test showed that although there was an increase in nitrogen, sulfur and aromatics conversion, only nitrogen conversions were statistically significant. According to the t-test, increase in sulfur and aromatics conversions due to the pretreatment of the light gas oil were not statistically significant.

5.2 Recommendations

Based on the results observed in this thesis, the recommendations below are proposed for additional studies.

1. The effectiveness of the PGMA-DAP(3)-TENF polymer could also be tested on different feedstocks such as naphtha and heavy gas oil to determine how change in feedstock affects adsorption studies.

2. The polymer PGMA-DAP(3)-TENF was used in this thesis on the basis of having the highest nitrogen adsorption on a batch scale. However, scaling up the polymer reduced the nitrogen adsorption. Studies on how scaling up a polymer affects polymer activity should also be considered.

3. In this thesis, the hydrotreatment studies were completed using a commercial NiMo/α-Al$_2$O$_3$ catalyst. It is highly recommended that additional hydrotreatment studies be performed using different catalyst compositions such as bimetallic catalysts containing CoMo, NiW and CoW to compare their effectiveness with NiMo/ α-Al$_2$O$_3$ catalysts.

4. It is recommended to investigate further into the reasons for the decrease in performance following regeneration. This thesis focused on physical (BET) and chemical(FTIR) differences between the fresh polymer and regenerated feeds. More insights into the chemical characteristic of the regenerated feed would shed more light into their effectiveness.

5. It is recommended to use a different solvent than toluene for regeneration of the polymers, as this may increase polymer effectiveness and nitrogen adsorption.

6. Overall mass balance is recommended using C, N and S analysis to determine the total nitrogen, sulfur and aromatic compounds contained in the polymer before and after adsorption studies with light gas oil.

