Denitrogenation of Thermally Cracked Naphtha

by

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Abstract

Three main areas were investigated: characterization of the thermally cracked naphtha, development of novel denitrogenation reactions to remove basic nitrogen compounds from the naphtha, and fundamental study of chemistry that removes neutral nitrogen compounds from model oil.

Identification and quantification of nitrogen-containing compounds in thermally cracked naphtha was the first to be investigated, to understand the nature of the nitrogen compounds, in order to strategically plan the development of denitrogenation methods. A base pretreatment method using nickel (II) carbonate, along with silica column chromatography was conducted to remove the complex matrix of the naphtha, and extract nitrogen compounds for qualitative and quantitative analysis. Gas chromatography coupled with mass spectrometry (GC-MS) was used to identify nitrogen compounds. Quantification was conducted with gas chromatography coupled with both flame ionization detector (FID) and nitrogen phosphorus detector (NPD). Measurements of NPD response to different classes of nitrogen compounds were performed, thus the results have revealed that the response would be structure dependent.

A non-hydrotreating denitrogenation reaction with bromoacetic acid, through N-alkylation, was developed to selectively remove basic nitrogen containing compounds from the thermally cracked naphtha. In addition, a recycling method of basic nitrogen compounds was discovered. Strong base sodium hydroxide was used to break carbon nitrogen bond of the product from bromoacetic acid reaction, to achieve the recovering of the basic nitrogen compounds. Around 75 % of basic nitrogen compounds removal was measured by gas chromatography coupled NPD. Concentrations of neutral (95 ppm) and basic (263 ppm) nitrogen compounds in naphtha were calculated based on the concentrations of total nitrogen compounds (358 ppm) and the basic nitrogen compounds removal from dichloromethane and acetone fractions of the silica column chromatography.

Furthermore, denitrogenation methods that specifically targeted the neutral nitrogen compounds from naphtha were explained. Combinations of chemical reactions with liquid-liquid extractions have been studied in detail. Sulfonic group extractions, acid extractions, and oxidative acid extractions were conducted. Hydrochloric acid and peroxide acid treatments in combination with aqueous phase extraction were proven to be effective for neutral nitrogen compounds removal. Both hydrochloric acid and peroxide acid treatments had 100% neutral nitrogen compounds removal when it was tested with pyrrole (2000 ppm) and indole (2000 ppm) in toluene model oil. Fundamental chemistry behind these extractions was explained, for better understanding of how neutral nitrogen compounds were removed by strong acid and peroxy acid.

Acknowledgement

It was my great pleasure and honor to study the characterization and denitrogenation of naphtha under supervision of Prof. Arno De Klerk. Prof. De Klerk was always patient and helpful. He was encouraging whenever I was facing challenges during the exploration. I highly appreciate that he had an open mind to the ideas I had and the valuable advices he provided to help me overcome the problems during the research.

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1 Introduction

1.1 Background

To produce a commonly used transportation fuels, crude oil has to go through a series of refining processes. The lighter fraction, naphtha, is the main product that is converted into gasoline. Due to the large demand of the gasoline in the North American market, additional naphtha can be produced by thermal cracking of the heavier fractions. However, the heavier fractions usually contain more organic compounds with heteroatoms like sulfur, nitrogen and oxygen. The possible nitrogen-containing compounds in the thermally cracked naphtha would be aliphatic amines, anilines and heterocyclic aromatic compounds.[1] Nitrogen-containing compounds can be classified into two categories, basic and neutral nitrogen-containing compounds. Basic nitrogen-containing compounds like aliphatic amines, pyridines and quinolines have two lone pair electrons on the nitrogen atom, therefore, it is acting like a base that available for protonation (Figure 1-1). Neutral nitrogen-containing compounds such as pyrrole, indole and carbazole are not basic because the lone pair electrons on the nitrogen atom can delocalize into the aromatic ring, and these electrons are therefore not available for protonation under acidic conditions [2] (Figure 1-2).

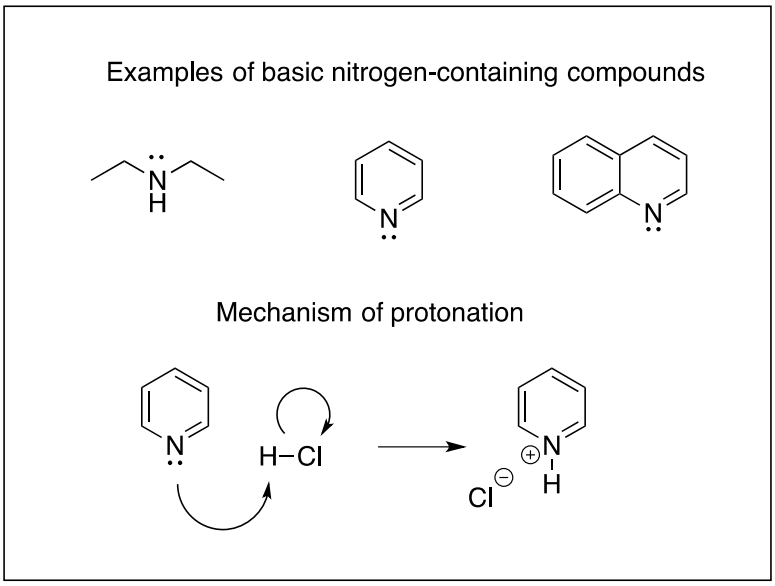

Figure 1-1. Basic nitrogen-containing compounds in naphtha and the mechanism of protonation.

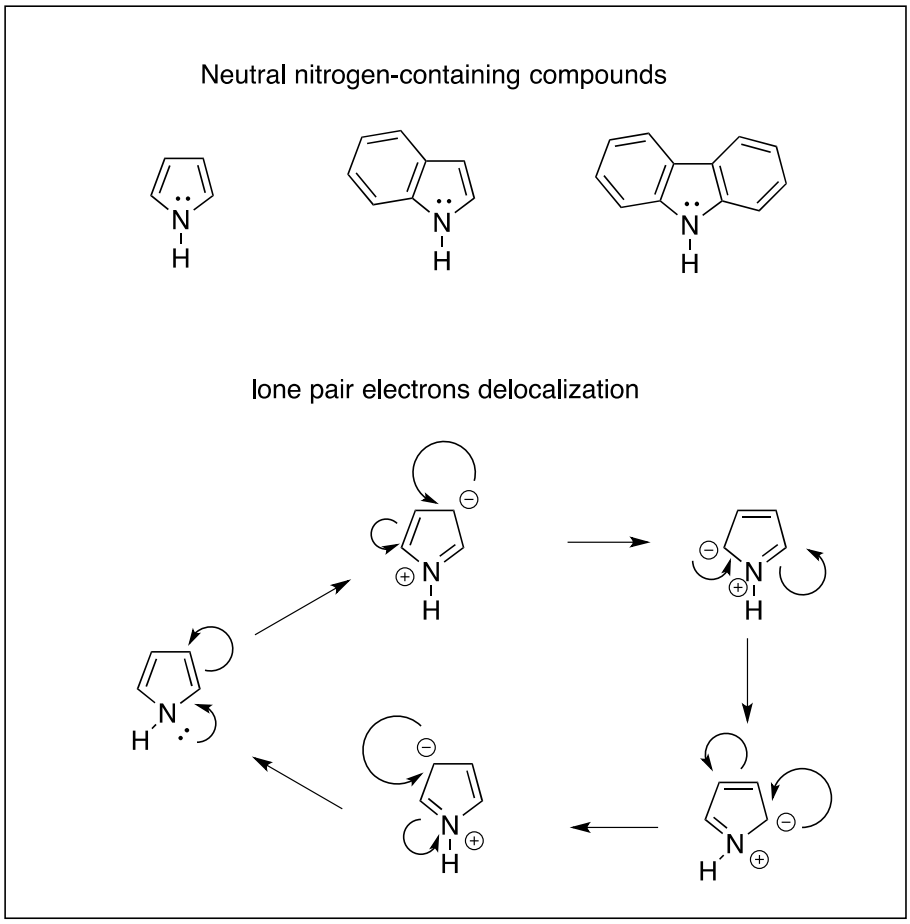

Figure 1-2. Neutral nitrogen-containing compounds in naphtha and lone pair electrons delocalization.

Sulfur- and nitrogen-containing compounds in oil has been a problem in the refining industry. For processes that involve acid and metal heterogeneous catalysts. For example, high octane number gasoline is required for high performance gasoline engines to avoid engine knocking. Low octane number naphtha can be converted into high octane number gasoline in a catalytic naphtha reformer. During this catalytic reforming process, aromatic and cyclic compounds are produced to boost the octane number. Conventional naphtha reforming employs platinum on chlorided alumina ($Pt/Cl^-/Al_2O_3$) catalysts. Basic nitrogen-containing compounds in the naphtha can cause inhibition of the acid function of the catalyst and the naphtha feed destined for reforming is usually hydrotreated beforehand.

Hydrodenitrogenation (HDN) is the standard industrial denitrogenation method to remove compounds that contain nitrogen from oil. It is a powerful hydrotreating method that removes both basic and neutral nitrogen compounds along with sulfur and oxygen compounds. In addition, the hydrotreating process also hydrogenates olefins into aliphatic products. Hydrodenitrogenation (HDN) is the most difficult hydrotreating reaction, which requires more severe conditions (higher pressure and temperature), in comparison with hydrodesulfurization (HDS) and hydrodeoxygenation (HDO). It is due to the hydrodenitrogenation that only occurs after the conversion of aromatic C=N bonds into

aliphatic C-N bonds (Figure 1-3), while sulfur atom does not form aromatic bonds with carbon atoms.[3] When hydrodenitrogenation reaction conditions are applied, hydrodesulfurization would occur simultaneously.

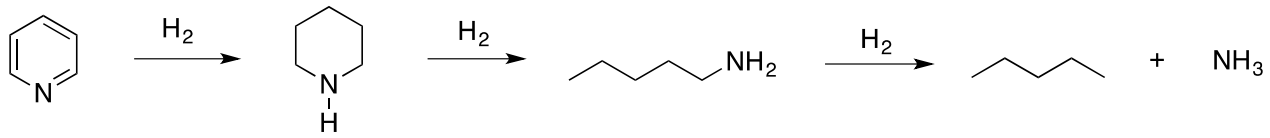

Figure 1-3. Reaction sequence of hydrodenitrogenation of pyridine.

The products of hydrodenitrogenation and hydrodesulfurization of crude oil contain paraffinic oil, ammonia gas and hydrogen disulfide gas, which can then be separated and removed from hydrogen gas for hydrogen gas recycle. Although hydrogenation is effective, it involves high pressure and high temperature reaction conditions.

In oil refining, the catalytic naphtha reformer usually generates sufficient hydrogen needed for hydrotreating processes. When extra volume of hydrogen is required, the hydrogen must be generated by processes such as electrolysis of water and synthesis gas from gas reforming. Water electrolysis is far less popular, only 5% worldwide hydrogen production comes from this way, because it is limited to the capacities of 5000 m^3/h, and requires the availability of low cost electricity. About 95% of worldwide hydrogen production is generated by synthesis gas from hydrocarbons and natural gas though steam reforming. [4]

$$CH_4 + H_2O \leftrightarrow CO + 3\,H_2$$

In addition to electrolysis and steam reforming of hydrocarbons, gasification of oil refining residues can also produce some hydrogen.

$$Heat \rightarrow H_2 + CO + CH_4 + Other\ products$$

Once hydrogen is generated, the storage and transportation of the hydrogen are also challenging. The most widely used method for hydrogen storage is compressing hydrogen into a metal tank or cylinder at high pressure. Sometimes hydrogen can be compressed and stored as liquid hydrogen at low temperature. This compression and low temperature storage method also requires enormous amount of energy. [5]

In Canada, the Alberta oil sand bitumen has high viscosity. Oil sand bitumen has to be upgraded to reduce its viscosity for pipeline transportation. Hydrogen is usually needed to upgrade oil sand bitumen, however it is highly impractical to transport hydrogen from refineries, or hydrogen production facilities to the bitumen production field. On the other hand, building complex natural gas reforming facilities at the bitumen production field costly. Without access to hydrogen, field-upgrading facilities can only perform partial upgrading of the oil sand bitumen. For example, a field upgrader concept

(Figure 1-4) developed by Nexen Energy ULC, includes steam assisted gravity drainage (SAGD) and partial bitumen upgrader, and is aiming to produce the partially upgraded oil that meets pipeline specifications (viscosity of < 350 cSt at 7.5 °C, density of > 19 °API (< 940 kg·m^{-3}) and olefin content of < 1 wt% as 1-decene equivalent). [6]

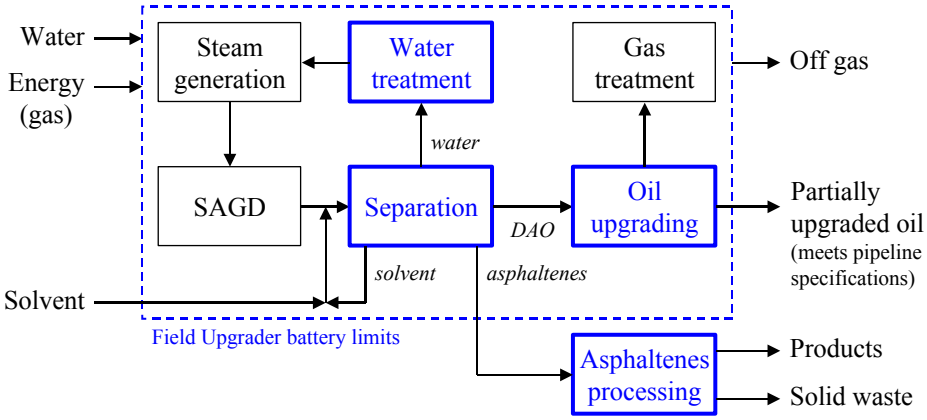

Figure 1-4. Generic process flow diagram of a Field Upgrader. [6]

The olefin treatment, which is part of the oil upgrading in this field upgrader, is an acid catalyzed process. The nitrogen containing compounds that are present in the oil can deactivate the acid catalyst. Traditional hydrotreating methods like hydrodenitrogenation is not an option here at the oil sand production field, as there is no access to hydrogen. The development of non-hydrotreating denitrogenation methods that can remove basic nitrogen compounds from oil is required.

Cracked naphtha is also a source of olefins. In some cases it is preferable to exploit the olefins in the naphtha rather than hydrotreating and reforming the naphtha. Olefins are readily converted into a variety of products through acid catalysis. Another example of refining process is aliphatic alkylation, which is applied to olefins rich naphtha, with the purpose of producing high octane number paraffinic gasoline blending material called alkylate. This conversion process is carried out with sulfuric acid or hydrofluoric acid catalyst at low temperature.[7] When basic nitrogen-containing compounds are present in the naphtha, the feed is considered unsuitable for acid catalysis, because the basic compounds will inhibit or deactivate the acid catalysts. There is consequently a need to find a simple and cheap way to selectively remove nitrogen-containing compounds from cracked naphtha so that it can be used as feed for acid catalyzed refining technologies.

1.2 Objectives

To identify and quantify the nitrogen-containing compounds in the thermally cracked naphtha, which is produced during thermal processing of oil sands bitumen. The work is focused on the naphtha fraction, because this fraction is the primary feed to the olefin treatment process.

To evaluate methodologies that selectively remove nitrogen-containing compounds from the thermally cracked naphtha without using hydrotreating. The method will have to be compatible with the later aromatic alkylation process.

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2 Identification and quantification of nitrogen-containing compounds in thermally cracked naphtha.

2.1 Introduction

As a very first step, it is important to identify what types of nitrogen-containing compounds are in the thermally cracked naphtha, and also determine the quantity of these nitrogen-containing compounds. The information obtained from this research will provide a great help to the design of removal strategies. Our main targets are the basic nitrogen-containing compounds in the cracked naphtha. Because acidic catalyst will be used in further refining process, basic nitrogen-containing compounds have to be removed to prevent catalyst from deactivation.

The challenge in qualitative and quantitative analysis comes from the relatively low concentration of the nitrogen-containing compounds in the lighter fractions of oil. For example, average nitrogen content of industrial naphtha from Anqing, China is between 3 to 5 ug/g.[1] Nitrogen-containing compounds in the light oil and light cycle oil can be in the range of 80-240 ppm.[2] Thermally cracked and fluid catalytic cracked (FCC) naphtha could be around 40 ppm.[3] In the case of identification, it is difficult to determine the nitrogen-containing compounds in naphtha directly, because it is a small amount compared to the hydrocarbon matrix. Even with careful chromatographic separation, separation is not always complete and peak overlapping makes subsequent identification by mass spectrometry difficult.

To overcome the problems of low concentration and complex hydrocarbon matrix, several methods including solvent extraction,[4] acid-base treatment of fractionation,[5] ionic liquid extraction,[6-7] silica solid phase extraction,[8-9] aluminum oxide coupled with resin extraction,[10] were used to pre-concentrated nitrogen-containing compounds from diesel, distillate, and vacuum gas oil. Gas chromatography coupled with mass spectrometry (GC-MS), flame ionization detector (GC-FID), atomic emission detector (GC-AED), nitrogen phosphorous detector (GC-NPD) and two dimensional gas chromatography coupled with mass spectrometry (2D GC-GC-MS),[11-12] were commonly used analytical instruments for characterization of nitrogen-containing compounds in oil.

An early analytical method developed by Qi, et al.[4], measured total nitrogen content in catalytic cracked diesel involving solvent extraction. Ethanol (95%) with some metal ions like $FeCl_3$, $ZnCl_2$ and $AlCl_3$ were used to extract nitrogen-containing compounds from the cracked diesel. Nitrogen-containing compounds formed metal complex in the solvent, which significantly improved the capability of solvent extraction. Addition of metal ions in ethanol also increased the selectivity of the extraction, because ethanol may also extract polar organic compounds other than nitrogen-containing compounds. Quantitative analysis was performed with coulometry. In coulometry, the extracted sample of nitrogen-containing compounds was reduced and cracked into ammonia under hydrogen flow with Ni catalyst at high temperature. Then ammonia gas went through a titration cell and reacted with

hydrogen ion. By measuring electric quantity of hydrogen ion, the total nitrogen content can be determined. Although this early method provided a simple way to extract nitrogen-containing compounds from the oil and also quantify nitrogen content in the oil, it suffered relatively poor extraction selectivity, and failed to identify nitrogen-containing compounds at molecular level.

Shiraishi, et al.[5] have applied an acid-base treatments of fractionation method to isolate the basic and neutral nitrogen-containing compounds from the light oil. The light oil was first mixed with *n*-hexane and 10% sulfuric acid aqueous solution. In this process, basic nitrogen-containing compounds were acidified and converted to the salt form, and extracted into aqueous layer. Then the aqueous layer was separated and basified with solid NaOH until pH was adjusted between 12-13. Salt forms of basic nitrogen-containing compounds were converted back into the base form in this process. Dichloromethane was then used to extract the basic nitrogen-containing compounds. The light oil and *n*-hexane mixture contained neutral nitrogen-containing compounds was concentrated and separated with aluminum oxide column. The mixture of solvents with dichloromethane and *n*-hexane (2:3) was used to remove hydrocarbons matrix. Dichloromethane was then used to elute neutral nitrogen-containing compounds. Gas chromatography coupled with atomic emission detector (GC-AED) and mass spectrometry (GC-MS) was employed to analyze separated basic and neutral nitrogen-containing compounds in dichloromethane.

Ionic liquids were popular within the denitrogenation technologies because the properties of the ionic liquids can be altered to extract both basic and neutral nitrogen-containing compounds. Chen, et al [6] have investigated Lewis acidic and Bronsted acidic ionic liquids and their ability in two types of nitrogen-containing compounds extractions from model oil. Pyridine and carbazole were used as basic compound and neutral compound in model oil. The results shown all the acidic ionic liquids were excellent for basic nitrogen-containing compound extraction. However, they appeared differently for their ability of neutral nitrogen-containing compound extraction (Figure 2-1). The total nitrogen content was obtained with high-pressure liquid chromatography (HPLC) coupled with an ultra violet (UV) detector. Wavelengths 240 mm and 330 mm were chosen for pyridine and carbazole respectively. The method discovered the important properties of ionic liquids and it indicated that basic and neutral nitrogen-containing compounds could both be removed with appropriate ionic liquid. However, the entire research was based on model oil, it would not be simply apply to the real industrial produced oil.

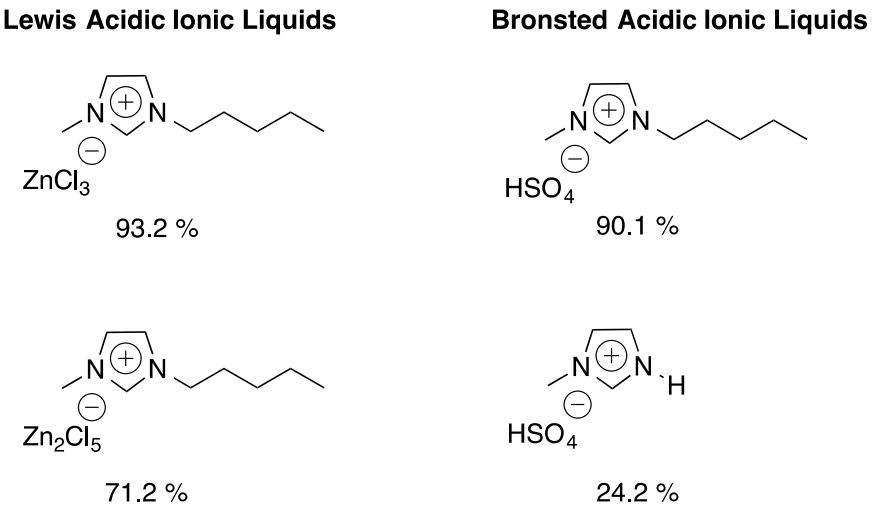


Figure 2-1. Chemical structures of Lewis acidic ionic liquids and Bronsted acidic ionic liquids and their extraction efficiency for neutral nitrogen-containing compounds.[6]

Seventeen ionic liquids were synthesized by Laredo, et al. [7], they were tested the extraction ability of nitrogen-containing compounds from model oil and straight run gas oil. The results shown only two ionic liquids (Figure 2-2) were suitable for extraction of nitrogen-containing compounds from straight run gas oil, although, most of them indicated good extraction capability when they were tested with model oils. Some ionic liquids either failed to extract sufficient amount of nitrogen-containing compounds, or failed to retain the chemical or physical states in experimental conditions. For example, ionic liquids may dissolve into the real feed so that there was no layers separation. On the other hands, some ionic liquids may turn into solid state once they were mixed with the real oil feed.

Figure 2-2. The only two ionic liquids that were proved suitable for extraction of nitrogen-containing compounds from straight run gas oil among the tests performed by Laredo et al.[6]

Total nitrogen content in the straight run gas oil was measured with ANTEK equipment (ASTM D-4639). This instrument performed elemental analysis of nitrogen, sulfur and halides with combustion ion chromatography, ultraviolet fluorescence and chemiluminescence technologies. The research was mainly focusing on synthesis of ionic liquids and their extraction capability. It did not involve identification of nitrogen containing compounds at molecular level.

Briker, et al.[9] developed an silica phase extraction (SPE) method to extract nitrogen-containing compounds from distillates. In this method, nitrogen-containing compounds were extracted with HCl pretreated silica in a cartridge. A nonpolar solvent, *n*-heptane, was used to elute the hydrocarbons.

Dichloromethane (DCM) was used to elute the neutral nitrogen-containing compounds. Then elution was continued with deionized water to collect the basic nitrogen hydrochloride salt. The elution was followed by a second glass cartridge with pH 9 adsorbent. In this cartridge the salt is converted back into basic nitrogen-containing compounds. The last step was using DCM to elute the basic nitrogen-containing compounds. The advantage of this method over methods employing only acid-base extraction is that both and neutral nitrogen-containing compounds were extracted and separated. The main drawback of this method is that HCl acid pretreatment of the silica is time consuming, and introducing the second pH 9 absorbent cartridge further complicated the process.

Oliveira, et al.[10] performed analysis of nitrogen-containing compounds in residue heavy gas oil. Neutral aluminum oxide was used to extract nitrogen-containing compounds from the complex matrix of residue heavy gas oil. Several solvents were used to elute the matrix. Hydrocarbons were eluted by n-hexane. Aromatic compounds and sulfur compounds were eluted by combination (3:2) of n-hexane and dichloromethane. Nitrogen-containing compounds were eluted by dichloromethane, then methanol was applied to elute most polar fraction. The second part of the method involved resin extractions. Basic resin was used to extracted acids, followed by dichloromethane to elute nitrogen-containing compounds. In the third part of this method, acidic resin was used to separate neutral nitrogen-containing compounds from basic nitrogen containing compounds. Neutral nitrogen-containing compounds were eluted by dichloromethane, then basic nitrogen-containing compounds were eluted with isopropylamine in hexane (10% v/v). This method not only separated nitrogen-containing compounds from the complex matrix, but also separated basic and neutral nitrogen-containing compounds. The qualitative analysis was performed with GC-MS. The disadvantage of this method is that large volume of solvent was needed and it is very time consuming. Selectivity of the separation may be hard to control, as all the separation relied on column chromatography.

Maciel, et al.[11] analyzed the nitrogen-containing compounds in diesel fuel with two-dimensional gas chromatography coupled with mass spectrometry. This method involved two gas chromatography separation systems. A non-polar column was used in the first dimension, while another polar column was used in the second dimension. Nitrogen-containing compounds in the diesel fuel can be separated from the matrix, however, quantitative analysis required standard addition calibration, because of the low concentration of nitrogen-containing compounds in diesel. The standard addition calibration method could suffer from matrix interference effects because diesel contains a variety of different polarity compounds. Polar organic compounds appear to be higher ionization than the non-polar compounds. Although standard addition calibration complicates this method, it has advantage of avoiding sample pretreatment and fractionation before analysis. Another drawback is the high cost of two-dimensional gas chromatography system.

Muhlen, et al.[12] combined a separation method with two-dimensional gas chromatography for quantitative analysis of heavy gas oil. Neutral aluminum oxide was the stationary phase in column chromatography for the separation. Heavy gas oil was separated into hydrocarbons, resins and asphalthenes. Then acidic and basic silica were used to separate resins fraction. Ion exchange resins

(Amberlyst A-27 and A-15) were employed to separate basic and neutral nitrogen-containing compounds. Analysis was performed with two-dimensional gas chromatography coupled with nitrogen phosphors detector (NPD). The NPD detector selectively detect nitrogen-containing compounds, therefore significantly reduced the peak overlapping by other matrix. Four types of materials were applied as stationary phase in the separation steps, in order to provide very good separation. Two-dimensional gas chromatography couple with NPD has obvious advantage over the normal one-dimensional GC system, that it provides better separation. Again, these combined methods share the common problems: extremely time consuming and involving expensive analytical instruments. Although NPD detector is capable of selectively detecting nitrogen-containing compounds, it could response to non-nitrogen compounds when they are present in a very high concentration, and it also response to phosphor compounds.

Most of analytical instruments used for the characterization of nitrogen-containing compounds in oil are gas chromatography coupled with specific detectors and mass spectrometry. Recently new methods with high performance liquid chromatography (HPLC) and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) were developed to study nitrogen-containing compounds in gas oil. Instead of using open column separation, Lucy, et al. [13] separated gas oil with high-performance liquid chromatography (HPLC) before analysis of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has higher resolution than normal mass spectrometry techniques. Dinitrophenyl (DNAP) column was selected to separate polycyclic aromatic hydrocarbons from nitrogen-containing compounds. Elution solvent is a mixture of dichloromethane and hexane with increasing gradient of dichloromethane. Four fractions were collected after the separation. The first fraction contained polycyclic aromatic hydrogen carbons and sterically hindered pyridine derivatives; The second fraction contained nitrogen-containing compounds with oxygen and sulfur containing compounds. The third fraction contained less sterically hindered nitrogen-containing compounds. The last fraction did not contain nitrogen-containing compounds. Four fractions were all analyzed by FT-ICR MS in positive and negative modes. Basic nitrogen-containing compounds like pyridine derivatives were detected in positive mode through protonation, while neutral nitrogen-containing compounds like pyrrole derivatives were detected in negative mode through deprotonation. This work avoided using open column chromatography and sample pretreatments, however, high performance liquid chromatography (HPLC) with DNAP column could not separate nitrogen-containing compounds into basic and neutral fractions. HPLC is not a direct replacement of open columns and sample pretreatment methods. Analysis with FT-ICR MS on positive and negative modes could distinguish between pyridines and pyrroles, therefore determine amount of basic and neutral nitrogen-containing compounds in the gas oil. This type of analysis could not distinguish between structures of nitrogen-containing compounds and its isomers.

In this work, we have investigated the nature of nitrogen-containing compounds in thermally cracked naphtha. A more simplified silica extraction procedure including an inorganic base pretreatment was developed and applied to the identification of nitrogen-containing compounds in thermally cracked naphtha. A small database was built with authentic sample so that tentative assignment based on

analysis by gas chromatography coupled with mass spectrometry (GC-MS) could be confirmed and assisted with the identification of isomers. Quantitative analysis was performed with gas chromatography coupled with flame ionization detector (FID) and nitrogen phosphorous detector (NPD).

2.2 Experimental

Materials. Thermally cracked naphtha (Table 2-1.) was obtained from an industrial visbreaking unit processing a deasphalted oil from steam assisted gravity drainage produced Athabasca oilsands bitumen.

Table 2-1. Characterization of thermally cracked naphtha

Property	Units	Thermally cracked naphtha
Fractionation	wt %	NA
Density	Kg/m^3 @ 20 ℃	762.7
API Gravity		53.5
Sulphur	% wt	0.9
Nitrogen	% wt	0.09
Carbon	% wt	83.34
Hydrogen	% wt	13.76
Oxygen	% wt	0.25
Viscosity	cSt @ 25 ℃	0.85
Viscosity	cSt @ 40 ℃	0.72
Viscosity	cSt @ 100 ℃	NA
Viscosity	cSt @ 150 ℃	NA
Aromatics	%wt C	8.51
Aliphatic saturate	mol %	96.42
Aliphatic olefin	mol %	1.26
aromatic	mol %	2.32
Olefin content	wt % equiv. as 1-decene	4.7
Diene number	g I_2/100 g	0.62
Bromine number	g Br_2/100 g	27.84
CCR	%wt	45.12 ± 2.55
Acid number	mg KOH/g	0.123 ± 0.003

HPLC grade solvents used in the study, including *n*-pentane (99.7%), *n*-heptane (99%), acetone (99.7%), dichloromethane DCM (99.9%) and diethyl ether (99.9%), were purchased from Fisher Scientific, Canada. Chemical reagents including sodium carbonate (99.5%), 2-methyl pyridine (98%), 3-methyl pyridine (99%), 4-methyl pyridine, 2,3-lutidine (99%), 2,5-lutidine (95%), 2,6-lutidine (98%), 2-ethyl pyridine (97%), 3-ehtyl pyridine (98%), 4-ethyl pyridine (98%), m-toluidine (99%), aniline (99.5%), 2,3,4 trimethyl pyridine (99%), 2,4 dimethyl aniline (99+%), alpha methyl benzyl amine (99%), acetamide (99%), acetic hydrazide (90%), isoprocarb, pyrazine (99%), lepidine (99%), indole (99%), quinoline (98%), 1,8-Diazabicycloundec-7ene (98%), 3,4-dihydro 2H-1,4 benzoxazine and meta-tolylurea were purchased from Sigma Aldrich, Canada. The supplied provided no concentration

guarantee for the last two reagents. Nickel (II) carbonate and cobalt (II) carbonate hydrate were purchased from ACROS.

Procedure. Thermally cracked naphtha was first pretreated with inorganic base nickel (II) carbonate to eliminate the fatty acids in the naphtha, because these fatty acids would have very broad and hight intensity peaks in the chromatogram that could overlap with the peaks of the nitrogen-containing compounds. Details of the procedure is as follows: Thermally cracked naphtha (200 mL) was treated with Ni(II) Carbonate (1.231 g, 10.378 mmol) and stirred overnight at room temperature.[14]

The reaction mixture was filtered. The solid residue of the base pretreatment was washed with n-heptane (50 mL). Then the residue was acidified with 1N HCl (16 mL) and extracted with diethyl ether (3×20 mL), followed by washing with water (2×20 mL). The diethyl ether was dried with $MgSO_4$ and evaporated under reduced pressure and the remaining residue was dissolved in acetone (2 mL) for analysis.

The filtrate from the base pretreatment was passed through a silica stationary phase column chromatography setup. *n*-Pentane (80 mL), DCM (420 mL) and acetone (240 mL) were used to elute the column respectively as shown in Figure 2-3. The DCM fraction and acetone fraction were collected and concentrated separately under reduced pressure. The n-pentane was used to wash out the hydrocarbons. The polarity of DCM is suitable of eluting oxygen-containing compounds like ketones and alcohols, as well as neutral nitrogen containing compounds. The most polar acetone was responsible for collecting the basic nitrogen-containing compounds. The DCM and acetone fractions were analyzed.

In order to confirm the identity of the basic nitrogen-containing compounds in the residue, where possible authentic samples (model compounds) were commercially obtained and analyzed in the same way as the cracked naphtha. A database of authentic samples of basic nitrogen-containing compounds was built over time for analysis. This should benefit future research and assist with confirmation of the identification of basic nitrogen-containing compounds.

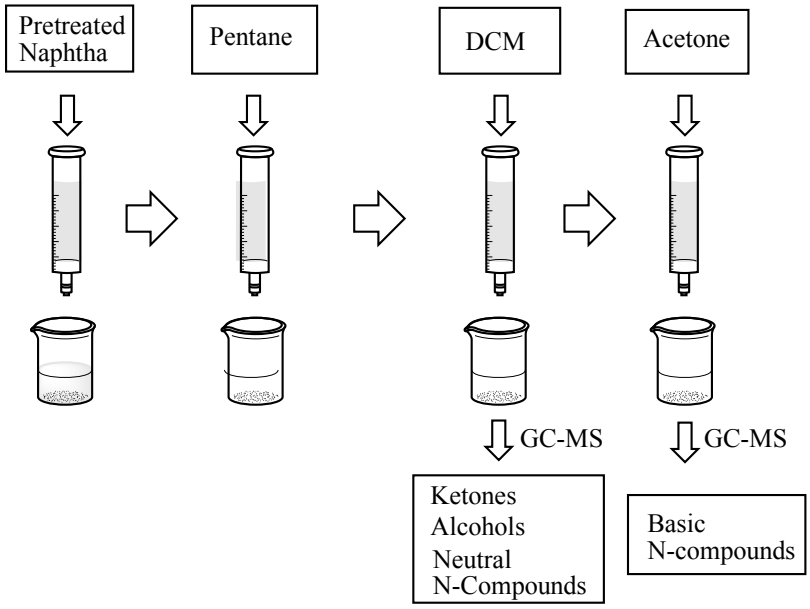


Figure 2-3. Column chromatography with silica stationary phase to separate the basic nitrogen-containing compounds from neutral nitrogen containing compounds, hydrocarbons, ketones and alcohols.

Analysis. Identification of the compounds was performed using an Agilent 7820A gas chromatography (GC) with 5977E MSD mass spectrometer (MS). The sample separation was achieved with Agilent 19091S-433 column (length: 30 m, diameter: 250 μm, film thickness: 0.25 μm, max temperature 325 °C). Helium was the carrier gas with flow of 1 mL/min. Split ratio was 1:100. The oven initial temperature was 80 °C, which was increased to 170 °C with a ramp rate of 6 °C/min and then increased to 300 °C with a ramp rate of 15 °C/min and held at 300 °C for 5 min.

Quantification of nitrogen-containing compounds was carried out with an Agilent 7890A gas chromatography (GC) equipped with both a flame ionization detector (FID) and a nitrogen phosphorus detector (NPD). The same column and temperature program were employed as for the GC-MS analysis.

Measurement of FID relative response factors. An acetone solution (250 mL) of known concentration of seven nitrogen-containing compounds including 2-ethyl pyridine (395.5 mg, 2000 ppm), 2-methyl pyridine (395.5 mg, 2000 ppm), 3-methyl pyridine (395.5 mg, 2000 ppm), 2,4,6-trimethyl pyridine (395.5 mg, 2000 ppm), 2,3-lutidine (395.5 mg, 2000 ppm), 2,5-lutidine (395.5 mg, 2000 ppm), 2,6-lutidine (395.5 mg, 2000 ppm), and *n*-heptane (395.5 mg, 2000 ppm, internal standard) were prepared and analyzed by GC-FID. The relative response factors for the flame ionization detector that were determined are given in Table 2-2.

Table 2-2. Experimentally determined FID relative response factors for authentic nitrogen-containing compounds

Compounds	Area	Response factors	FID relative response factors
2-ethyl pyridine	98.99	0.250	0.923
2-methyl pyridine	93.03	0.235	0.868
3-methyl pyridine	86.00	0.217	0.802
2,4,6-trimethylpyridine	88.57	0.224	0.826
2,3-lutidine	95.10	0.240	0.887
2,5-lutidine	89.76	0.227	0.837
2,6-lutidine	98.61	0.249	0.920
Heptane	107.21	0.271	
Average relative response factor:			0.866

Response factor and relative response factor for each compounds were calculated with equation (1) and (2).

(1)

$$\text{Response factor of A} = \frac{\text{Peak area of A}}{\text{Mass of A}}$$

(2)

$$\text{Relative response factor of A} = \frac{\text{Response factor of A}}{\text{Response factor of heptane}}$$

It was impractical to determine response factors for all of the nitrogen-containing compounds. An average relative response factor of 0.866 was calculated (Table 2-2) and applied to estimate the total mass of the nitrogen-containing compounds in the cracked naphtha. By comparing the chromatogram of GC-FID and GC-NPD, we were able to know which peaks in GC-FID were nitrogen-containing compounds, even if the chemical structures were not confirmed with authentic samples. The sum of the peak areas of all the nitrogen-containing compounds was obtained. The total mass of nitrogen-containing compounds in certain amount of naphtha was calculated with equation (3), using the average calculated response factor and sum of the peak area of all the nitrogen-containing compounds.

(3)

$$\text{Mass of A} = \frac{\text{Peak area of A} \times \text{mass of heptane}}{\text{Peak area of heptane} \times \text{relative response factor of A}}$$

Response of nitrogen compounds to the nitrogen phosphorus detector (NPD). A stock solution of pyrazine (78.47 mg, 699.2 ppm N) and quinoline (253.09 mg, 699.2 ppm N) was prepared in acetone (50 mL). Equations (4) and (5) were applied to calculate the weight of pyrazine (78.47 mg) and quinoline (253.09 mg) which were dissolved in the acetone solution (50 mL). Several diluted solutions were made to have various concentrations (349.2 ppm N, 174.8 ppm N and 87.4 ppm N).

Equations in calculation:

(4)

$$\text{Weight of N atoms in compound} = \text{concentration of N atom} \times \text{weight of acetone solution}$$

(5)

$$\text{Weight of compound} = \text{weight of N atoms in compound} \times \frac{\text{Molar Mass of compound}}{\text{n} \times \text{molar mass of N atom}}$$

Where the weight of acetone solution (50 mL) is 39.24 g; Concentration of N atom is 699.2 ppm N; **n** is number of nitrogen atoms in the molecule.

NPD quantitative analysis of nitrogen compounds in naphtha. In external standard calibration method, a stock solution was prepared by dissolving 2-methyl pyridine (348 mg, 1600 ppm) 2,6-lutidine (348 mg, 1600 ppm), 2-ethyl pyridine (348 mg, 1600 ppm), aniline (348 mg, 1600 ppm), m-toluidine (348 mg, 1600 ppm), 2,4-dimethyl aniline (348 mg, 1600 ppm), quinoline (348 mg, 1600 ppm), lepidine (348 mg, 1600 ppm) and indole (348 mg, 1600 ppm) into toluene (250 mL). This stock solution was then diluted to 800 ppm and 400 ppm solutions as external calibration standard. NPD detector analyzed the DCM fraction and acetone fraction from the silica extraction (Figure 2-3). The same procedure was used to analyze the samples from bromoacetic acid denitrogenation of the naphtha.

2.3 Results and Discussion

Base pretreatment. Sodium carbonate, cobalt (II) carbonate and nickel (II) carbonate were tested for their ability of removing fatty acids from the cracked naphtha. The sodium carbonate was capable of altering the physical state of the naphtha, which reaction mixture was turned into a more sticky solution. During the filtering process, the filter was blocked and the solution could not go through the filter. Alternatively, Cobalt (II) carbonate hydrate is very fine powder and could not be completely filtered out. It was found that the fine powder even went through the silica column. Both sodium and cobalt carbonate were abandoned, although they were able to remove fatty acids.

Nickel (II) carbonate was chosen, because it is capable of removing all the fatty acids from the naphtha in very high selectivity. The only alcohol that was removed along with those fatty acids was 2,6-di-*tert*-butyl-4-methyl-phenol. The 2,6-di-*tert*-butyl-4-methyl-phenol is easily deprotonated, because the

charge can be delocalized through the aromatic ring, as shown in Figure 2-4, which makes the phenol slightly acidic.

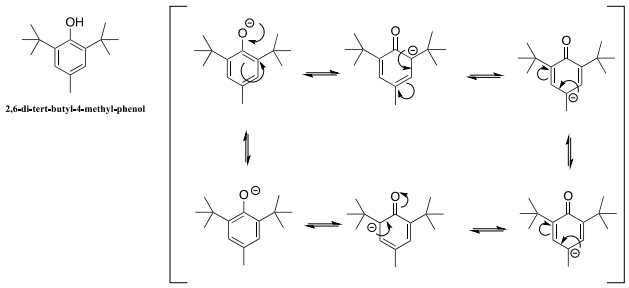


Figure 2-4. Structure of 2,6-di-*tert*-butyl-4-methyl-phenol and lone pair delocalization through the aromatic ring after deprotonation.

Heating the sample to 60 °C accelerated the reaction between nickel (II) carbonate and the organic acids, but it deteriorated the selectivity. At 60 °C more phenol derivatives were removed together with the carboxylic acids. Therefore, temperature control is essential to this base pretreatment.

Carboxylic acids in base pretreatment residue. The solid residue collected from the base pretreatment reaction was a mixture of the nickel salt of mainly carboxylic acids. The residue was acidified with hydrochloric acid and extracted by diethyl ether.

The GC-MS analysis shown that the acidic compounds that were present in the cracked naphtha were mainly aliphatic carboxylic acids in the range of 4 carbons to 11 carbons (Figure 2-5). Isomers of these fatty acids were also found as the smaller peaks shown between the big peaks.

The only non-carboxylic acid found in this extraction was 2,6-di-*tert*-butyl-4-methyl-phenol. The phenol acted like a weak acid, because the lone pair electrons could be delocalized into the aromatic ring, as was shown in Figure 2-4. The negative charged is stabilized by this delocalization effect so that it readily formed the metal salt with nickel. It was suspected that the 2,6-di-*tert*-butyl-4-methyl-phenol in the cracked naphtha was not a thermal cracking product, but came from a small amount of oxidation inhibitor that was added for shipping. This was found not to be the case, no oxidation inhibitor was added, and 2,6-di-*tert*-butyl-4-methyl-phenol is indeed a product in the cracked naphtha.

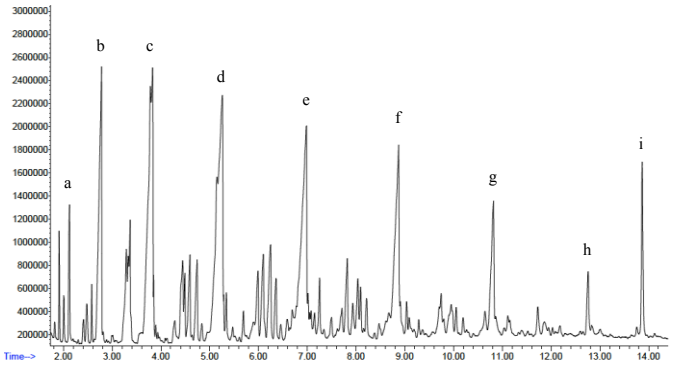


Figure 2-5. GC-MS analysis of the fatty acids extraction. a: Butyric acid, b: Pentanoic acid, c: Hexanoic acid, d: Heptanoic acid, e: Octanoic acid, f: Nonanoic acid, g: Decanoic acid, h: Undecanoic acid, i: 2,6-di-tert-butyl-4-methyl-phenol. The smaller peaks between larger labeled peaks are mainly isomers of the fatty acids.

Identification of basic nitrogen-containing compounds. Analysis of the acetone fraction from silica column extraction indicated that the fraction contained mainly nitrogen-containing compounds (Figure 2-6).