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APPENDIX A

Reactor Catalyst Loading

The commercial catalyst was loaded into the reactor alongside with silicon carbide diluent. The purpose of the different sized silicon carbide is to prevent flow limitations that is usually associated with laboratory reactors. The reactor length used over the course of this research was 25cm in length and1cm in diameter. At the end of the reactors, filters were kept in place to prevent the catalyst and diluent from falling out. The lowest part of the reactor was filled with 22mm length of 3 mm diameter glass beads. This was followed by a 25 mm length layer of 16-size mesh silicon carbide. Following this layer, 10mm depth of 40 mesh and 60 mesh silicon carbide layers of material was added. The catalyst section of the reactor involved the addition of 5ml of catalyst mixed with 12ml of 90 mesh silicon carbide and carefully loaded in alternating layers, ensuring adequate mixing and interaction between the catalyst and the 90 sized mesh. The next diluent loading used was 60, 40 and 16 mesh, respectively for a layer depth of 8mm each. To complete the loading section, a layer of 20mm length of 3mm glass beads was added. There were a few millimeters of empty sections on top of the reactor before the filter was used to cover the reactor top. Figure A.1 shows a general representation of the catalyst loading used in the lab.
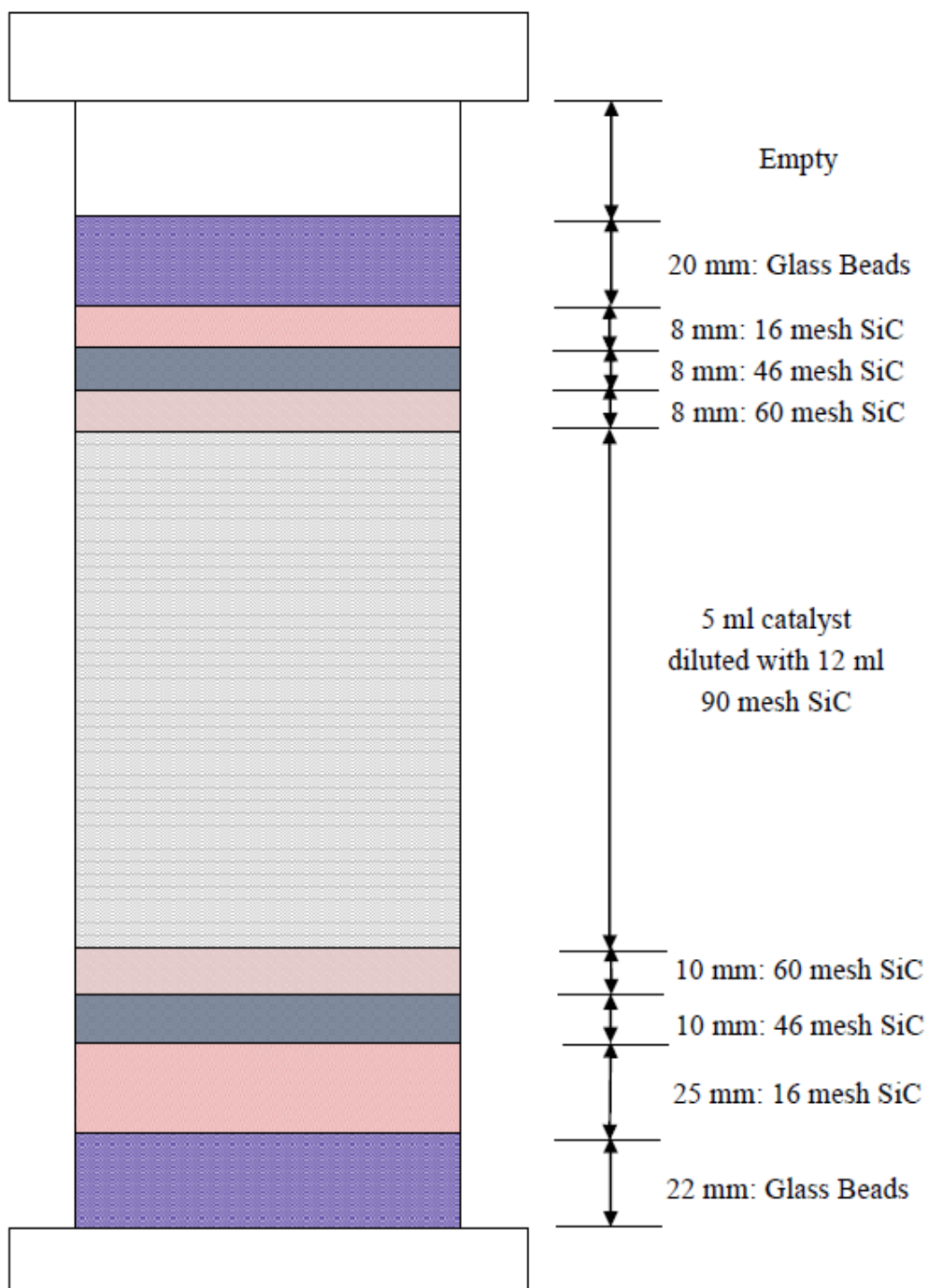
Figure A.1: Schematics for reactor catalyst loading (Prabhu, 2011)

APPENDIX B

Time on Stream

T (°c)	Sulfidation	Pre-coking	Temperature studies at 8.96 MPa and 1hr^{-1}	Temperature studies at 9.65 MPa and 1hr^{-1}	Temperature studies at 8.27MPa and 1hr^{-1}	Temperature studies at 8.27MPa and 2hr^{-1}	Temperature studies at 8.96 MPa and 2hr^{-1}	Temperature studies at 9.65 MPa and 2hr^{-1}
370		3	1.5	1.5	0.5 Sample Discard 1.5	1.5	0.5 Sample Discard 1.5	1.5
360			1.5	1.5	1.5	1.5	1.5	1.5
350			1.5	0.5 Sample Discard 1.5	1.5	0.5 Sample Discard 1.5	1.5	0.5 Sample Discard 1.5
343	1							
193	1							

Number of days for each sample

Figure B.1: Time on Stream (34.5 days) for the hydrotreatment of untreated LGO showing, temperature, pressure and LHSV

T(°c)	Sulfidation	Pre-coking	Temperature studies at 8.96 MPa and 1hr⁻¹	Temperature studies at 9.65 MPa and 1hr⁻¹	Temperature studies at 8.27MPa and 1hr⁻¹	Repeat Temperature studies at 8.96 MPa and 1hr⁻¹
370		3	1.5	1.5	0.5 Sample Discard 1.5	0.5 Sample Discard 1.5
360			1.5	1.5	1.5	
350			1.5	0.5 Sample Discard 1.5	1.5	
343	1					
193	1					

Number of days for each sample

Figure B.2: Time on Stream (21.5 days) for the hydrotreatment of Pretreated LGO showing, temperature, pressure and LHSV

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