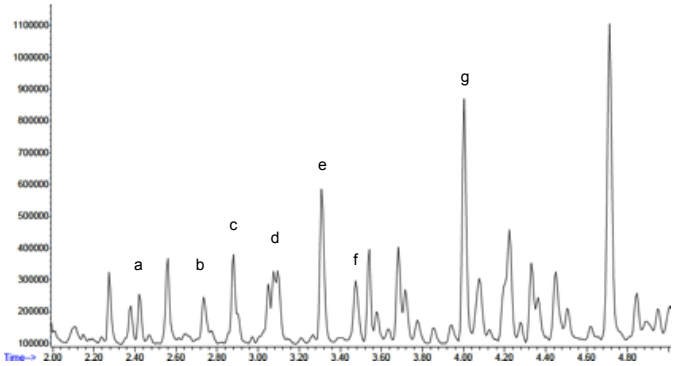


Figure 2-6. Section of chromatogram of the acetone extracted fraction. a: 2-methyl pyridine, b: 3-methyl pyridine, c: 2,6 lutidine, d: 2-ethyl pyridine, e: 2,5 lutidine, f: 2,3-lutidine, g: 2,4,6-trimethyl pyridine.

The identity of some of the compounds could be confirmed by comparison with the authentic sample database that was built using the same analytical protocol (Table 2-3).

The majority of the nitrogen-containing compounds in the cracked naphtha were identified as heterocyclic molecules (Figure 2-7). Pyridine derivatives were the major nitrogen-containing compound class in the cracked naphtha. Quinoline derivatives were also found. For practical reasons it was not possible to confirm all the tentative compound identifications based on mass spectrometry with authentic samples.

Table 2-3. GC-MS Retention Times of Authentic Compounds with Compounds Identified in Cracked Naphtha in Italics.

Compounds	GC-MS retention time
2-methyl pyridine [a]	*2.413*
Acetic hydrazide	2.68
3-methyl pyridine [a]	*2.727*
4-methyl pyridine	2.734
2,6-lutidine [a]	*2.874*
2-ethyl pyridine [a]	*3.068*
2,5-lutidine [a]	*3.322*
2,3-lutidine [a]	*3.482*
3-ethyl pyridine	3.643
4-ethyl pyridine	3.689
aniline	3.904
2,4,6 trimethyl pyridine [a]	*4.017*
alpha methyl benzyl amine	4.839
2,4 dimethyl aniline	6.971
3,4 dihydro 2H-1,4 benzoxazine	10.646
acetamide	11.127
isoprocarb	14.434
meta-tolylurea	17.06

[a] Present in thermally cracked naphtha

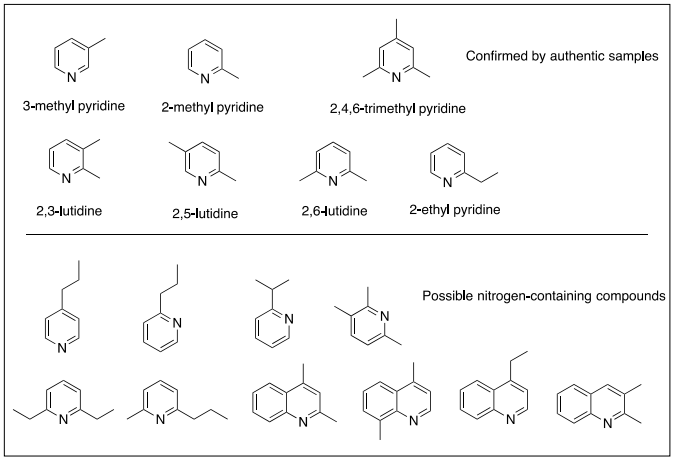


Figure 2-7. Nitrogen-containing compounds identified in thermally cracked naphtha.

A very small amount of the peaks in the chromatogram of the acetone-extracted fraction were identified as alcohols and conjugated ketones. The DCM extraction failed to remove these oxygenates from the silica column. Fortunately these peaks did not overlap with many of the nitrogen-containing compounds in the GC-MS chromatogram and did not hinder mass spectrometric identification.

Identification of nitrogen-containing compounds in the DCM extract was complicated by overlap in the chromatogram. At the time of writing it was not yet possible to overcome this obstacle. It is anticipated that the nitrogen-containing compounds in the DCM extract would be mainly neutral species, i.e. pyrroles and indoles.

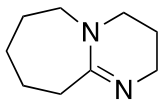
Quantification of nitrogen-containing compounds. The amount of basic nitrogen-containing compounds in acetone fraction of silica extraction of the cracked naphtha was determined by GC-FID in combination with GC-NPD. GC-NPD and GC-FID analyses were performed using identical temperature program and column. The retention times of the same compound on the two chromatograms were very close. Comparison of the two chromatograms allowed us to distinguish between the peaks from nitrogen-containing compounds. The concentration of basic nitrogen-containing compounds in the thermally cracked naphtha was found to be 199.6 ppm (basic nitrogen-compound concentration not nitrogen content).

It should be noted that higher values for the amount of nitrogen-containing compounds were found when the acid compounds were not fully removed from the sample. Co-elution of acids caused peak overlap that increased the apparent concentration of the nitrogen-containing compounds. It also appears that some the acids occur in association with the nitrogen-containing compounds as acid–base pairs, causing the mass of nitrogen-containing compounds (not nitrogen) determined by analysis to be higher.

There were some neutral nitrogen containing compounds were eluted into the dichloromethane (DCM) fraction of the silica extraction. These neutral nitrogen-containing compounds were not quantified by FID because their peaks are hardly recognized under heavily overlapping with oxygen containing compounds. Instead, they were quantified by nitrogen phosphorus detector (NPD).

Response of nitrogen compounds to the nitrogen phosphorus detector (NPD). The nitrogen phosphorus detector (NPD) is widely used for quantitative analysis of inseticides[15]or pharmaceutical compounds that contain nitrogen atoms.[16] However, it is rarely used for analysis of nitrogen-containing compounds in the oil. To better understand how NPD detector response to nitrogen compounds, a few simple experiments were performed. For example, it was expected that molecules contain two nitrogen atoms are more sensitive than the molecules contain only one nitrogen atom. Furthermore, it is necessary to know whether the sensitivity of nitrogen atom to the detector has a proportional relationship.

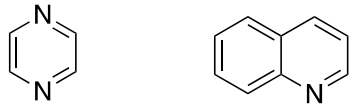
An experiment with an acetone solution of 1,8-Diazabicycloundec-7-ene (DBU) and quinoline was designed to test their response to the NPD detector. DBU contains two nitrogen atoms (Figure. 2-8) while quinoline (Figure 2-9) contains only one nitrogen atom. The purpose of this comparison is to see whether DBU would have the same peak area as the quinoline, when the standard solution contains same concentration of nitrogen atom (ppm N). However, it was observed that the peak represents the DBU disappeared one day after the standard solution was prepared. It turned out the experiment was not successful because the DBU was found easily decomposed in a short period of time.



1,8-Diazabicycloundec-7-ene (DBU)

Figure 2-8. Molecular structures of 1,8-Diazabicycloundec-7ene.

Pyrazine was then chosen as a replacement of 1,8-Diazabicycloundec-7-ene (DBU) simply because it also has two nitrogen atoms in its molecular structure (Figure 2-9) and extra advantage in its stability. A solution of pyrazine and quinoline was prepared with the same nitrogen concentration (ppm N) in acetone to test the sensitivity of the NPD detector.



Pyrazine Quinoline

Figure 2-9. Molecular structures of pyrazine and quinoline.

The result proves our first hypothesis that the molecule contains more nitrogen atoms (pyrazine), has higher sensitivity than the molecule (quinoline) with single nitrogen atom. However, it is not a simple proportional relationship. As shown in Table 2-4., the peak area of pyrazine is more than double the peak area of the quinoline when nitrogen concentrations were 87 ppm N, 174 ppm N and 349 ppm N. Interestingly, when nitrogen concentration was 699 ppm N, it seems that the peak area of pyrazine is double the peak area of quinoline. However, this observation is only a coincidence, because both pyrazine and quinoline have linear response to the NPD detector, which were shown in Figure 2-10. The result suggests that the response of nitrogen-containing molecules to NPD detector is more likely to be structural depended, rather than a simple proportional relationship. It leads to another question that whether nitrogen compounds with similar structures would have similar responses to the NPD detector.

Table 2-4. NPD peak area comparison of pyrazine and quinoline.

Concentration ppm N	Pyrazine peak area (pA*s)	Quinoline peak area (pA*s)
87	449.75	103.25
174	994.12	261.89
349	2015.5	852.67
699	4042.90	2216.9

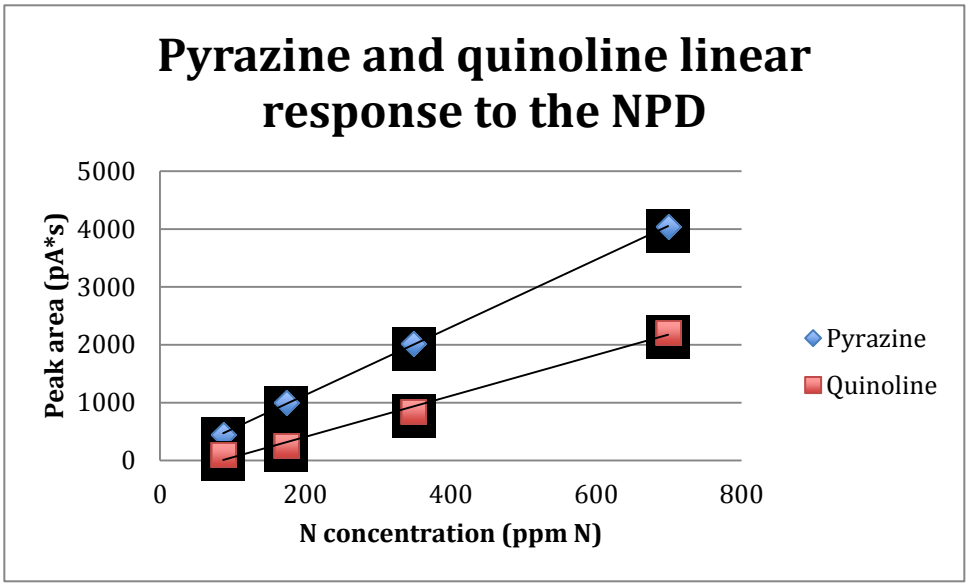
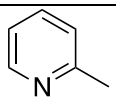
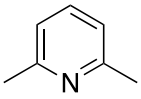
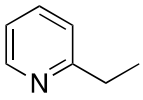
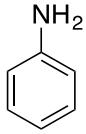
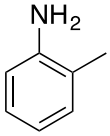
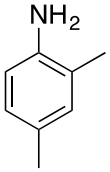
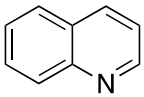
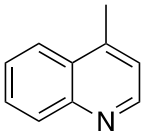
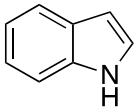


Figure 2-10. Linear response of pyrazine and quinoline to the NPD detector.

To answer the question, pyridine derivatives, aniline derivatives, quinoline derivatives and indole (Table 2-5) were chosen to be external calibration standards for quantitative analysis of nitrogen compounds in DCM and acetone fractions of the silica extraction of naphtha. The responses of those calibration standards to the NPD detector reveal nitrogen compounds that have similar molecular structure might have similar responses to the NPD detector.

Linear responses were obtained for all the compounds of calibration standard. The results indicate that, pyridine derivatives are having similar response to the NPD detector, which is dependent on the concentration of nitrogen atom in the pyridine derivatives. Consistent results were observed from aniline derivatives and quinoline derivatives, which supports the idea that nitrogen-containing compounds with similar structures would have similar response to NPD detector. However, a larger number of nitrogen-containing compounds have to be tested in order to further confirm this observation. The calibration standards also reveal that the NPD detector trend to give different response to structurally different nitrogen compounds.

Table 2-5. Responses of calibration standard (1600 ppm) to the NPD detector.

Compounds	Retention time (mins)	Formula	Molar mass (g/mol)	Fraction of N	Response (pA.s/ppm substance)*	Response (pA.s/ ppm N)*
 2-methyl pyridine	2.101	C_6H_7N	93.13	0.15	0.73	4.86
 2,6 lutidine	2.400	C_7H_9N	107.15	0.13	0.54	4.18
 2-ethylpyridine	2.671	C_7H_9N	107.15	0.13	0.62	4.77
 Aniline	3.441	C_6H_7N	93.13	0.15	0.34	2.29
 m-toluidine	4.864	C_7H_9N	107.15	0.13	0.29	2.20
 2,4 dimethyl aniline	6.462	$C_8H_{11}N$	121.18	0.12	0.24	1.99
 Quinoline	7.964	C_9H_7N	129.16	0.11	0.43	3.89
 Lepidine	10.925	$C_{10}H_9N$	143.19	0.10	0.35	3.48
 Indole	9.039	C_8H_7N	117.15	0.12	0.32	2.71

*Response (pA.s/ppm substance) is the slope of calibration curve for each standard compound.
*Response (pA.s/ ppm N) = Response (pA.s/ppm substance) / Fraction of N.

With nitrogen phosphorous detector (NPD), quantitative analysis of both DCM and acetone fractions gave total concentration of nitrogen compounds in the naphtha. The NPD detector has a major advantage over the frame ionization detector (FID) for analysis of neutral nitrogen-containing compounds. The neutral nitrogen containing compounds of naphtha were eluted into DCM fraction in the silica extraction, along with large amount of oxygen containing compounds, for example, ketones and alcohols. In fact, the major compounds in DCM fraction were oxygen-containing compounds, which covered the peaks of neutral nitrogen containing compounds. Therefore, quantitative analysis of neutral nitrogen compounds in DCM fraction with frame ionization detector (FID) will give very large error. This was the reason that FID was only chosen for quantitative analysis of basic nitrogen compounds in acetone fraction. In that case, non-nitrogen compounds did not cover the peaks of basic nitrogen compounds that were the major compounds in the acetone fraction.

The NPD has extremely high sensitivity to nitrogen containing compounds. In opposite, molecules without nitrogen atoms would have extremely low sensitivity to this detector, as oxygen-containing compounds in the DCM fraction have ignorable response to NPD detector. With the N-selective advantage of the NPD, the peaks in the chromatogram were truly representing the nitrogen containing compounds in the DCM fraction. Neutral nitrogen compounds were the majority of nitrogen compounds in DCM fraction, although it possibly also contains small amount of basic nitrogen compounds that did not separate properly during the silica extraction. In Table 2-6, the concentration of basic nitrogen compounds in naphtha was calculated with equation (7), and concentration of neutral nitrogen compounds in naphtha was calculated with equation (8). This method of calculation assume that all the basic nitrogen compounds were in acetone fraction, and all the neutral nitrogen compounds were in the DCM fraction, which did not take into account the minor basic nitrogen compounds in DCM fraction.

Table 2-6. NPD quantitative analysis of nitrogen compounds in naphtha.

Calibration compounds	m_D (ug)	m_A (ug)	m_T (ug)	C_D (ppm)	C_B(ppm)	C_T (ppm)
2-methyl pyridine	19938.9	28861.2	48800.1	133.9	193.8	327.7
2,6 lutidine	10191.4	27835.8	38027.2	68.4	186.9	255.3
2-ethylpyridine	21147.0	32085.8	53232.8	142.0	215.4	357.4
Aniline	43304.6	57883.3	101187.9	290.8	388.7	679.5
m-toluidine	55313.4	70343.2	125656.6	371.5	472.4	843.9

2,4-dimethyl aniline	21718.8	54859.1	76577.9	145.9	368.4	514.3
Quinoline	63675.4	64146.1	127821.5	427.6	430.8	858.4
Lepidine	4170.5	39192.1	43362.6	28.0	263.2	291.2
Indole	68523.6	74855.8	143379.4	460.2	502.7	962.9
Average	55367.1	50006.9	100623.3	229.8	335.8	565.6

Equations for calculation of concentration of N compounds in naphtha (ppm):

(6)

$$C_T = \frac{m_T}{m_{naphtha}}$$

(7)

$$C_B = \frac{m_B}{m_{naphtha}}$$

(8)

$$C_D = \frac{m_D}{m_{naphtha}}$$

C_T: Total concentration of N compounds in naphtha
C_B: Concentration of basic N compounds in naphtha
C_D: Concentration of neutral N compounds in naphtha
m_A: Mass of N compounds in acetone fraction
m_D: Mass of N compounds in DCM fraction
m_T: Total mass of N compounds in naphtha
$m_{naphtha}$: Mass of naphtha (148.12 g, 200 mL)

In addition, types of nitrogen-containing compounds in the fuel oil like naphtha are diversified. Depending on which calibration compound was used to calibrate the peaks in the chromatogram, the quantification results were not a fixed number (Table 2-6). This is also consistent with the observation on the responses of calibration standards to the NPD, that the responses of nitrogen compounds are structural dependent (Table 2-5). So NPD can be used to estimate the total concentration of nitrogen-containing compounds in naphtha, rather than providing an absolute number. This number would be closer to the real number if one type of nitrogen compound is the dominated compound in the oil, and that type of compound is chosen for calibration. In the thermally cracked naphtha, pyridine derivatives are dominated. Therefore, the basic nitrogen compounds in the naphtha would be around 186 to 215

ppm. The quantitative analysis with FID was 199 ppm, which is also within the right range. Knowing this range also provide valuable information for the later design of denitrogenation reaction. A close to stoichiometric amount of denitrogenated reagent would be employed in the experimental trails, instead of starting with random amount of reagent that would further complicate the research. Furthermore, NPD analysis is capable of giving a standard of what percentage of nitrogen-containing compounds has been removed by denitrogenation reactions. In chapter 3, the nitrogen phosphorous detector (NPD) was used in this purpose to measure the nitrogen compounds removal ability of the bromoacetic acid denitrogenation reaction.

2.4 Conclusion

The identification and quantification of nitrogen-containing compounds in thermally cracked naphtha were performed. Due to the low abundance of these compounds in a complex matrix, it was necessary to extract and concentrate these compounds prior to analysis. This was achieved by base pretreatment followed by adsorption and selective extraction. The main outcomes of this study were:

(a) Most nitrogen containing compounds in thermally cracked naphtha was heterocyclic. Pyridinic compounds were the dominant class, followed by quinolinic compounds.

(b) The basic nitrogen-compound concentration was 200 μg/g, measured by GC-FID with calculated relative response factor.

(c) Base pretreatment had to be conducted at ambient conditions. At 60 °C reaction with nickel (II) carbonate also converted phenolic compounds to their respective nickel phenolate salts.

(d) The acids in thermally cracked naphtha were mostly C_4-C_{11} fatty acids, i.e. linear and branched carboxylic acids.

(e) The response of nitrogen-containing compounds to nitrogen phosphorus detector (NPD) is structure dependent.

(d) Nitrogen phosphorus detector (NPD) was used for quantitative analysis of nitrogen-containing compounds in the thermally cracked naphtha, the concentration range of basic nitrogen compounds in the naphtha was186-215 ug/g.

2.5 Reference

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3 Denitrogenation of basic nitrogen compounds from thermally cracked naphtha.

3.1 Introduction

Denitrogenation of oil is needed before many desirable catalytic conversion processes to avoid catalyst deactivation. Even nitrogen-containing compounds are present in a very low concentration in the feed, their strong adsorption to the catalyst can make significant negative impacts and slow down the conversion such as hydrocracking and hydrodesulfurization. For example, in the hydrodesulfurization (HDS) process, nitrogen-containing compounds have to be removed to achieve ultra low sulfur content oil. Similar to hydrodesulfurization (HDS), the practical method available for industrial removal of nitrogen-containing compounds from oil is hydrodenitrogenation (HDN). It is known that hydrotreating is a high temperature, high pressure, high cost method. Depending on the feed composition, the actual hydrotreating process also involves hydrodesulfurization (HDS), hydrodeoxygenation (HDO), and hydrogenation of olefins or aromatics and heat control. It is a complicated process as the products from these different hydrotreating reactions may affect the catalyst. In addition, the olefins and aromatics are sometimes valuable compounds in the feed, it is not always desirable to hydrogenate these compounds. In this case, non-hydrodenitrogenation methods are required to remove nitrogen-containing compounds selectively, and leave olefins and aromatics remaining in the oil.

Non-hydrodenitrogenation methods can be classified as precipitation,[1] photo irradiation,[2] solvent extraction,[2-3] acid treatment,[2] adsorption,[4-6] chemical conversion.[7] Precipitation is using chemical or physical treatment to allow formation of solid residue of nitrogen-containing compounds in the naphtha. Photo irradiation utilizes the UV irradiation to decompose oxidized nitrogen-containing compounds in the oil. In solvent extraction normally one of the solvent or combination of solvents can be introduced to the oil and form two liquid layers. Solvents can extract nitrogen-containing compounds and then removal is achieved by layer separation. Some of the solvent extraction methods such as ionic-liquid extractions were mention in the introduction of chapter 2. Acid treatment is acid-base chemical reaction, which is capable of removing basic nitrogen-containing compounds from oil. Adsorption is mainly the physical separation method involves zeolite, silica, alumina or activated carbon. New research in adsorption area is focusing on polymers. Chemical conversion is basically applying chemical reagents to react with nitrogen-containing compounds. These methods can be combined to achieve a maximum removal ability of nitrogen-containing compounds from naphtha, and also avoid disadvantages of using single method would have.

One of the precipitation methods developed by Shiraishi, et al. was applied to remove nitrogen-containing compounds from model oil and light oil.[1] Aniline, indole, and carbazole were dissolved in xylene to make the model oil. Alkylating reagents methyl iodide and silver tetrafluoroborate were tested with three model compounds in xylene and all of them formed precipitate. Nuclear magnetic resonance (^{1}H and ^{13}C NMR) was used to confirm the structures of the precipitates (Figure 3-1). Both aniline and carbazole were alkylated and formed the salt with tetraborate ion. Although indole was

alkylated at its nitrogen atom, it was alkylated on the aromatic ring as well. The N-alkylation product is not the major product. The precipitate of indole is a mixture of complicated alkylated products rather than tetraborate salt as a single product.

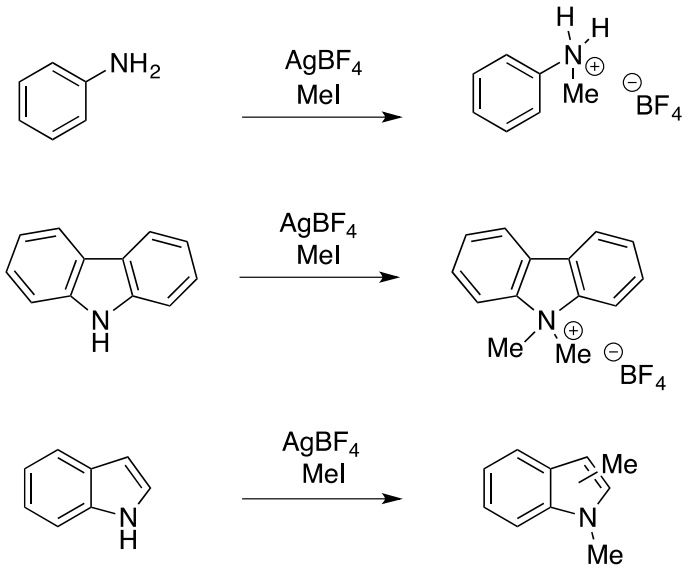


Figure 3-1. Alkylation reaction of nitrogen model compounds with methyl iodide and silver tetrafluoroborate.[1]

This alkylation method was then tested on the light oils. The results shown nitrogen-containing compounds in the light oil were alkylated and formed precipitate in the light oil. This method successfully removed 80% of the nitrogen-containing compounds from light oils. The great advantage of this method is that sulfur-containing compounds were removed with nitrogen-containing compounds by the similar fashion. However, the nature of alkylation reaction has a drawback that nitrogen-containing compounds with large carbon number are not easily alkylated. The reason is that less electron density on the nitrogen when it is in a large carbon number molecule, for example, when carbazole are attached with long carbon chain substituents. Another problem of this method is the reaction with indole type nitrogen-containing compounds. Although alkylation on the nitrogen atom occurred, alkylation also occurred on the aromatic ring. Alkylation on the aromatic ring has less benefit to the precipitation and this cost extra amount methyl iodide that is a relatively expensive reagent.

The same research team, Shiraishi, et al.[2] developed photochemical denitrogenation method, employing UV irradiation with liquid-liquid extraction to remove nitrogen-containing compounds from model oil and light oil. Aniline, indole and carbazole were added into xylene to make the model oil. Two liquid-liquid extraction systems were tested including oil-water and oil-acetonitrile. While under UV irradiation by a 300 W high-pressure mercury lamp, the oil was stirred with water with volume ratio of 100/300 mL. Air bubbling through the mixture at 500 mL/min in atmospheric pressure to oxidize the nitrogen-containing compounds. Hydrogen peroxide can be alternative oxidation reagent and actually

accelerate the photodecomposition of nitrogen-containing compounds. Similar reaction procedure was adapted to oil-acetonitrile mixture with 200/200 mL volume ratio. The analysis was carried out with gas chromatography coupled mass spectrometry (GC-MS), gas chromatography coupled flame ionization detector (GC-FID), and gas chromatography coupled atomic emission detector (GC-AED). Nitrogen-containing compounds in light oils were not analyzed directly, fractionation of basic and neutral nitrogen compounds had to be performed because the nitrogen emission spectrum is overlapping with C-H band in aromatic hydrocarbons. Aromatic hydrocarbons have to be removed before analysis with gas chromatography coupled atomic emission detector (GC-AED). The detail fractionation method was discussed earlier in the chapter 2 introductions.

The photochemical denitrogenation method required assistant of liquid-liquid extraction and oxidation. In the light oil photochemical denitrogenation, more than 97% of nitrogen-containing compounds were removed into acetonitrile in the present of hydrogen peroxide. Oil-water system could also remove 80% of nitrogen-containing compounds from the light oil in the present of hydrogen peroxide and UV irradiation. The method also removed certain amount of sulfur containing compounds along with the nitrogen-containing compounds.

Ionic-liquid extraction has ability of removal nitrogen-containing compounds from oil, which has been discussed in the chapter 2 introductions. It has advantage of low volatility, alterable solvent properties that extracts both basic and neutral nitrogen-containing compounds and produced by relatively simple synthetic procedures. However, when it applies to the real oil feed, most of ionic liquid have stability issue or simply loss removal capability. Alternative class of ionic liquid solvent known as eutectic solvents has shown promising ability of removal nitrogen-containing compound from model oil. From economic point of view, eutectic solvents are lower prices, less toxic and usually generated by single step synthesis. They still share the advantages of normal ionic liquid such as low volatility and non-flammable. Ali, et al.[3] have studied some eutectic solvents (Table 3-1) and their nitrogen-containing compounds removal ability. Synthesis of eutectic solvents is one-step heating (353-373 K) reaction of two components. Produced eutectic solvents were dried under vacuum without further purification process.

Table 3-1. The compositions of eutectic solvent used by Ali et al. [3]

Component 1	Component 2
Choline chloride	Malonic acid
Choline chloride	Glycolic acid
Choline chloride	Phenylacetic acid
Choline chloride	Phenylpropionic acid
Choline chloride	Glycerol
Choline chloride	Urea
Glycerol	Citric acid
Fructose	Malic acid

Eight eutectic solvents were tested to extract pyridine and carbazole from model oil (*n*-heptane). Best results were achieved, which more than 98 % of pyridine and carbazole were removed, when choline chloride and phenylacetic acid were used to make the eutectic solvent (Figure 3-2). Quantitative analysis was performed by high performance liquid chromatography (HPLC). The eutectic solvents have not been tested with real oil feed, however, the solubility of *n*-heptane in most of eutectic solvents are very low.

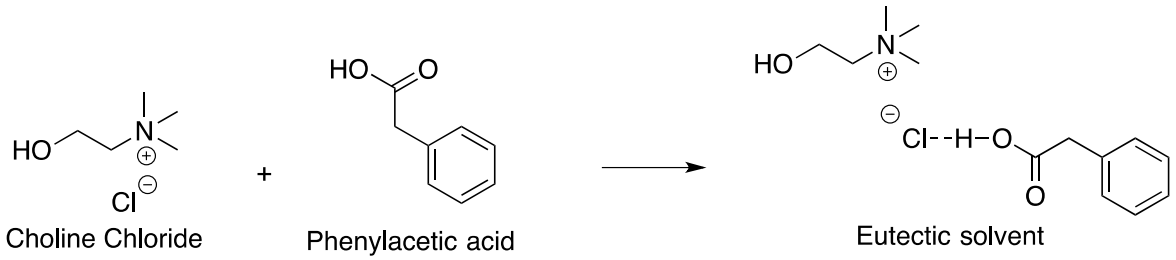


Figure 3-2. Eutectic solvent made by the reaction of choline chloride and phenylacetic acid.

Adsorption can also be used to extract nitrogen-containing compounds from oil. Activated carbon has high adsorptive ability in the removal of nitrogen-containing compounds, due to interactions between oxygen functional groups on the activated carbon and nitrogen-containing compounds in the oil. This could be simple acid-base interaction between acid groups and basic nitrogen-containing compounds, and hydrogen-bonding between oxygen functional groups and neutral nitrogen-containing compounds.

Han, et al.[4] has developed a denitrogenation method using oxidized activated carbon. Oxidizing reagents like tert-butyl hydroperoxide solution, sodium hypochlorite solution, saturated ammonium persulfate solution, concentrated nitric acid, and a mixture of concentrated sulfuric acid and nitric acid were used to introduce oxygen functional group on to the activated carbon. Temperature program desorption (TPD) was used to characterize oxygen functional groups on the oxidized activated carbon. The oxidized activated carbons were tested with light cycled oil to study their ability of removal nitrogen-containing compounds. Quantification of nitrogen-containing compounds in oil was performed with gas chromatography coupled nitrogen phosphorus detector (GC-NPD). Total N content was measured with NS-9000 analyzer from Antek Instruments Inc. In their study, nitrogen-containing compounds were classified by ring numbers: 1-ring, 2-ring, 3-ring and 4-ring. For normal activated carbon, 61%, 50%, 32% and 34% removal ratio were observed for 1-ring, 2-ring, 3-ring and 4-ring nitrogen-containing compounds. Oxidized activated carbons which were treated by different oxidizing reagents shown different ability of removing these four types of nitrogen-containing compounds. For example, activated carbon that oxidized by ammonium persulfate and t-butyl hydroperoxide can remove more 3-ring and 4-ring nitrogen-containing compounds than the normal activated carbon. Oxidation with nitric acid and sodium hypochlorite did not increase the adsorbed amount of nitrogen-containing compound on activated carbon. The mixture of nitric acid and sulfuric acid was so strong that it damaged the pore in activated carbon, it lose ability to adsorb 2-ring and 3-ring nitrogen-containing compounds, however, selectively removed 4-ring nitrogen-containing compounds. This denitrogenation method dose not have very high removal efficiency, but it opened the door to

selectively removal of nitrogen-containing compounds base on ring-size. And the selectivity can be control by changing oxidizing reagents.

In order to achieve specific control on selectivity of denitrogenation from oil, peoples are paying more attention to the polymers, particularly functionalized polymers. Misra, et al.[5] have synthesized poly glycidyl methacrylate supported fluorenone derived π-acceptors for denitrogenation of bitumen derived gas oil. The concept is based on formation of charge transfer complex between electron rich nitrogen-containing compounds and electron deficient π-acceptors.[6] This concept would solve one of the problem in solvent extraction. Large carbon number alkylated carbazoles are hard to be extracted by solvent extraction. But alkylated carbazoles are electron rich nitrogen-containing compounds, which should readily form charge transfer complex with π-acceptors. The polymers made by Misra, et al.[5] contains poly glycidyl methacrylate (PGMA), hydroxyl amine linker and fluorenone derivatives (Figure 3-3). These functionalized polymers were thermally stable under 200 ℃.

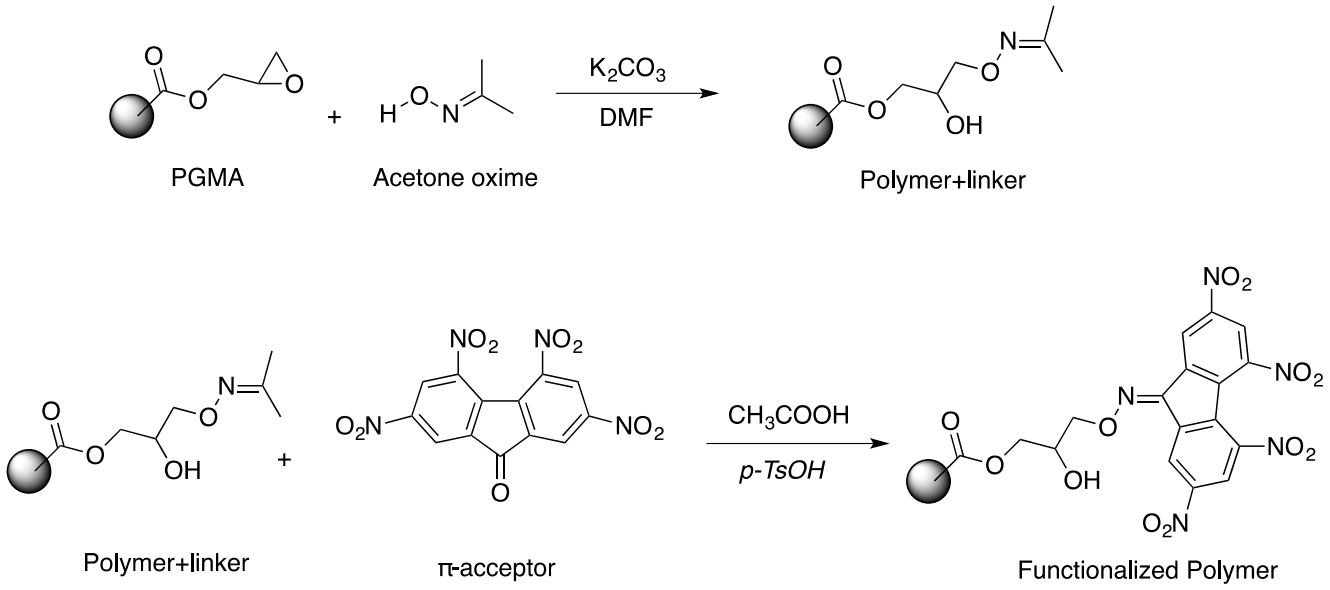


Figure 3-3. Synthesis of functionalized polymer for denitrogenation of gas oil.[5]

There were three types of fluorenone derivatives served as π-acceptor including 2,7-dinitro-9-fluorenone (DNF), 2,4,7-trinitro-9-fluorenone (TriNF) and 2,4,5,7-tetranitro-9-fluorenone (TENF). Structures of these π-acceptors are shown in Figure 3-4. The functionalized polymers were tested with bitumen derived gas oil and quantitative analysis was performed by Antek-Model 9000 Nitrogen/Sulfur analyzer. The polymer that functionalized by TriNF has the best denitrogenation ability that 14.4% of nitrogen-containing compounds were removed, while DNF and TENF could only removed 9.4% and 11.2% of nitrogen-containing compounds from gas oil. The reason behind this trend is that DNF has only two nitro electron-withdrawing groups, which makes it the weakest π-acceptor. TeNF has four nitro electrion-withdrawing groups it is the best π-acceptor. However, two of the nitro groups are too close to each other, the resulting constrain on the ring force the original plane geometry to distort,

which prevent the formation of charged transfer complex with nitrogen-containing compounds.

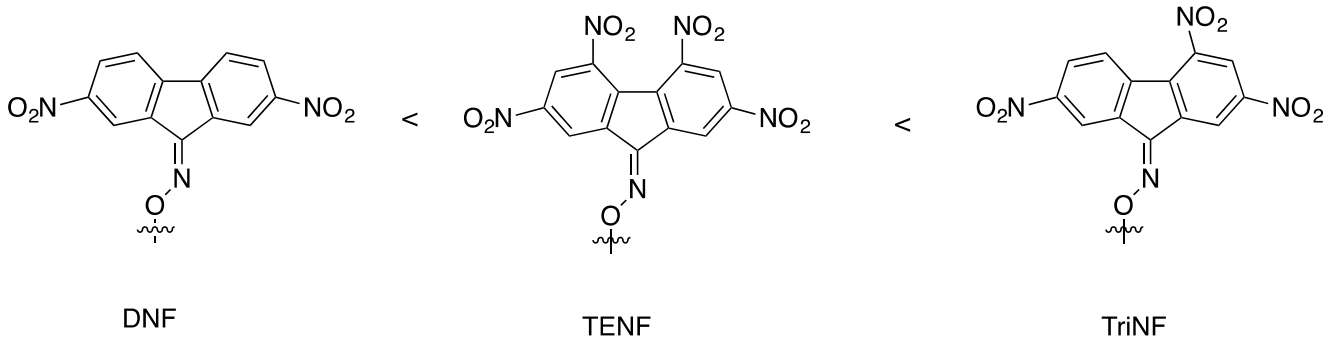


Figure 3-4. Structures of π-acceptors linked on the polymer and their denitrogenation ability to gas oil.

Although the best denitrogenation result from TriNF functionalized polymer is only 14.4%, it provides an idea of selectively removal of alkylated carbazole compounds from real oil. More investigation on using different π-acceptors on polymer may lead to a better result. And the method can also be combined with other denitrogenation strategies such as solvent extraction to achieved a better result that can not be achieved with single method.

Most chemical conversion methods are oxidative denitrogenation.[7] There are three types of oxidants including hydrogen peroxides or related compounds, ozone and air or oxygen, which are commonly used for denitrogenation and desulfurization. Oxidative denitrogenation reactions with hydrogen peroxides based oxidants were two phase reaction. Water reduced the rate of oxidation of nitrogen containing compounds in oil.

In order to avoid two phases oxidative denitrogenation, an oil phase peroxided based oxidative denitrogenation method was developed by Lin, et al.[7] The peracetic acid (CH_3COOOH) they made is capable of being dissolved in organic oil phase and reaction dose not involve aqueous solution. Traditionally, preparation of peracetic acid (CH_3COOOH) was made by reacting acetic acid with hydrogen peroxide in aqueous solution (Figure 3-5).

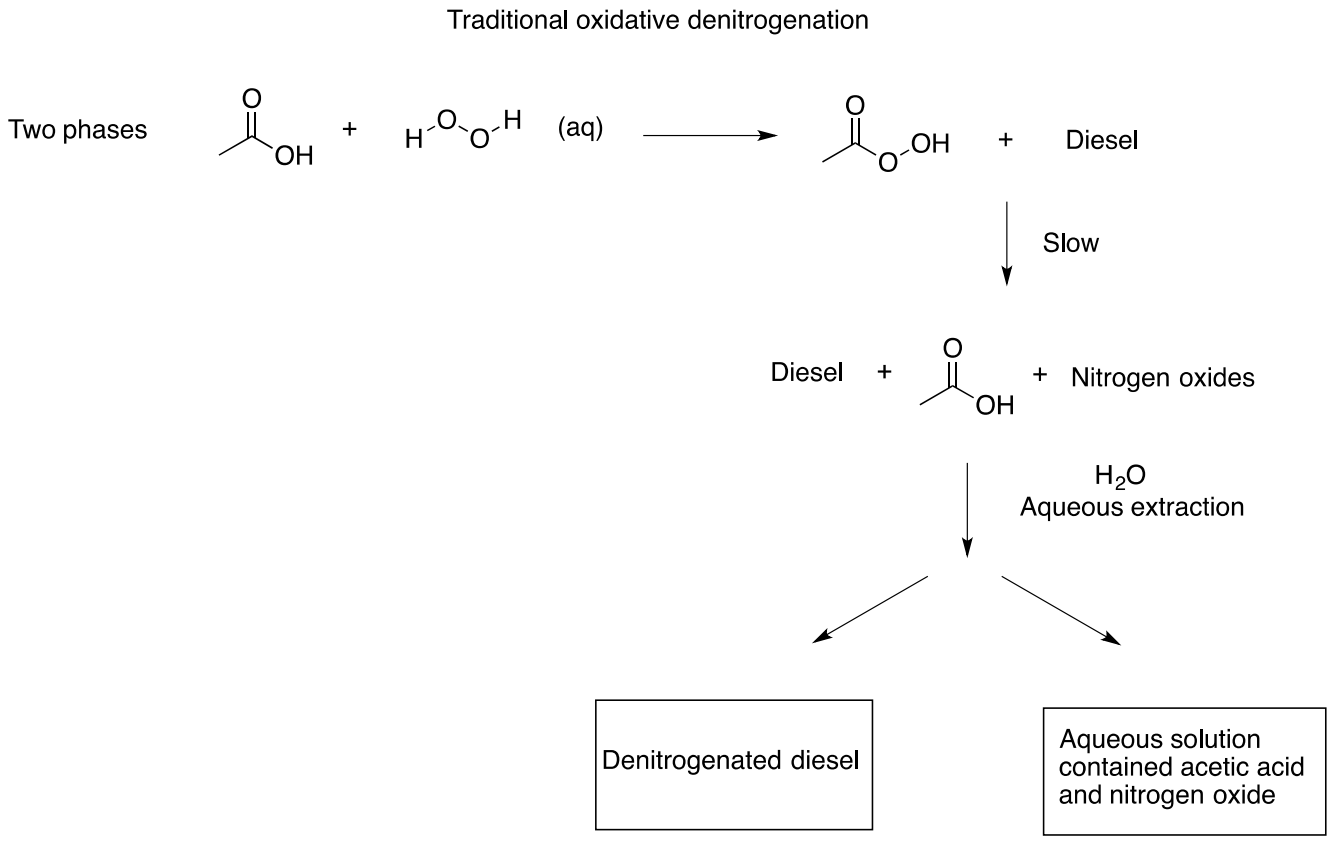


Figure 3-5. Traditional oxidative denitrogenation process of diesel.

In Lin's non-aqueous synthetic method of peracetic acid,[7] formaldehyde reacted with molecular oxygen in the present of homogenous catalyst Fe (III) acetylacetonate in acetone. The following oxidative denitrogenation reaction with peracetic acid in diesel was single phase. The nitrogen-containing compounds were oxidized to form N-oxides, which were later extracted by water (Figure 3-6). The non-aqueous oxidative denitrogenation reaction was effective as nitrogen concentration was reduced from 213 ppm down to 68 ppm. The quantitative analysis was performed with gas chromatography coupled atomic emission detector (GC-AED). This method also removed sulfur-containing compounds from diesel through oxidative desulfurization.

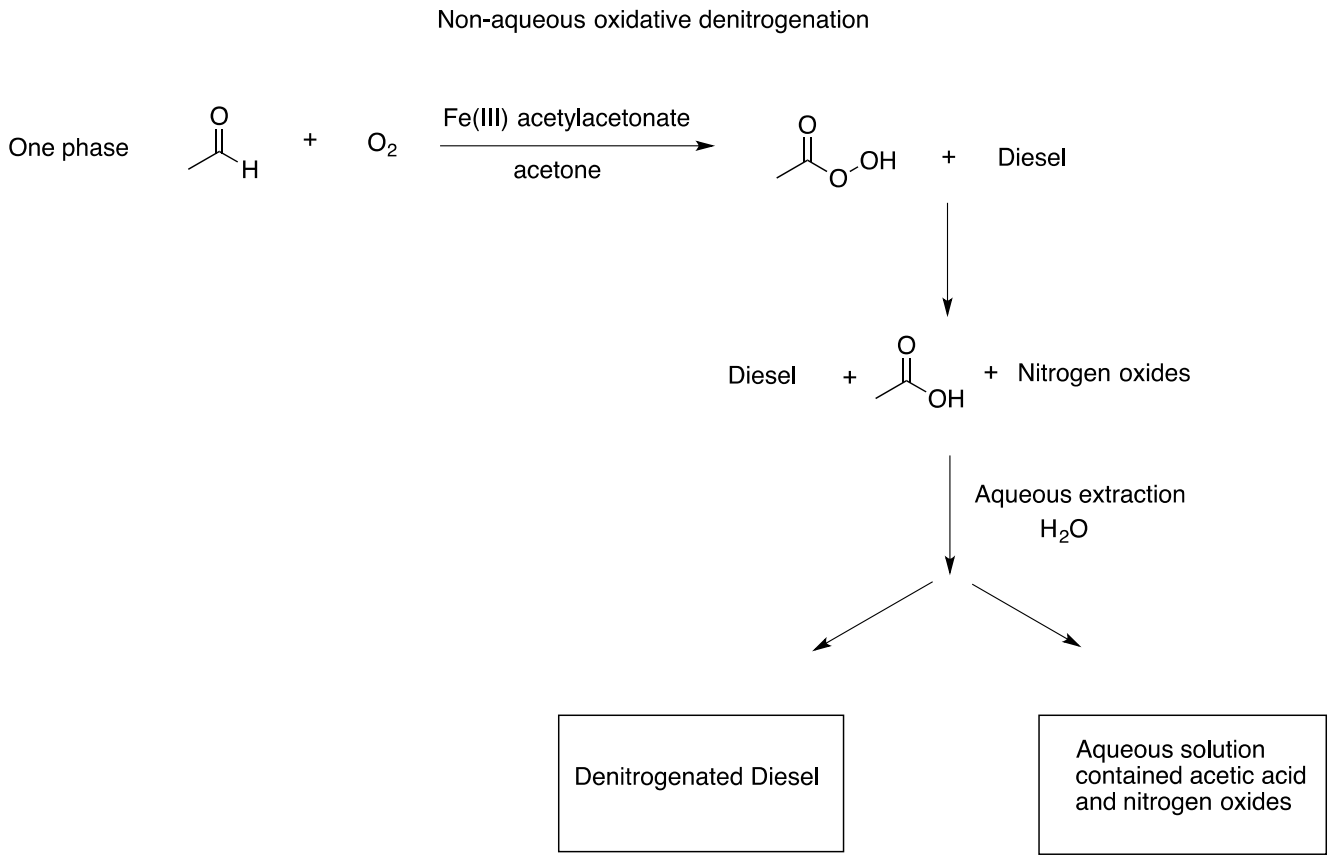


Figure 3-6. Non-aqueous oxidative denitrogenation process of diesel.

Oxidation reactions dominate the chemical conversion methods in removing nitrogen-containing compounds from oil, because they turn nitrogen-containing compounds into a much polar compounds that would be dissolved in polar solvents. However, oxidative denitrogenation reactions generate side-products like acetic acids in oil, which requires additional purification process to remove them. Some oxidizing reagents are classified as dangerous goods because of potential risks on combustion and explosion.

Our work on denitrogenation of thermally cracked naphtha is an alkylated chemical conversion method. The concept of this alkylated denitrogenation based on chemical reaction of pyridine derivatives with bromoacetic acid. The method was the first step of Zhang, et al.'s work for preparation of indolizines (Figure 3-7).[8] These two reagents were simply stirred in ethyl acetate (EtOAc) at room temperature for 3 hours. The product is extremely polar pyridinium bromide salt that forms precipitate in ethyl acetate. Interestingly, this is an Sn2 alkylation reaction at nitrogen atom, instead of a simple acid-base reaction. The pyridinium bromide salt can be removed by filtration or liquid-liquid extraction with polar solvent.

The same alkylation reaction occurs between quinoline derivatives and bromoacetic bromide at slightly different conditions, which was proved by Mehranpour, et al. (Figure 3-8). The idea implies that basic nitrogen-containing compounds in oil may react with bromoacetic acids to form products that can be removed by filtration or liquid-liquid extraction. The only reagent needed would be bromoacetic acid that is safe, inexpensive and reaction occurs at room temperature in a short time without requirement of complicated purification process.

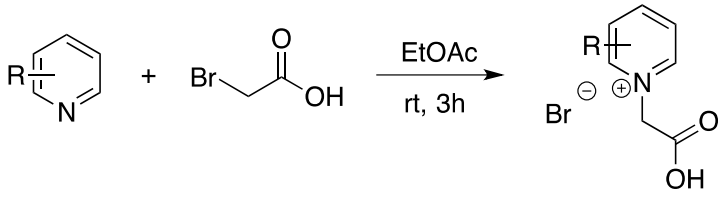


Figure 3-7. Reaction of bromoacetic acid with pyridine derivatives to form pyridinium bromide salt.[8]

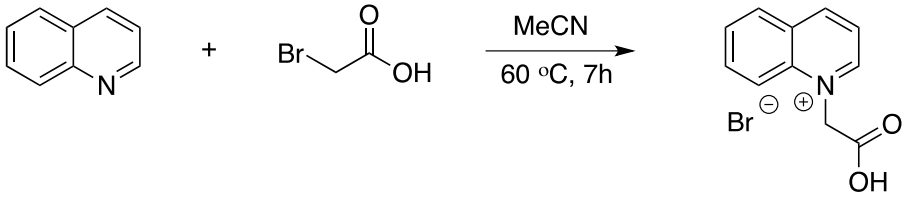


Figure 3-8. Reaction of bromoacetic acid with quinoline to form quinolinium bromide salt.[9]

Bogardus, et al.[10] discovered that quaternary ammonium derivatives of tertiary amines could be cleaved by hydrolysis at basic conditions. For example, hydrolysis of N-(4-hydroxy-3,5-dimethylbenzyl)pyridinium bromide in water would cleave the nitrogen-carbon bond and generate pyridine and 4-Hydroxymethyl-2,6-dimethylphenol (Figure 3-9). It was found that rate of hydrolysis was proportional to pH of the solution. In other words, the more basic of solution, the faster the hydrolysis reaction would occur. This idea can be applied to cleave the nitrogen-carbon of pyridinium or quinolinium bromide salt, resulting pyridine or quinoline derivatives can be valuable products for other purpose. Liquid-liquid extraction is able to recover these basic nitrogen-containing compounds from the aqueous solution. In addition, hydrolysis of pyridinium or quinolinium bromide would allow us to analyze what types of pyridine and quinoline derivatives are present in the oil. Pyridine and quinoline derivatives are the most common basic nitrogen-containing compounds in lighter fraction of oil. Qualitative analysis of these basic nitrogen-containing compounds can be performed by gas chromatography coupled mass spectrometry (GC-MS).

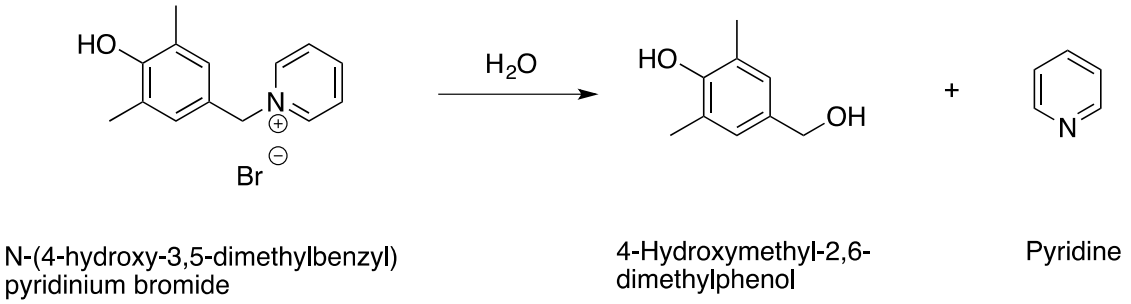


Figure 3-9. Hydrolysis of quaternary ammonium derivatives of tertiary amine.[10]

3.2 Experimental

Materials. Thermally cracked naphtha was obtained from an industrial visbreaking unit processing a deasphalted oil from steam assisted gravity drainage produced Athabasca oilsands bitumen.

HPLC grade solvents used in the study, including *n*-pentane (99.7%), *n*-heptane (99%), acetone (99.7%), dichloromethane DCM (99.9%), diethyl ether (99.9%), toluene (99.9%) were purchased from Fisher Scientific, Canada. Chemical reagents including bromoacetic acid (99%), chlorosulfonic acid (99%), sodium hydroxide (98%), 2-methyl pyridine (98%), 2,6-lutidine (98%), 2-ethyl pyridine (97%), aniline (99.5%), m-toluidine (99%), 2,4-dimethyl aniline (99%), quinoline (98%), lepidine (99%) and indole (99%) were purchased from Sigma Aldrich, Canada. Nickel (II) carbonate, Magnesium sulfate were purchased from ACROS.

Analysis. Qualitative analysis was carried out using an Agilent 7820A gas chromatography (GC) with 5977E MSD mass spectrometer (MS). Agilent 19091S-433 column (length: 30 m, diameter: 250 μm, film thickness: 0.25 μm, max temperature 325 °C) was used for separation. Helium was the carrier gas with flow of 1 mL/min. Split ratio was 1:100. The oven has initial temperature 80 °C, which was increased to 170 °C with a ramp rate of 6 °C/min, followed by a raise to 300 °C with a ramp rate of 15 °C/min and held at 300 °C for 5 min.

Quantitative analysis of nitrogen-containing compounds was carried out with an Agilent 7890A gas chromatography (GC) equipped with both a flame ionization detector (FID) and a nitrogen phosphorus detector (NPD). The same column and temperature program was employed as for the GS-MS analysis.

NPD quantitative analysis of bromoacetic acid denitrogenation. A stock solution was prepared by dissolving 2-methyl pyridine (348 mg, 1600 ppm) 2,6-lutidine (348 mg, 1600 ppm), 2-ethyl pyridine (348 mg, 1600 ppm), aniline (348 mg, 1600 ppm), m-toluidine (348 mg, 1600 ppm), 2,4-dimethyl aniline (348 mg, 1600 ppm), quinoline (348 mg, 1600 ppm), lepidine (348 mg, 1600 ppm) and indole (348 mg, 1600 ppm) into toluene (250 mL). This stock solution was then diluted to 800 ppm and 400 ppm solutions as external calibration standard. This is the same method that has been used for NPD

quantitative analysis of nitrogen compounds in naphtha in the chapter 2 experimental sections. The only difference is the naphtha sample in the analysis here was denitrogenated by bromoacetic acid.

The internal standard calibration method was also applied to measure the nitrogen compounds removal ability of bromoacetic acid denitrogenation. The following Table 3-2 shows how acetone fraction and DCM fraction from original naphtha and bromoacetic acid treated naphtha were prepared for analysis. The equations were used in the calculation of the percentage of nitrogen compounds removal.

Table 3-2. Sample preparation of NPD analysis (internal standard method), A: Acetone fraction, B: DCM fraction.

Samples	Acetone fraction (mg)	Internal standard: lepidine (mg)	Solvent: Toluene (mg)
Original naphtha	44.4	6.9	846.5
Denitrogenated naphtha	45.1	6.8	842.0

A

Samples	DCM (mg)	Internal standard: lepidine (mg)	Solvent: Toluene (mg)
Original naphtha	45.0	6.1	855.2
Denitrogenated naphtha	45.3	6.3	849.3

B

Equations for calculation of percentage of nitrogen compounds removal

(1)

$$Area\ N = Area\ T - Area\ IS$$

(2)

$$Area\ N'\ (original) = \frac{Mass\ (original)}{Mass\ (denitrogenated)} \times\ Area\ N\ (denitrogenated)$$

(3)

$$Area\ N'\ (denitrogenated) = Area\ N'\ (original)\ \times \frac{Area\ IS\ (Origeinal)}{Area\ IS\ (denitrogenated)}$$

(4)

$$Area\ N\ (removed\ from\ original) = Area\ N\ (original) - Area\ N'(denitrogenated)$$

(5)

$$Percentage\ of\ N\ compounds\ removal = \frac{Area\ N\ (removed\ from\ original)}{Area\ N\ (originial)} \times 100\%$$

Area N: Area of peaks that represent nitrogen compounds.
Area IS: Area of peak that represent internal standard lepidine.
Area T: Total area of all the peaks in chromatogram.
Area N (original): Area of peaks that represent nitrogen compounds in original sample.
Area N′ (original): Area N (denitrogenated) that is corrected with mass difference of extracted fractions, which represents Area N (denitrogenated) in the scale of original sample.
Area N (denitrogenated): Area of peaks that represent nitrogen compounds in denitrogenated sample.
Area N′ (denitrogenated): Internal standard calibrated Area N′ (original), which represents the real Area N (denitrogenated) in the scales of original sample.
Mass (original): Mass of acetone/DCM fraction from original sample.
Mass (denitrogenated): Mass of acetone/ DCM fraction from denitrogenated sample.

Procedure.

Bromoacetic acid denitrogenation reaction with model compounds

To a mixture of pyridine (0.791 g, 10 mmol), quinoline (1.29 g, 10 mmol) and indole (1.17 g, mmol) in ethyl acetate (30 mL), bromoacetic acid (4.167 g, 30 mmol) was added. The reaction mixture was stirred at room temperature overnight. White residue was observed. Reaction was quenched with distilled water (20 mL). Aqueous layer was separated from organic solvent and water was evaporated under reduced pressure. The resulting white residue was identified as a mixture of pyridinium acid salt ^{1}H NMR (60 MHz, D_2O): δ 5.38 (s, 2H, NCH_2), and quinolinium acid salt ^{1}H NMR (60 MHz, D_2O): δ 5.75 (s, 2H, NCH_2). Aromatic peaks are around δ 7.86-9.46.

Denitrogenation of naphtha with bromoacetic acid

Thermally cracked naphtha (148.9 g, 200 mL) was treated with bromoacetic acid (0.1 g, 0.72 mmol) and reaction mixture was stirred overnight at room temperature. The resulting solution was washed with H_2O (3×50 mL) to remove the salt products. Then the inorganic base nickel (II) carbonate (1.32 g, 11.098 mmol) was added to the denitrogenated naphtha to neutralize the fatty acids. This solution was stirred overnight at room temperature and brown solid residue was filtered and collected. The liquid filtrate is acids free denitrogenated naphtha. The acids free denitrogenated naphtha was passed through a silica stationary phase column chromatography setup. *n*-Pentane (80 mL), DCM (420 mL) and acetone (240 mL) were used to elute the column respectively as shown in Figure 2-3. The DCM fraction and acetone fraction were collected and concentrated separately under reduced pressure. The

product fractions were analyzed by GC-MS, GC-FID and GC-NPD. Figure 3-10. shows the general procedure of this denitrogenation process.

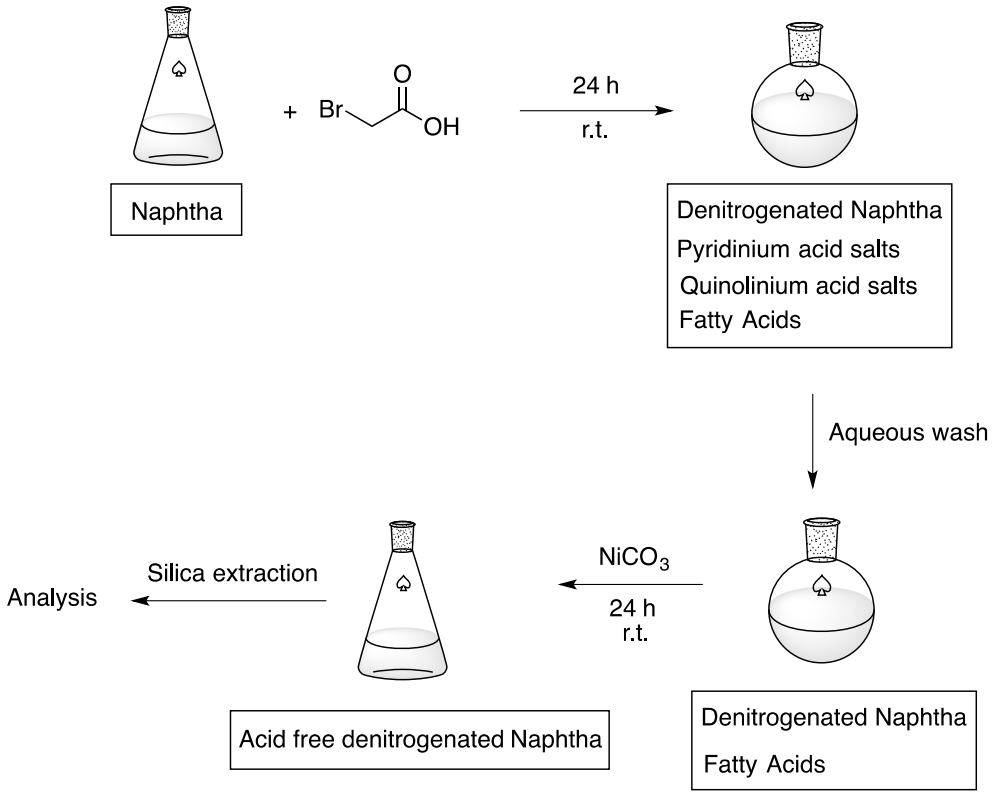


Figure 3-10. General procedure of denitrogenation reaction of naphtha with bromoacetic acid.

Analysis of fatty acids from thermally cracked naphtha

The filtered brown solid residue from the $NiCO_3$ base pretreatment was acidified with 1N HCl until pH≈2 and extracted with diethyl ether (3×20 mL), followed by washing with water (2×20 mL). The diethyl ether was dried with $MgSO_4$, and then evaporated under reduced pressure and the remaining residue was analyzed by GC-MS.

Cleavage of the quaternary ammonium carbon bond

To the aqueous solution that contains the salt products of bromoacetic acid denitrogenation reaction of naphtha, sodium hydroxide (1 g, 0.025 mol) was added and the mixture was stirred for 10 minutes. The aqueous solution was then extracted by diethyl ether (3×30mL). The organic layer was separated from aqueous solution and dried with magnesium sulfate. The dried organic layer was evaporated under

reduced pressure and liquid residue (80 mg) was collected. This liquid residue was purified with pipette column with silica gel as stationary phase. Pentane (10 mL), dichloromethane (10 mL) and Acetone (6 mL) were used as mobile phases to elute the column respectively. Dichloromethane (15 mg) and acetone fractions (41 mg) were collected and concentrated under reduced pressure. The acetone fraction was analyzed by GC-MS.

Chlorosulfonic acid reaction with pyridine

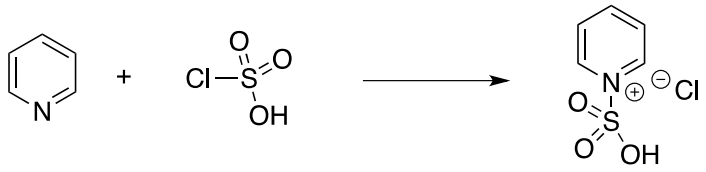


Figure 3-11. Chlorosulfonic acid reaction with pyridine to form pyridinium sulfonic acid salt.

Pyridine (1.04 g, 13.2 mmol) in dichloromethane (40 mL) was added dropwise to a stirring solution of chlorosulfonic acid (1.54 g, 13.2 mmol) in dichloromethane (40 mL) over a period of 10 minutes. The reaction mixture was stirred for 25 minute. Solvent was evaporated and the white solid residue was washed with dichloromethane (100 mL). The white solid residue (1.63 g, 8.33 mmol) was collected and identified as desired product ^{1}H NMR (60 MHz, DMSO-d6): δ 13.53 (s, 1H, OH). Aromatic peaks are around δ 8.06-8.87.[11] Yield of reaction is 63%.

Chlorosulfonic acid reaction with naphtha

Chlorosulfonic acid (0.60 g, 5.149 mmol) was added dropwise into naphtha (50.00 g) and reaction mixture was stirred at room temperature overnight. The treated naphtha has turned red and black residue was observed on the bottom of the flask. The treated naphtha was then removed. To the black residue (0.61 g), H_2O (60 mL) and dichloromethane (40 mL) was added. The two phases solution was stirred vigorously overnight, and the organic layer was separated from the aqueous layer and concentrated under reduced pressure to obtain organic residue (0.194 g). Aqueous layer was concentration under reduced pressure as well to obtain residue (0.58 g). Both residues from organic layer and aqueous layer were dissolved in ethanol (1.5 mL) and analyzed by GC-MS.

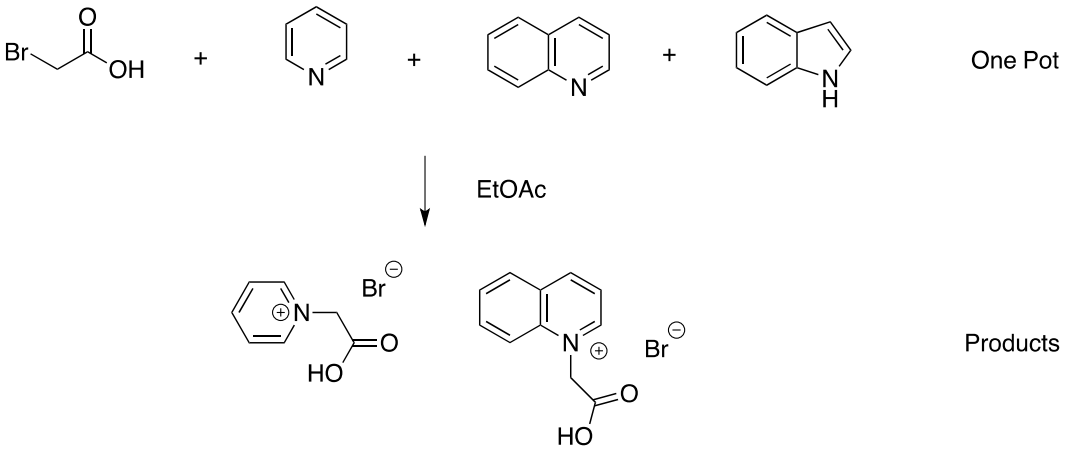
p-toluenesulfonyl chloride reaction with naphtha

p-toluenesulfonyl chloride (0.5 g, 2.62 mmol) was dissolved into naphtha (84.98 g) and reaction mixture was stirred at room temperature overnight. Residue (0.03 g) was observed and separated with treated naphtha. The residue was dissolved in ethanol for GC-MS analysis.

3.3 Results and discussion

Bromoacetic acid denitrogenation reaction with model compounds

It is known that pyridine reacts with bromoacetic acid in ethyl acetate to form a pyridinium acid.[8] In order to confirm the reliability of this chemistry, basic pyridine and quinoline and neutral indole were selected as model compounds, which reacted with bromoacetic acid in ethyl acetate at room temperature. We observed that pyridinium acid and quinolinium acid were successfully generated (Figure 3-12 A). In the ^{1}H NMR (60 MHz) spectrum of the product residue (Figure 3-12 B), the peaks represent the CH_2 in pyridinium acid (5.38 ppm) and quinolinium acid (5.75 ppm) were indicated by the arrows. The solvent peak of H_2O was identified at 4.72 ppm. The reaction was completed because the CH_2 peaks at 4.02 ppm which represent bromoacetic acid was not found in this spectrum. The peaks in the aromatic range (7.5-9.0 ppm) were highly overlapped, however, they also proved that the two desired products were successfully synthesized. The resolution of peaks can be improved and the noise can be reduced with higher magnetic frequency NMR instrument. In the case of the identification of pyridinium acid and quinolinium acid, 60 MHz NMR instrument is sufficient because the peaks of CH_2 can be easily identified. As expected, the neutral indole was not found in the reaction products. The lone pair electrons on the nitrogen atom are able to delocalize into aromatic ring, which makes it not a good nucleophile. The product mixture contains pyridinium acid and quinolinium acid can be easily removed by water extraction or filtration. Therefore, we believed that reaction of bromoacetic acid with cracked naphtha could be a potential method, which selectively removes basic nitrogen-containing compounds.



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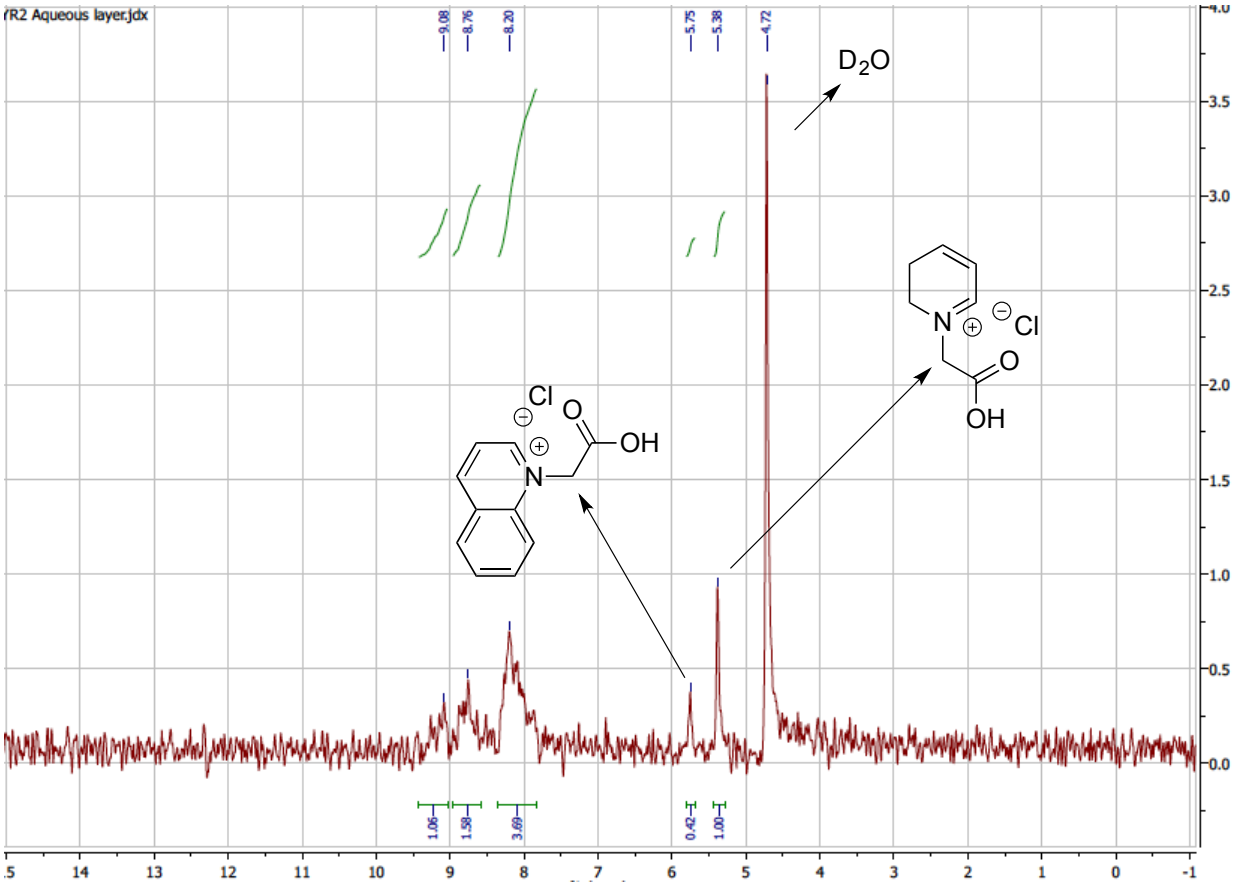


B

Figure 3-12. A: Bromoacetic acid denitrogenation reaction with model compounds. B: ^{1}H NMR (60 MHz) spectrum of the product residue.

Bromoacetic acid denitrogenation reaction with thermally cracked naphtha

When a reagent is applied to the real industrial naphtha, the selectivity of the reaction is one of the most crucial aspects. The thermally cracked naphtha contains several types of nitrogen containing compounds, as well as oxygen and sulfur containing compounds that are sometimes chemically more active than nitrogen compounds. These active non-nitrogen-containing compounds can consume the reagent for denitrogenation reaction, therefore, significantly reduce its ability to remove nitrogen compounds.

In our naphtha, the present of oxygen containing compounds, for example, ketones, alcohols, and fatty acids have been confirmed with gas chromatography coupled mass spectrometry (GC-MS) in the earlier characterization work. The results of naphtha denitrogenation reaction with bromoacetic acid shown that bromoacetic acid specifically targeted to those basic nitrogen-containing compounds like pyridine and quinoline derivatives in our thermally cracked naphtha, without being affected by other

present non-nitrogen-containing compounds. For the purpose of analysis, base pretreatment and silica extraction that were described in experimental section were used after bromoacetic acid denitrogenation reaction. The GC-MS analysis of the acetone fractions before and after bromoacetic acid denitrogenation reaction of the naphtha is shown in Figure 3-13. The majority of the peaks that represent basic nitrogen-containing compounds have been removed by this reaction. The remaining peaks in the "after reaction" chromatogram indicate polar alcohols and conjugated ketone, which were not successfully fractionated by silica extraction. The selectivity of bromoacetic acid denitrogenation reaction in the naphtha is excellent. Rather than simple acid-base reaction, the mechanism of this bromoacetic acid reaction is nucleophilic substitution to form a quaternary ammonium cation (Figure 3-14.) Those non-nitrogen containing compounds in the naphtha are not good nucleophiles, therefore are not reactive to bromoacetic acid, which well explains the excellent selectivity of this bromoacetic acid reaction.

In general, nitrogen compounds with larger molecular weight are more resistant to be removed by traditional liquid extraction methods. While in bromoacetic acid reaction, the larger quinoline derivatives were removed along with those smaller pyridine derivatives.

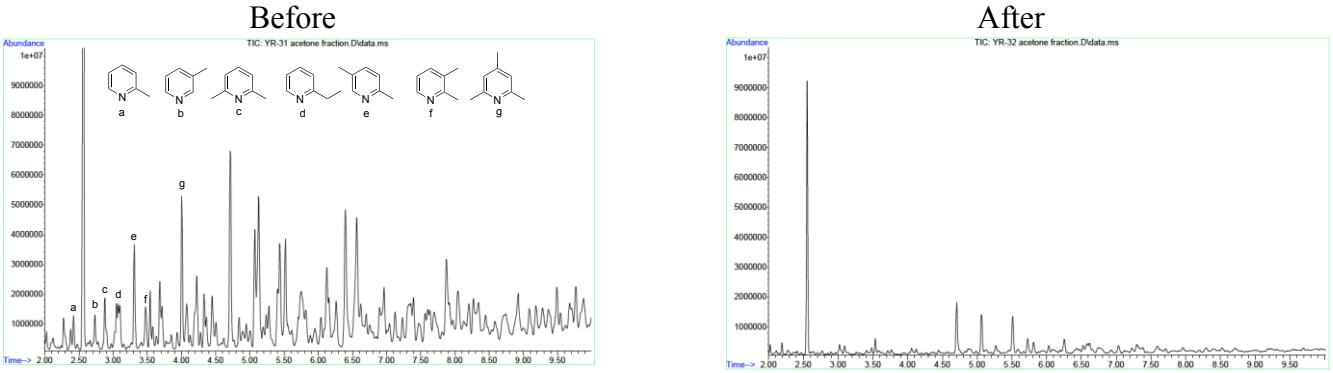


Figure 3-13. GC-MS chromatograms of the acetone fractions before and after bromoacetic acid denitrogenation reaction of naphtha. (Quinoline derivatives were not labeled in the chromatograms)

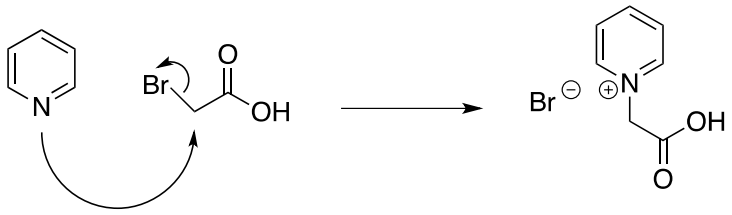


Figure 3-14. Reaction mechanism of bromoacetic acid reaction with basic nitrogen compound pyridine.

Removal of fatty acids from thermally cracked naphtha

In chapter 2, the work of characterization of naphtha reveals that fatty acids from C4 to C11 (Figure 2-5) are present in the thermally cracked naphtha. They have to be removed because the polarity of these fatty acids are similar with the nitrogen-containing compounds, therefore, can be eluted along with basic nitrogen-containing compounds in acetone fraction during silica extraction. In the GC-MS chromatogram, big peaks from these fatty acids could cover with the peaks from basic nitrogen-containing compounds, which cause problems on interpretation. In fact, the fatty acids were only removed for this analysis purpose. Fatty acids removal is not necessary when bromoacetic acid denitrogenation is used for sample preparation of olefin alkylation.

Cleavage of the quaternary ammonium carbon bond

The cleavage of the quaternary ammonium carbon bond was achieved by hydrolysis in the basic solution of sodium hydroxide[10] (Figure 3-15.). The aqueous wash after the bromoacetic acid denitrogenation of the naphtha contains pyridinium and quinolinium salt derivatives. These salt derivatives are not suitable for GC-MS analysis because these highly polar compounds are likely to stay in the column. In addition, they are dissolved in the water, which is not compatible with our column in the gas chromatography. Therefore, one of the benefits from the cleavage of the quaternary ammonium carbon bonds in the salts is that the final products from this cleavage reaction provide direct evidences to prove what types of nitrogen-containing compounds were removed from naphtha. In addition, the cleavage reaction is a potential recycling method of nitrogen-containing compounds.

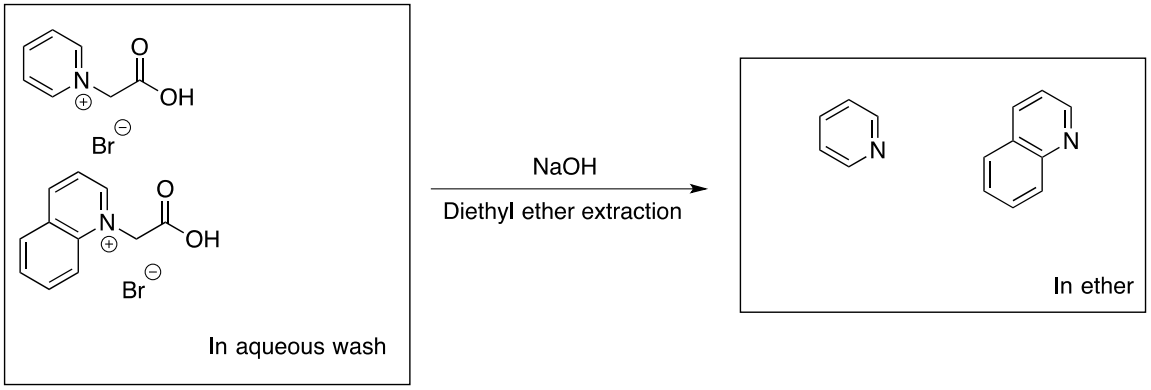
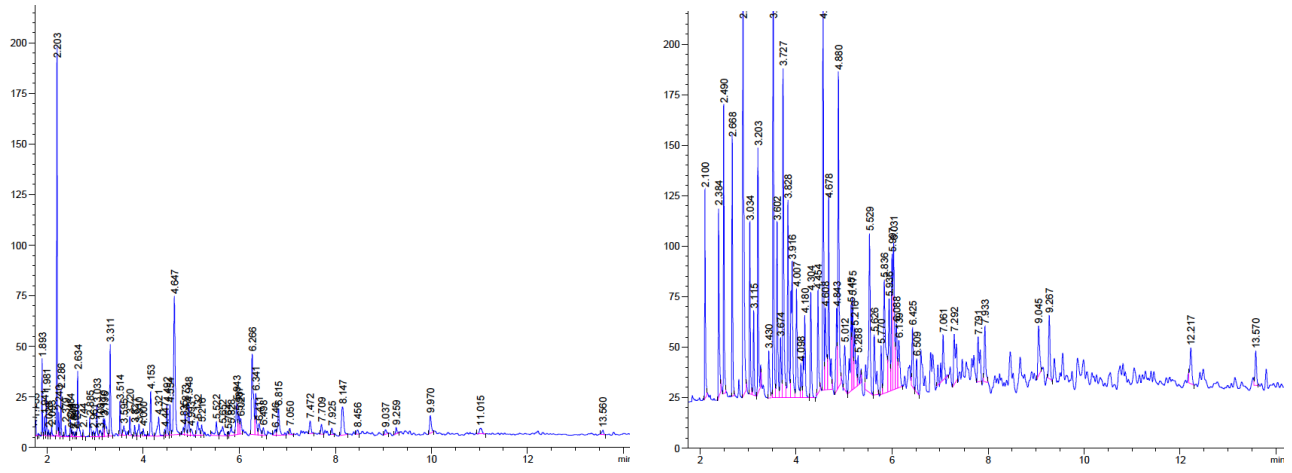


Figure 3-15. Examples of recycle of nitrogen-containing compounds from bromoacetic acid denitrogenation reaction. (not all the N-compounds are shown here)

GC-NPD analysis of bromoacetic acid denitrogenation reaction of naphtha

The residues of acetone fraction before and after bromoacetic acid denitrogenation reaction were analyzed by gas chromatography coupled with nitrogen phosphorus detector (GC-NPD), in order to determine the ability that this reaction can remove basic nitrogen-containing compounds from the thermally cracked naphtha. Nitrogen phosphorus detector (NPD) was chosen instead of flame ionization detector (FID) because of its excellent sensitivity to nitrogen-containing compounds. Denitrogenation reaction has removed most of nitrogen compounds from acetone fraction. The remaining nitrogen compounds have very low concentration, which do not have peaks in FID chromatogram, whereas do have peaks in NPD chromatogram Figure (3-16).



GC-FID GC-NPD

Figure 3-16. Comparison of GC-FID and GC-NPD chromatograms of the same acetone fraction of the silica extraction of naphtha.

Bromoacetic acid denitrogenation reaction of naphtha was quantified by GC-NPD, with external standard calibration (Table 2-5). The results reveal that the majority of basic nitrogen compounds were successfully removed from the naphtha. The nitrogen compounds in the acetone fraction, where the most basic nitrogen compounds of naphtha were extracted, have been removed. Depending on which nitrogen compound was used in the calibration, the removal percentage varied from 65% to 96% (Table 3-3). An average number 75% was calculated. It is believed that this average number is closed to the real removal capability, because this number is similar with the percentages (74%, 84% and 75%) when pyridine derivatives were used for calibration. And pyridine derivatives are the dominated class of nitrogen compounds in acetone fraction.

Table 3-3. NPD quantitative analysis of removal of basic N-compounds in acetone fraction from bromoacetic acid denitrogenation reaction.

Calibration compounds	Before reaction (Acetone fraction ppm)	After reaction (Acetone fraction ppm)	Basic N compounds removal (%)
2-methyl pyridine	193.8	49.9	74
2,6 lutidine	186.9	29.2	84
2-ethylpyridine	215.4	53.2	75
Aniline	388.7	106.3	73
m-toluidine	472.4	134.6	72
2,4-dimethyl aniline	368.4	60.4	84
Quinoline	430.8	150.5	65
Lepidine	263.2	10.8	96
Indole	502.7	163.4	67
Average	335.8	84.3	75

In DCM fraction, the dominated class of nitrogen compound is neutral. There were also some basic nitrogen compounds that were eluted into DCM fraction during the silica extraction. Quantitative analysis of DCM fraction shows around 36% (average value) of nitrogen compounds have been removed from this fraction. Base on the mechanism of bromoacetic acid denitrogenation reaction (Figure 3-16), only basic nitrogen compounds would react with bromoacetic acid. This means at least 36% of nitrogen compounds in the DCM fraction were basic nitrogen compounds. It is important to understand that it is not 36% of DCM fraction was basic nitrogen compounds. The majority of chemicals in the DCM fractions are oxygen-containing compounds.

When 2-methyl pyridine was the compound for calibration, the data shown higher concentration of nitrogen compound was obtained after denitrogenation reaction. This indicates 2-methyl pyridine is not a suitable compound for calibration of this sample. Except 2-methyl pyridine, all other calibration standard compounds indicate certain amount of basic nitrogen compounds were removed from DCM fraction by bromoacetic acid denitrogenation. The numbers are varied, depending on which compound was employed for calibration (Table 3-4). This observation has further confirmed that the response of nitrogen containing compounds to the nitrogen phosphorus detector is structural dependent.

Table 3-4. NPD quantitative analysis of removal of basic N-compounds in DCM fraction from bromoacetic acid denitrogenation reaction.

Calibration compounds	Before reaction (DCM fraction ppm)	After reaction (DCM fraction ppm)
2-methyl pyridine	133.9	179.4
2,6 lutidine	68.4	38.3
2-ethylpyridine	142.0	82.7
Aniline	290.8	170.0

m-toluidine	371.5	217.5
2,4-dimethyl aniline	145.9	81.9
Quinoline	427.6	252.7
Lepidine	28.0	16.7
Indole	460.2	271.1
Average	229.8	145.6

Alternatively, internal standard calibration method was used for NPD quantitative analysis for bromoacetic acid denitrogenation of naphtha. Lepidine was the internal standard. It was chosen because its peak is not overlapping with any other nitrogen compounds in the sample. This method was applied to test the removal capability of bromoacetic acid denitrogenation in percentage, rather than to obtain a certain number for quantity. The results are shown in Table 3-5, where section A is the measurement of denitrogenation of acetone fraction, and section B is the measurement of DCM fraction. Equations (1-5) that were described in the experimental were used for the calculations. There were two corrections were made in the calculations. In equation (2), the Area N (denitrogenated) was corrected with mass difference of original and denitrogenated extracted fractions, to give Area N′ (original) the corrected area of peaks that represent nitrogen compounds in the scale of original sample. In equation (3), Area N′ (original) was corrected with Internal standard difference to give Area N′ (denitrogenated), which represents the real Area N (denitrogenated) in the scales of original sample. These two corrections are essential because the masses of extracted fractions were different between original and denitrogenated (samples), and the mass of internal standard added into the sample were theoretically the same. To make these calculations more comprehensive, an example using equations (1-5) is provided for the calculation of the percentage of N compounds removal in acetone fraction. The percentage of nitrogen compounds removal in DCM fraction can also be calculated in the same manner.

Table 3-5. NPD quantitative analysis of nitrogen compounds removal of bromoacetic acid denitrogenation of naphtha. (Internal standard calibration) A: Acetone fraction, B: DCM fraction.

	Mass of extracted fractions (g)	Area T (pA*s)	Area IS (pA*s)	Area N (pA*s)	Area N′ (pA*s)	Area N removed (pA*s)	N compounds removal %
Original	0.238	4737.5	2735.2	2002.3	408.2	1589.9	79
Denitrogenated	0.159	2979.7	2707.1	272.7	412.4		

A

	Mass of extracted fractions (g)	Area T (pA*s)	Area IS (pA*s)	Area N (pA*s)	Area N′ (pA*s)	Area N removed (pA*s)	N compounds removal %
Original	1.327	1988.9	1920.0	69.0	48	17.7	25
Denitrogenated	1.578	1883.4	1825.4	58.0	51.3		

B

Example of calculations of the percentage of N removal in acetone fraction.

(1)

$$Area\ N\ (original) = 4737.5\ (\mathrm{pA} * \mathrm{s}) - 2735.2\ (\mathrm{pA} * \mathrm{s}) = 2002.3\ (\mathrm{pA} * \mathrm{s})$$

$$Area\ N\ (denitrogenated) = 2979.7\ (\mathrm{pA} * \mathrm{s}) - 2707.1\ (\mathrm{pA} * \mathrm{s}) = 272.7\ (\mathrm{pA} * \mathrm{s})$$

(2)

$$Area\ N'(original) = \frac{0.238\ (g)}{0.159\ (g)} \times\ 272.7\ (\mathrm{pA} * \mathrm{s}) = 408.2\ (\mathrm{pA} * \mathrm{s})$$

(3)

$$Area\ N'(denitrogenated) = 408.2\ (\mathrm{pA} * \mathrm{s}) \times \frac{2735.2\ (\mathrm{pA} * \mathrm{s})}{2707.1\ (\mathrm{pA} * \mathrm{s})} = 412.4\ (\mathrm{pA} * \mathrm{s})$$

(4)

$$Area\ N\ (removed\ from\ original) = 2002.3\ (\mathrm{pA} * \mathrm{s}) - 412.4\ (\mathrm{pA} * \mathrm{s}) = 1589.9\ (\mathrm{pA} * \mathrm{s})$$

(5)

$$Percentage\ of\ N\ compounds\ removal = \frac{1589.9\ (\mathrm{pA} * \mathrm{s})}{2002.3\ (\mathrm{pA} * \mathrm{s})} \times 100\% = 79\ \%$$

The percentage N compounds removal of acetone fractions 79 %, in comparison with the results from external standard calibration method (average of all standards used 75%), is mostly consistent to each other. If the external standard method exclusively use the average number of three pyridine derivatives (78%) to calibrate the results, there is only 1% difference to the 79% that was obtained with internal standard calibration method. However, in terms of DCM fraction, there is larger disagreement between internal (25%) and external (36%) standard method. The error is larger in DCM fraction because the majority of compounds in this fraction are non-nitrogen containing compounds (ketones and alcohols).

With the assistant of the NPD quantitative analysis on basic nitrogen compound removal, it was found that at least 25-36% nitrogen compounds in DCM fraction were actually basic nitrogen compounds. This detail important information can be used to correct the result in chapter 2: Quantitative analysis of nitrogen compounds in naphtha. In chapter 2, the quantitative analysis was based on the assumption that all the neutral nitrogen compounds were extracted into DCM fraction. Now it is necessary to

recalculate the results, which taking into account the part of basic nitrogen compounds in the DCM fraction. For example, when 2-ethylpyridine was chosen as calibration standard, the nitrogen compounds in acetone fraction and DCM fraction were 32085 ug and 21147 ug respectively. 25% of the nitrogen compounds (5286 ug) in DCM fraction were removed during the bromoacetic acid denitrogenation reaction. Assuming that the removal rate of the basic nitrogen compounds from DCM fraction is 75%, which is the same removal rate measured from acetone fraction. There are about 7049 ug of basic nitrogen compounds was extracted into DCM fraction, along with the basic nitrogen compounds (32085 ug) in acetone fraction, the total basic nitrogen compounds in naphtha (200 mL) would be 39134 ug. The neutral nitrogen compounds in the naphtha (200 mL) would be 21147-7049 = 14098 ug.

Chlorosulfonic acid reaction

The reaction between chlorosulfonic acid and pyridine occurred at room temperature in a short time. The 1H NMR confirmed the formation of white residue was the desired product, although the reaction yield was moderate. The reaction shares the same nucleophilic substitution reaction mechanism (Figure 3-17) as the bromoacetic acid reaction and it is kinetically more favorable than the bromoacetic acid reaction with pyridine. Apparently, chlorosulfonic acid is much more reactive than bromoacetic acid, as the reaction finished in 30 minutes, rather than overnight. In terms of industrially application, short reaction time usually means that the production would be economically more favorable. Thus, chlorosulfonic acid was selected to improve the denitrogenation reaction in the cracked naphtha.

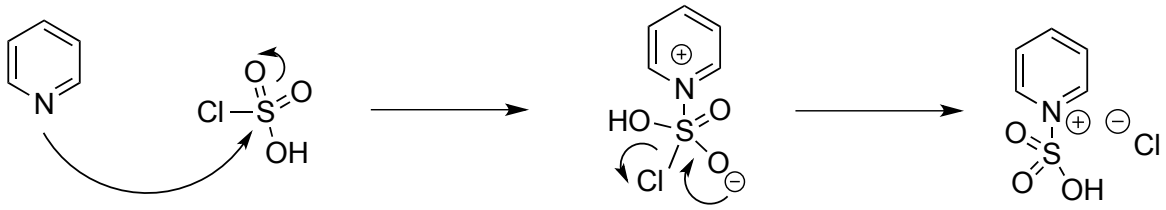


Figure 3-17. Reaction mechanism of chlorosulfonic acid reacts with pyridine.

Residue from aqueous phase was dissolved into ethanol and analyzed by GC-MS. In the residue from aqueous phases, nitrogen-containing compounds were not found in this sample. The GC-MS chromatogram indicated that the residue containd thiophenes, tetrahydrothiophenes and aromatic sulfonic acids (Figure 3-18). Thiophenes and tetrahydrothiophenes are not chemically active to chlorosulfonic acid. Hydrogen bonding between the OH in sulfonic acid and sulfur atom in thiophenes and tetrahydrothiophens could be the reason that these sulfur compounds were extracted in the residue. On the other hand, the present of aromatic sulfonic acid in the residue can be explained by the reaction between dimethyl benzene and chlorosulfonic acid.[12,13] There were some peaks shown silica in the GC-MS chromatogram reveals that chlorosulfonic acid in the sample could damage the column in the GC-

MS. The results of this experiment indicate that chlorosulfonic acid has failed to be denitrogenation reagent to remove nitrogen compounds from naphtha.

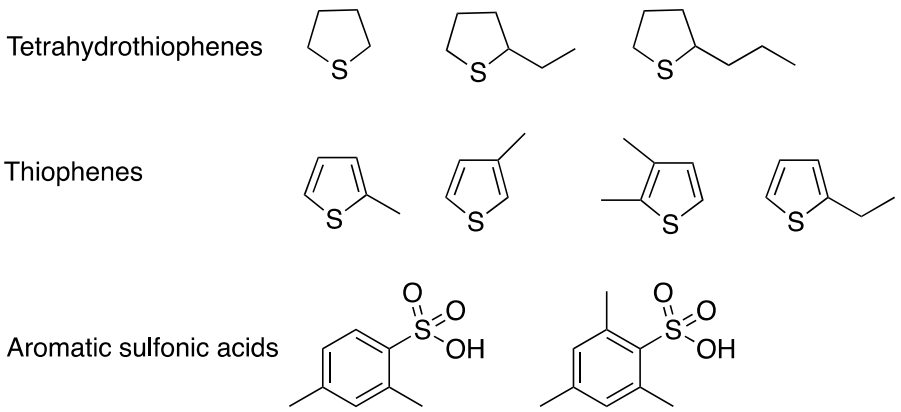


Figure 3-18. Chemical structures of the products from chlorosulfonic acid reaction with naphtha.

p-Toluenesulfonyl chloride reaction with naphtha

The reaction of *p*-Toluenesulfonyl chloride with pyridine to form a sulfonyl chloride/pyridine complex is a known reaction shown in figure 3-19.[14] The formation of sulfonyl chloride/pyridine complex can be completed within 30 minutes, a faster process than bromoacetic acid reaction. Comparing to the chlorosulfonic acid reaction, *p*-Toluenesulfonyl chloride is safer, easier for storage and less corrosive. It would not damage the GC column even excess amount of *p*-Toluenesulfonyl chloride is used in the reaction. In addition, it would avoid the formation of aromatic sulfonic acids in naphtha.

Figure 3-19. Reaction of *p*-Toluenesulfonyl chloride with pyridine to generate sulfonyl chloride/pyridine complex.

Therefore, *p*-Toluenesulfonyl chloride was selected as a replacement of chlorosulfonic acid to test whether it has denitrogenation effects on naphtha. The product residue collected after filtration of naphtha, contained several basic nitrogen containing compounds, as well as several alcohols like phenols (Figure 3-20). This result reveals that *p*-Toluenesulfonyl chloride is a potential denitrogenation reagent for naphtha that dose not contains alcohols or having extremely small amount of alcohols. The thermally cracked naphtha used in our experiment contains several types of phenols, therefore not compatible with *p*-Toluenesulfonyl chloride denitrogenation reaction. Furthermore, it is essential to understand the mechanism of the removal of basic nitrogen compounds with *p*-Toluenesulfonyl

chloride is not through an actual nucleophilic chemical reaction (Figure 3-21). The product residue contains basic nitrogen compounds, rather than the additional product of basic nitrogen compounds with *p*-Toluenesulfonyl chloride. It could be a certain type of physical interaction between *p*-Toluenesulfonyl chloride and those basic nitrogen compounds that was responsible for the denitrogenation.

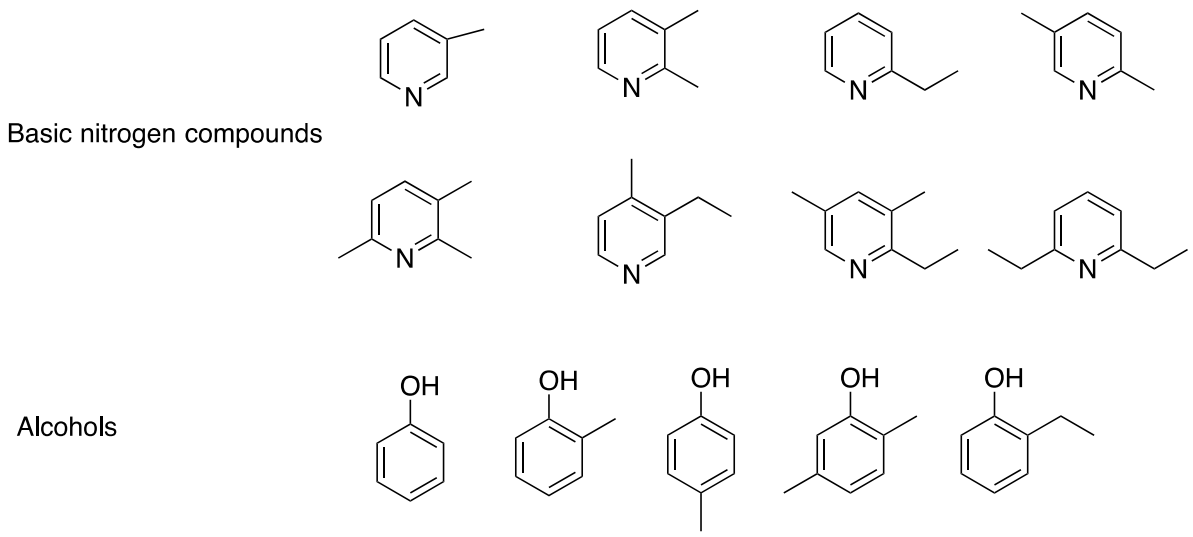


Figure 3-20. Basic nitrogen compounds and alcohols that were found in the residue of *p*-Toluenesulfonyl chloride reaction.

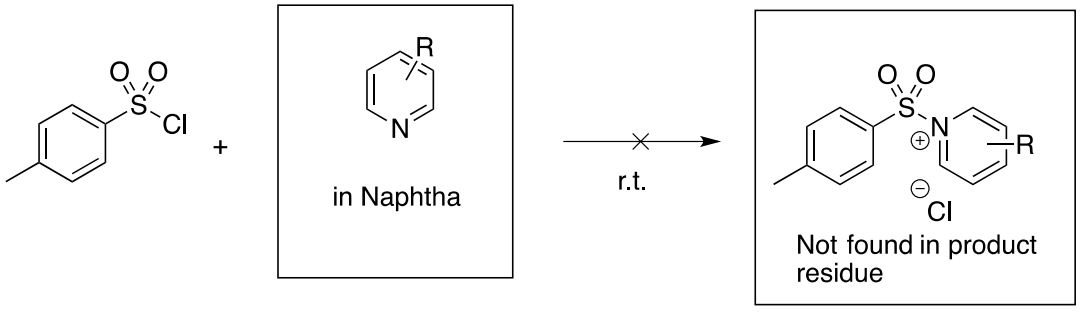


Figure 3-21. The expected reaction between basic nitrogen compounds with *p*-Toluenesulfonyl chloride reaction in naphtha.

3.4 Conclusion

The denitrogenation of basic nitrogen-containing compounds in thermally cracked naphtha was studied. Bromoacetic acid reaction was developed as a non-hydrotreating denitrogenation method, to selectively remove basic nitrogen-containing compounds at room temperature. Methods of quantitative analysis were developed to measure the capability of nitrogen compounds removal by the bromoacetic acid.

The main outcomes of this study were:

(a) Bromoacetic acid was proven chemically reactive to the basic nitrogen-containing model compounds, and not reactive to neutral nitrogen-containing compounds.

(b) The bromoacetic acid reaction successfully removed more than 75% basic nitrogen-containing compounds from the thermally cracked naphtha.

(c) The cleavage of the quaternary ammonium carbon bonds in the products of bromoacetic acid reaction was studied.

(d) Two methods were developed to use gas chromatography coupled with nitrogen phosphorus detector (GC-NPD) in the measurement of nitrogen compounds. Both methods gave highly consistent results that around 75% of basic nitrogen compounds were successfully removed from acetone fraction of the silica extraction after the bromoacetic acid denitrogenation reaction.

(e) It was found that 25-36% of nitrogen compounds in DCM fraction of the silica extraction after the bromoacetic acid denitrogenation reaction were basic nitrogen compounds. These basic nitrogen compounds can also be removed by bromoacetic acid denitrogenation.

(f) Quantitative analysis results on basic and neutral nitrogen compounds in naphtha were recalculated with more detail information obtained from GC-NPD on DCM fraction. New data suggests that the concentration of basic nitrogen compound and neutral nitrogen compound are 263 ppm and 95 ppm respectively.

(g) Studies of *p*-toluenesulfonyl chloride have revealed that it is a potential denitrogenation method for naphtha that is not containing alcohols.

3.5 Reference

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4 Denitrogenation of neutral nitrogen compounds from thermally cracked naphtha and model oil.

4.1 Introduction

Neutral nitrogen-containing compounds, such as pyrrol and carbazole, react with bromoacetic bromide in the basic condition. For instants, Saeidifar, et al.[1] synthesized 1-pyrrolacetate sodium salt by reacting bromoacetic acid and pyrrole in the present of two equivalent of sodium hydroxide in ethanol. Tian, et al.[2] prepared *N*-carbazolylacetate sodium salt by mixing carbazole, bromoacetic bromide and sodium hydroxide (3 equivalent) in dimethyl sulfoxide (DMSO) at 85 ℃ (Figure 4-1). In some case, tetrabutylammonium bromide, a phase transfer catalyst, may be used in N-alkylation reaction.[3]

In terms of identification, the sodium salt products can be acidified to acid form, which could be extracted by organic solvent and provide a method for identification of neutral nitrogen-containing compounds in the oil.

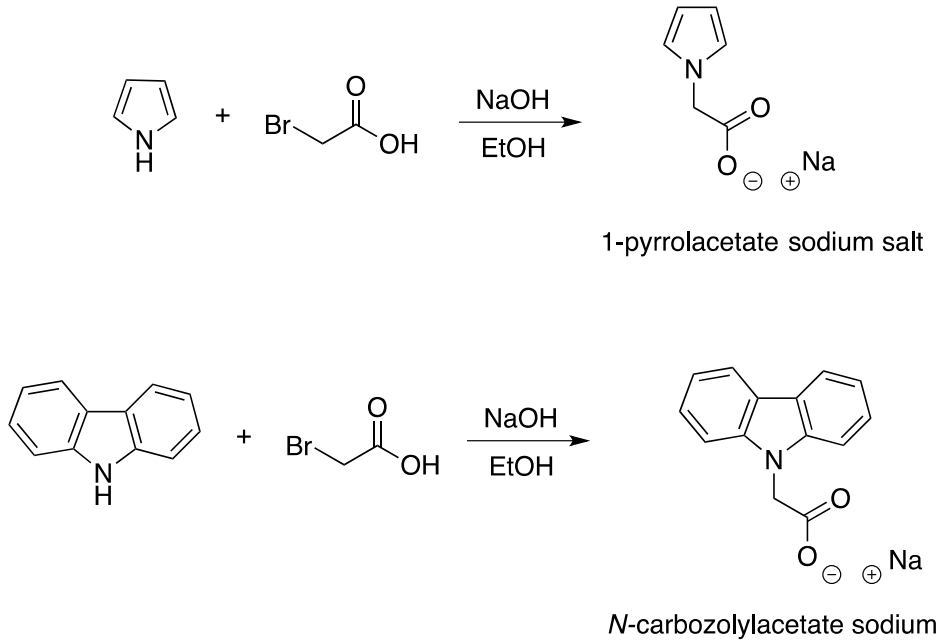

Figure 4-1. Reaction between neutral nitrogen-containing compounds and bromoacetic acids in basic condition.[1-2]

As described before, quaternary ammonium derivatives of tertiary amines could be cleaved by hydrolysis in basic conditions. This means the product of basic nitrogen-containing compounds with bromoacetic bromide is not stable in basic condition. However, reaction between neutral nitrogen containing-compounds and bromoacetic bromide requires basic condition. The N-alkylation

denitrogenation reaction with bromoacetic bromide and thermally cracked naphtha need to be performed separately to remove both basic and neutral nitrogen-containing compounds.

Recently, new adsorption method, discovered by Ahmed, et al.,[4] using sulfonated metal-organic frameworks (UiO-66-SO_3H) to remove neutral nitrogen containing compounds from model oil shown promising results. The sulfonated metal-organic frameworks (UiO-66-SO_3H) was synthesized by mixing zirconium chloride ($ZrCl_4$), benzenedicarboxylic acid (H_2-BDC), 2,5-dicarboxybenzenesulfonic acid 1-sodium salt ($NaSO_3H$-BDC), in a mixture of solvents (DMF to acetic acid 9:1 v/v) at 120 ℃. Model oil was prepared by dissolving quinoline, indole, pyrrole and methyl pyrrole in n-octane. The results of adsorption indicated that the adsorption of neutral nitrogen compound indole was increasing as the number of functionalized -SO_3H group increased on metal organic frameworks. It is believed that there are hydrogen bonding between the sulfonic groups and neutral nitrogen compounds (Figure 4-2.). In addition, an interesting observation shown that the adsorption of basic nitrogen compound quinoline was decreased as the number of sulfonic acid groups were increased. This observation was not expected because it is against the simple acid-base interactions between sulfonic acid and basic quinoline. Although the reason behind this observation was not explained, this method has potential application on selectively removal of neutral nitrogen containing compounds.

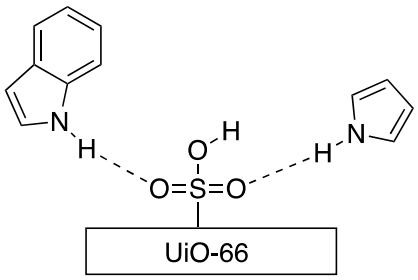

Figure 4-2. Hydrogen bonding between neutral nitrogen compounds and sulfonic groups on the metal-organic frameworks.[4]

The similar metal organic framework (UiO-66-COOH) was synthesized to test nitrogen compounds removal from model oil by Seo, et al.[5] The acid groups were functionalized on the metal organic framework to assist the adsorption of nitrogen compounds by both hydrogen bonding and acid-base interactions Figure (4-3). For neutral nitrogen compounds including pyrrole and indole, the functionalized acid groups have positive effect for the adsorption. The acid functionalized UiO-66 has lower quinoline adsorption than normal UiO-66, which is the same observation when sulfonic group was functionalized on the UiO-66. It was believed that addition of functional groups on the UiO-66 decreased the surface are of adsorbent. Then it was later proved that the adsorbed quinoline was increased per unit surface area of adsorbent, when acid groups were functionalized on adsorbent.

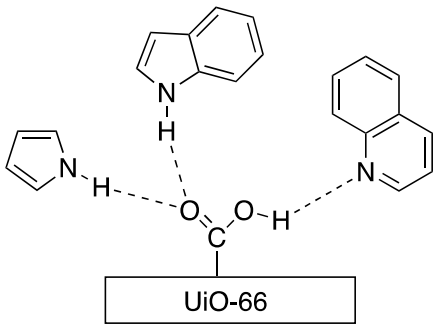

Figure 4-3. Hydrogen bonding between carbonyl groups of acid and neutral nitrogen compounds, and acid-base interaction between acid group and basic nitrogen compounds.

The preparation of adsorbents like functionalized organic frameworks are relatively time consuming. It is difficult to guarantee the consistency of the functionalized adsorbents. therefore, the results may not as reliable as other extraction methods like solvent liquid-liquid extractions.

Liquid-liquid extraction has been used as simple laboratory separation and purification methods for a very long time. As polar compounds are more likely to be dissolved in polar solvent, non-polar compounds are likely to be dissolved in non-polar solvent and polar water and one non-polar organic solvent is commonly applied in the process of liquid-liquid extraction. However, what we learn from nature is that chemical reactions and chemical phase transfer are often occurring between complex mixed-solvent systems, rather than a single-single solvent system. Theoretically, the mixed solvent system provides us a brilliant opportunity to alter the solubility parameter of the solvent to idealize not only the extraction ability of the solvent, but also the selectivity of the extraction.

The Hildebrand solubility parameter is a physical property of a solvent, which relates to the cohesive energy between molecules of solvent, as well as the heat of vaporization of the solvent. The solubility of solvent is depending on the cohesive energy density between molecules of that solvent. Solvent can only dissolve chemicals that have similar cohesive energy density.[6] The heat of vaporization is the energy that is needed to convert liquid form of the solvent into its gas form. Cohesive energy density of a liquid solvent is a representation of heat of vaporization in calories per cubic centimeter. The relationship between cohesive energy density and heat of vaporization can be expressed as the following equation (1). Hildebrand solubility parameter is the square root of the cohesive energy density, which can be expressed as the equation (2). When two miscible solvents are mixed to create a binary solvent system, the new mixed solvent has a unique solubility parameter. This mixed solvent parameter of binary solvent system can be calculated as equation (3).[6-7]

(1)

$$C = \frac{\Delta H - RT}{V_m}$$

(2)

$$\delta = \sqrt{C}$$

(3)

$$\delta_m = \frac{w_1\delta_1 + w_2\delta_2}{w_1 + w_2}$$

C: Cohesive energy density
ΔH: Heat of vaporization
R: Gas constant
T: Temperature
V_m: Molar volume
δ: Hildebrand solubility parameter
w: fraction of solvents
subscripts 1 and 2 represent co-solvent and water.

In addition to the influence of solubility parameter of solvent, the chemical property of solvent could play major role in the liquid-liquid extraction. For example, the aqueous acid extraction of nitrogen compounds from oil is a known technology. It utilizes the acid-base reaction between aqueous acid and basic nitrogen compounds to achieve the denitrogenation. It was reported by Qi, J. et al.[8] that neutral nitrogen compounds were partially removed by aqueous acetic acid extraction of catalytically cracked diesel oil, and the given explanation was that neutral nitrogen compounds are weakly basic, which would react with strong acids. The author suggested that the smaller of the molecule of the acid, the stronger of the acid. Although the formic acid (pKa: 3.75) is more acidic than acetic acid (pKa: 4.75), it was abandoned because of its weak thermal stability.[8] In the case of aqueous hydrochloric acid extraction, Yan Feng has reported that hydrochloric acid was used to extract basic nitrogen compound from gasoline, although the author did not mention whether hydrochloric acid was capable of removing neutral nitrogen compounds.[9] According to Qi, et al.[8] strong acids could remove neutral nitrogen compounds along with the basic nitrogen compounds from oil, hydrochloric acid (pKa: -7) is certainly considered to be a strong acid, thus it is possible to be used for neutral nitrogen compound removal. Although, the reason why neutral nitrogen compounds were removed by strong acids was not explained by the author.

Campton, who is the inventor of a patent stated that the neutral nitrogen compound pyrrole is unstable in the strong acidic and high temperature environment, resulting formation of pyrrole polymer.[10] The patent described a polymerization method Campton used to remove neutral nitrogen compound pyrrole from shale oil. Increasing temperature would increase the polymerization of the pyrrole, however, overheating would lead to undesired reactions with other chemicals in the shale oil. After the polymerization, shale oil was extracted with liquid propane leaving the polymer in the extraction column. Pyrrole polymerization can be used to explain why neutral nitrogen compounds were removed with strong acids. It is important to understand the fundamental of neutral nitrogen compounds removal is different from the acid-base reaction between pyridine (basic) and acids. In addition, Campton has also applied oxygen or air and actinic irradiation to the shale oil, leading to pyrrole polymerization.

Polymerization with oxygen or air can avoid heating in the process, therefore control the side-reactions that usually happening in the high temperature polymerization.

Oxidative peroxy acid extraction was found effective to remove neutral nitrogen compounds from oil.[11-12] The most common oxidizing reagent used in this purpose is hydrogen peroxide (H_2O_2). It is often mixed with organic acids, for example, formic acid or acetic acid, to generate the corresponding peroxy acids, as shown in Figure (4-4).

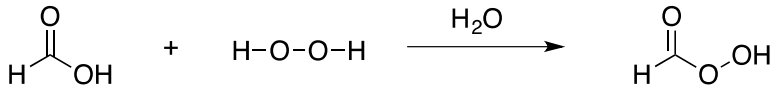

Figure 4-4. Reaction between formic acid and hydrogen peroxide to form peroxy acid.

Peroxy acid is highly reactive oxidant that oxidizes nitrogen compounds present in oil, the resulting oxidized nitrogen compounds are much more polar than the original nitrogen compounds. These polar oxidized nitrogen compounds are easily extracted into water. Oxidation reaction of pyrrole with peroxy acid is shown in Figure (4-5). Because peroxy acid is unstable, it is usually prepared by mixing acetic acid and hydrogen peroxide in situ. Oxidation of pyrrole generates a mixture of products, rather than a single product, because addition of pyrrole could occur resulting dimers.[13-14]

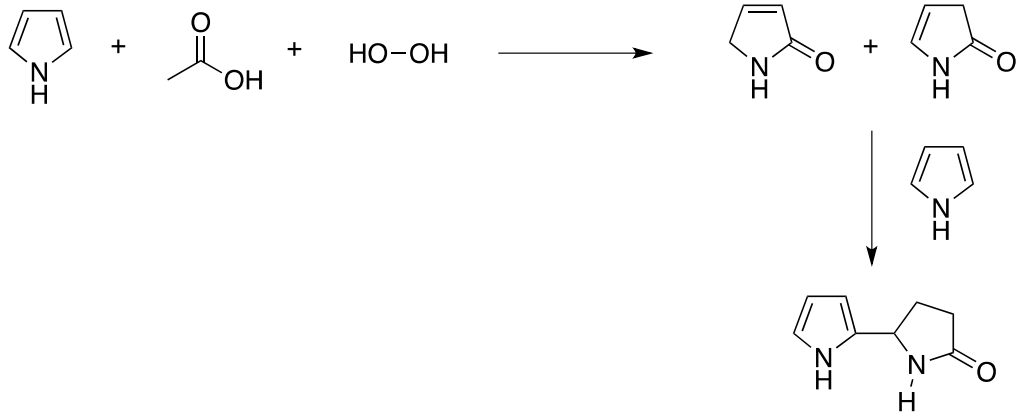

Figure 4-5. Oxidation reaction of pyrrole with peroxy acid.[13]

In terms of oxidation of basic nitrogen compounds with peroxy acid, pyridine can be oxidized to generate pyridine-N-oxide (Figure 4-6).[15] This pyridine-N-oxide is also polar compound that is readily extracted into water. It is also believe other basic nitrogen compounds like quinoline would react with peroxy acid, and can be removed with the same fashion.

Figure 4-6. Oxidation reaction of pyridine with peroxy acid. [15]

Although oxidative peroxy acid extraction is capable of removing both neutral and basic nitrogen compounds from oil, there is one limitation that this oil must has no olefin or extremely low olefin content. Peroxy acid is known as an effective oxidizing reagent to generate epoxide from olefin (Figure 4-7).[16] Epoxide is highly reactive compound that would further react with other chemicals in oil, eventually change the properties of oil. For example, thermally cracked naphtha would contain large amount of olefin, which would not compatible with peroxy acid extraction.

Figure 4-7. Oxidation reaction of olefin with peroxy acid.[16]

In our research of mixed solvent liquid-liquid extraction, methanol, ethanol and n-propanol were chosen to mix with water to adjust the solubility parameter of the solvent system. The extractions were performed with model oil that contained both basic and neutral nitrogen compounds to understand the fundamental of the extractions. In terms of aqueous acid extraction, formic acid, acetic acid, and propionic acid were selected to perform extraction on the same model oil. This would test the influence of acidity to the extraction outcome, as well as confirming the statement of strong acid is capable of removing neutral nitrogen compounds. Oxidative acid extractions were performed with the same model oil that was tested in the acid extractions to compare their nitrogen compounds removal capability. Furthermore, knowing oxidative acid extraction has ability to remove both neutral and basic nitrogen compounds, our experiments were also designed to know which type of nitrogen compound is more vulnerable to oxidative acid extraction.

4.2 Experimental

Materials. Thermally cracked naphtha was obtained from an industrial visbreaking unit processing a deasphalted oil from steam assisted gravity drainage produced Athabasca oilsands bitumen.

HPLC grade solvents used in the study, including toluene (99.9%), acetone (99.7%), and diethyl ether (99.9%), methanol (99.9%), n-propanol (99.9%) and acetic acid (glacial) were purchased from Fisher Scientific, Canada. Chemical reagents including bromoacetic acid (99%), sodium hydroxide (98%), tetrabutylammonium bromide (99%), 2,6-Naphthalenedisulfonic acid disodium salt (97%), Sodium 2-naphthalenesulfonate (95%), pyrrole (98%), lepidine (99%), indole (99%), quinoline (99%) were purchased from Sigma Aldrich, Canada. Propionic acid (99%), Magnesium sulfate were purchased from ACROS. Hydrogen peroxide (30%) was purchased from Caledon Laboratories Ltd. Hydrochloric acid (36.5-38%) and formic acid (98%), were purchased from EMD Canada. Ethanol anhydrous was purchased from Commercial Alcohols.

Analysis. Quantitative analysis of nitrogen-containing compounds was carried out using an Agilent 7890A gas chromatography (GC) equipped with both a flame ionization detector (FID) and a nitrogen phosphorus detector (NPD). A 19091S-433 column (length: 30 m, diameter: 250 μm, film thickness: 0.25 μm, max temperature 325 °C) was used for separation. Helium was the carrier gas with flow of 1 mL/min. Split ratio was 1:100. The oven has initial temperature 80 °C, which was increased to 170 °C with a ramp rate of 6 °C/min, followed by a raise to 300 °C with a ramp rate of 15 °C/min and held at 300 °C for 5 min.

Bromoacetic acid, sodium hydroxide two phases denitrogenation reaction

Bromoacetic acid (0.100 g, 0.72 mmol) and sodium hydroxide (0.115 g, 2.88 mmol) were dissolved into water (50 mL). Reaction mixture was stirred for 20 minutes. Tetrabutylammonium bromide (0.5 g, 1.55 mmol) was added into reaction mixture, followed by naphtha (200 mL), then stirred overnight at room temperature. The naphtha layer was separated from aqueous layer and washed by water (2×50 mL). Aqueous layers were combined and acidified with hydrochloric acid until pH ≈2. This acidic aqueous layer was extracted by diethyl ether (3×50 mL). The diethyl ether layer was separated and concentrated under reduced pressure to obtained brown residue (0.553 g). The collected residue was purified by pipette column chromatography with silica. GC-MS was used to identify compounds in the samples.

Sulfonic groups aqueous extraction of neutral nitrogen containing compounds from model oil

The model oil was prepared with indole (2000 ppm), pyrrole (2000 ppm), pyridine (2000 ppm), and quinoline (2000 ppm) in toluene (50 mL). In this extraction, model oil (4 mL) was extracted with aqueous solution (4 mL) of 2,6-naphthalenedisulfonic acid disodium salt (2.5 %) at room temperature for overnight. The organic layer was separated from aqueous layer, and analyzed by gas

chromatography coupled flame ionization detector (GC-FID) with internal standard method. Calibration solutions were prepared by diluting model oil (2000 ppm) into 1000 ppm and 500 ppm solutions. The internal standard Lepidine (6.3 mg) was added into three calibration solutions (1mL) and extracted sample solutions (1 mL) in GC vial for quantitative analysis. Extraction with aqueous solution of sodium 2-naphthalenesulfonate salt was performed in the same manner.

Water-alcohol mixed solvent liquid-liquid extractions

The model oil was prepared with indole (2000 ppm), pyrrole (2000 ppm), pyridine (2000 ppm), and quinoline (2000 ppm) in toluene (250 mL). In the experiment, to the three vials that each contains model oil (4 mL), aqueous solution (4 mL) of 20% methanol, 20% ethanol, and 20% n-propanol were added respectively. The mixtures of two phases solution were stirred vigorously at room temperature overnight. The organic layer was separated from aqueous layer, and analyzed by gas chromatography coupled flame ionization detector (GC-FID) with internal standard method. Calibration solutions were prepared by diluting model oil (2000 ppm) into 1000 ppm and 500 ppm solutions. The internal standard Lepidine (6 mg) was added into three calibration solutions (1mL), and extracted sample solutions (1 mL) in GC vial for quantitative analysis.

Water-acid mixed solvent liquid-liquid extractions

The model oil was prepared with indole (2000 ppm), pyrrole (2000 ppm), pyridine (2000 ppm), and quinoline (2000 ppm) in toluene (250 mL). Aqueous solution (4 mL) of 20% acetic acid, 20% propionic acid, and 20% hydrochloric acid were added respectively into three vials that contains model oil (4mL). The mixtures of two phases solution were stirred vigorously at room temperature overnight. Red precipitate was observed after the hydrochloric acid extraction, which was not found in other two aqueous acid extractions. The organic layer was separated from aqueous layer, and analyzed by gas chromatography coupled flame ionization detector (GC-FID) with internal standard method. Calibration solutions were prepared by diluting model oil (2000 ppm) into 1000 ppm and 500 ppm solutions. The internal standard Lepidine (6 mg) was added into calibration solutions (1mL), and extracted sample solutions (1 mL) in GC vial for quantitative analysis.

Oxidative acid liquid-liquid extractions

The model oil was prepared with indole (2000 ppm), pyrrole (2000 ppm), pyridine (2000 ppm), and quinoline (2000 ppm) in toluene (250 mL). Aqueous solution (4 mL) of 20% hydrogen peroxide, 20% formic acid, and the mixture of 20% hydrogen peroxide with 20% formic acid were added respectively into three vials that contains model oil (4mL). The mixtures of two phases solution were stirred vigorously at room temperature overnight. The organic layer was separated from aqueous layer, and analyzed by gas chromatography coupled flame ionization detector (GC-FID) with internal standard method. Calibration solutions were prepared by diluting model oil (2000 ppm) into 1000 ppm and 500

ppm solutions. The internal standard lepidine (6 mg) was added into calibration solutions (1mL), and extracted sample solutions (1 mL) in GC vial for quantitative analysis.

4.3 Results and discussion

Sodium hydroxide, bromoacetic acid two phases denitrogenation reaction

Neutral nitrogen-containing compounds are not good nucleophiles. Unlike basic nitrogen compounds, they are not reactive in the nucleophilic substitution reaction. The purposes of introducing inorganic base sodium hydroxide to bromoacetic acid reaction is to deprotonate the neutral nitrogen compounds, which convert them into better nucleophiles. Excess amount of base was used in this process, as bromoacetic acid has to be neutralized, before the deprotonation of neutral nitrogen compounds (Figure 4-8.) The reaction mixture contains both aqueous and organic phase, due to sodium hydroxide is not soluble in the naphtha. Tetrabutylammonium bromide (TBAB) was the phase transfer catalyst that assisted the transfer of reactants between aqueous and organic phases. The expected products were not found in the product mixture. Instead, GC-MS indicated that sodium hydroxide reacted with non-nitrogen containing compounds like thiols that are more acidic than the amine type neutral nitrogen compounds. The deprotonation of thiols led to nucleophilic substitution reaction with bromoacetic acid, generating thiocarbonic acid ethers. The GC-MS chromatogram and structures of thiocarbonic acid ethers are shown in Figure 4-9. It reveals that basic reaction condition is not suitable for our naphtha, because of the complexity of the matrix in this thermally cracked naphtha.

Moreover, because the chemical properties of neutral nitrogen compounds, it is believed that the development of a selective chemical reaction for the removal is extremely difficult when complex matrix is present in the fuel oil. Alternatively, liquid-liquid extraction and physical adsorption are known methods for the removal of neutral nitrogen compounds. Altering liquid solutions for extraction or manipulating functional groups on the solid absorbent could specifically target the neutral nitrogen compounds in fuel oil.

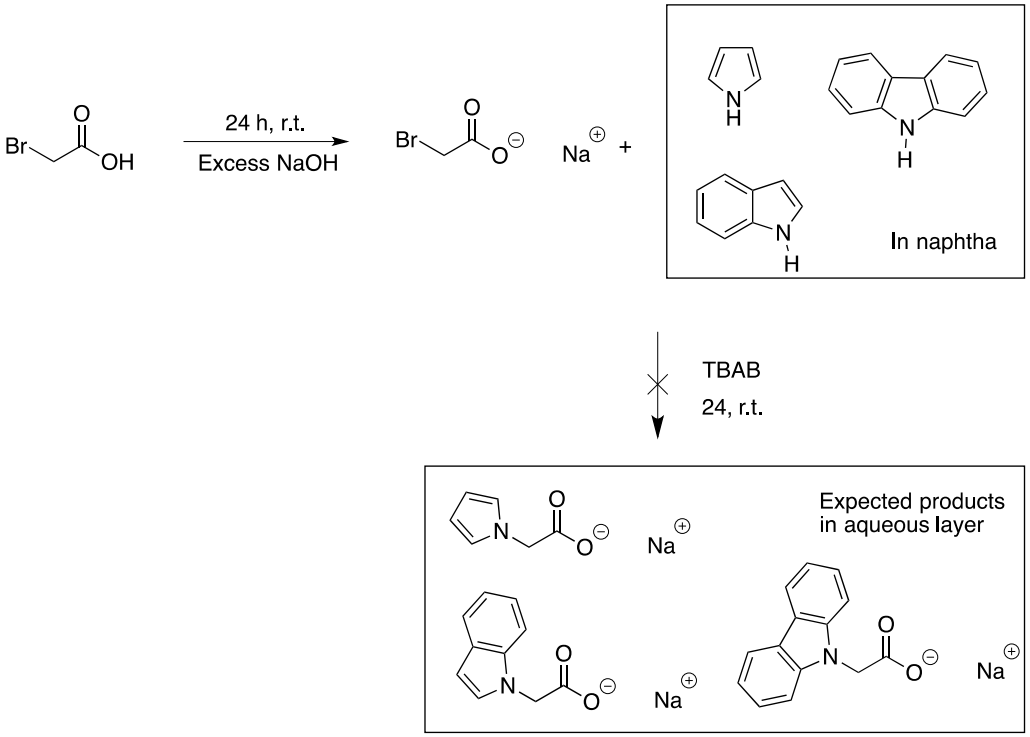

Figure 4-8: Two phases bromoacetic acid reaction in basic condition.

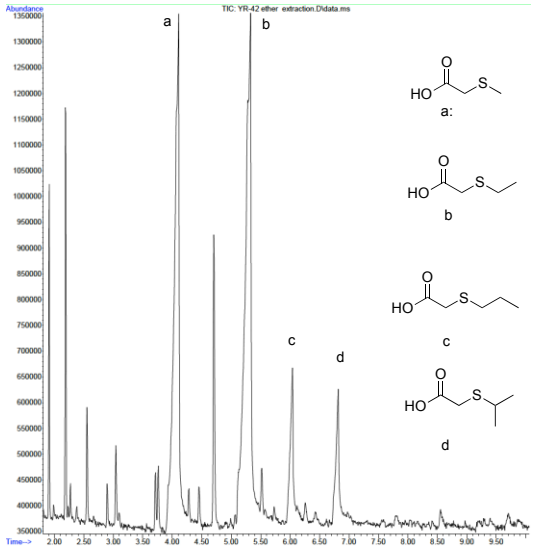

Figure 4-9. GC-MS chromatogram of the diethyl ether extraction of the sodium hydroxide bromoacetic acid denitrogenation reaction. Four major peaks were identified as additional products of thiols and bromoacetic acids. The rest of peaks are impurities.

Sulfonic groups aqueous extraction of neutral nitrogen containing compounds from model oil

Sulfonic groups aqueous extraction of neutral nitrogen compounds was designed depending on the hydrogen bonding theory between the sulfonic groups and the neutral nitrogen containing compounds. 2,6-naphthalenedisulfonic acid disodium salt and sodium 2-naphthalenesulfonate salt were chosen for the test, as they are attaching with different number of sulfonic groups in their molecular structures (Figure 4-10). 2,6-naphthalenedisulfonic acid disodium salt has double amount of sulfonic groups than sodium 2-naphthalenesulfonate salt, therefore was expected to extract more neutral nitrogen compounds.

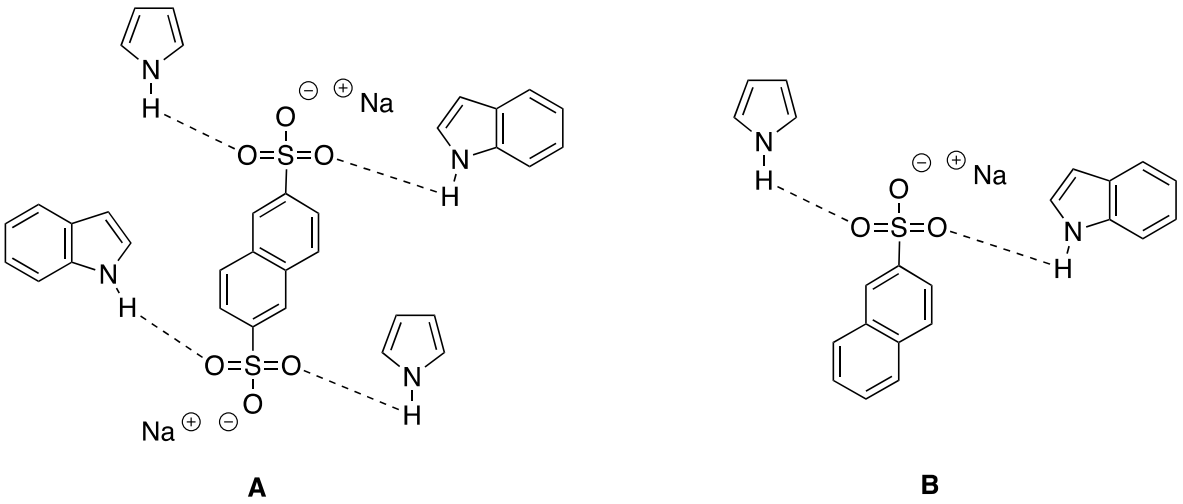

Figure 4-10. Hydrogen bonding between neutral nitrogen compounds and sulfonic groups in **A**: 2,6-naphthalenedisulfonic acid disodium salt and in **B**: sodium 2-naphthalenesulfonate salt.

The toluene model oil for extraction contains neutral nitrogen compounds pyrrole and indole, as well as basic nitrogen containing compounds pyridine and quinoline. The original concentration of the model oil was 2000 ppm for each model compound. The extractions with aqueous solution A: 2,6-naphthalenedisulfonic acid disodium salt (2.5%) and aqueous solution B: sodium 2-naphthalenesulfonate salt (2.5%) gave similar results for each specific model compound (Table 4-1). It is against the idea that solution of 2,6-naphthalenedisulfonic acid disodium salt would extract more neutral nitrogen compounds. This means the sulfonic groups may not have significant positive influences for the extraction of neutral nitrogen compounds and the reduced amount of pyrrole could only because of water extraction. The results also reveal that molecules with smaller molar weight are more readily to be extracted, which is consistent with the phenomena of purely water extraction.

Table 4-1. GC-FID quantitative analysis results of the nitrogen compounds extractions with solution A: 2,6-naphthalenedisulfonic acid disodium salt and solution B: sodium 2-naphthalensulfonate salt aqueous extraction.

Model Compounds	Retention time (min)	Before extraction (ppm)	Solution A extraction (ppm)	Solution B extraction (ppm)
Pyrrole	1.403	2000	818.3	812.1
Pyridine	1.809	2000	1386.3	1365.6
Quinoline	7.905	2000	1879.4	1872.7
Indole	8.999	2000	1906.7	1907.4
Lepidine*	10.869	7241		

*Lepidine was the internal standard for quantitative analysis with GC-FID.

To further confirm that sulfonic groups in the aqueous solution did not play an important role in the extraction of pyrrole, a control experiment with water were performed. In addition to water extraction as control, the aqueous solution of higher concentration of 2,6-naphthalenedisulfonic acid disodium salt (5%) was tested, to measure whether concentration of the sulfonic group would have any effects on the extraction results. Sodium 2-naphthalenesulfonate salt was not selected in this experiment because its low solubility in water limits the preparation of higher concentration solution. The higher water solubility of 2,6-naphthalenedisulfonic acid disodium salt comes from its extra sulfonic groups in the molecular structure. A second set of control was also introduced in this experiment to measure the adsorption capability of solid 2,6-naphthalenedisulfonic acid disodium salt to nitrogen containing compounds, without aqueous solution (Table 4-2). This isolated the influences of water extraction to have a clear measurement of the interaction between neutral nitrogen compounds and sulfonic 2,6-naphthalenedisulfonic acid disodium salt.

In table 4-2, the quantification results from GC-FID shows remaining amount of nitrogen compounds in model oil, after five different extractions. Some data were slightly higher than the original concentration 2000 ppm of stock solution, which reveals that a small amount of toluene was evaporated during the extraction process and the amount of nitrogen compounds were removed are almost ignorable. DiNa was used as the abbreviation of 2,6-naphthalenedisulfonic acid disodium salt in the table. The 3D bar charts (Figure 4-11) provide a direct view of the results from three extractions. Apparently, the results of water extraction and DiNa solution extraction were similar, which confirmed that water played the major role in the removal of pyrrole and pyridine. Interestingly, solid form of DiNa has certain capability to remove pyrrole and pyridine without present of water. It is not clear yet what kind of interactions are linking between basic pyridine and DiNa. In the comparison of the results from water extraction and DiNa solution extraction, it was not difficult to find out the removal effects from DiNa to pyrrole and pyridine were very few. In this case, water could have disabled the hydrogen bonding interactions between these nitrogen compounds and sulfonic groups. In terms of larger molecules like quinoline and indole, the extraction results of solid DiNa and solution DiNa were very

similar, only small amount of these compounds can be extracted, as larger molecules are less vulnerable to be extracted.

In order to investigate the effects from various concentrations, DiNa solutions were prepared in two different concentrations as 5% DiNa and 2.5% DiNa. The lowest concentration of DiNa was 2.5% that was higher than the concentration of any nitrogen compounds in the model oil. This made sure the maximum removal capacity was reached during extractions. In terms of DiNa solid extraction, two different masses 0.2 g and 0.1 g of DiNa were tested in the extractions. The results shown higher concentration of DiNa did not make significant difference on removal capability in both cases of solution and solid extractions.

In summary, this experiment shows that sulfonic groups in DiNa have weaker removal capability towards nitrogen compounds than water. Hydrogen-bonding interactions between sulfonic group and nitrogen compounds is a relatively weak interaction, therefore, dose not supply significant attraction to remove nitrogen compounds from model oil. However, more structurally different sulfonic compounds should be investigated before this conclusion can be confirmed.

Table 4-2. 2,6-naphthalenedisulfonic acid disodium salt extraction of nitrogen compounds

Model Compounds	Retention time (mins)	Water extraction (ppm)	0.2 g DiNa salt extraction (ppm)	0.1 g DiNa salt extraction (ppm)	5% DiNa solutiion extraction (ppm)	2.5% DiNa solution extraction (ppm)
Pyrrole	1.403	798.3	1831.9	1817.6	745.6	773.4
Pyridine	1.809	1467.2	1956.9	1945.1	1432.6	1461.4
Quinoline	7.905	2131.8	2122.1	2163.3	2109.7	2119.9
Indole	8.999	2149.0	2149.0	2181.0	2147.2	2152.5
Lepidine*	10.869	7085	7085	7085	7085	7085

*Lepidine was the internal standard for quantitative analysis with GC-FID.

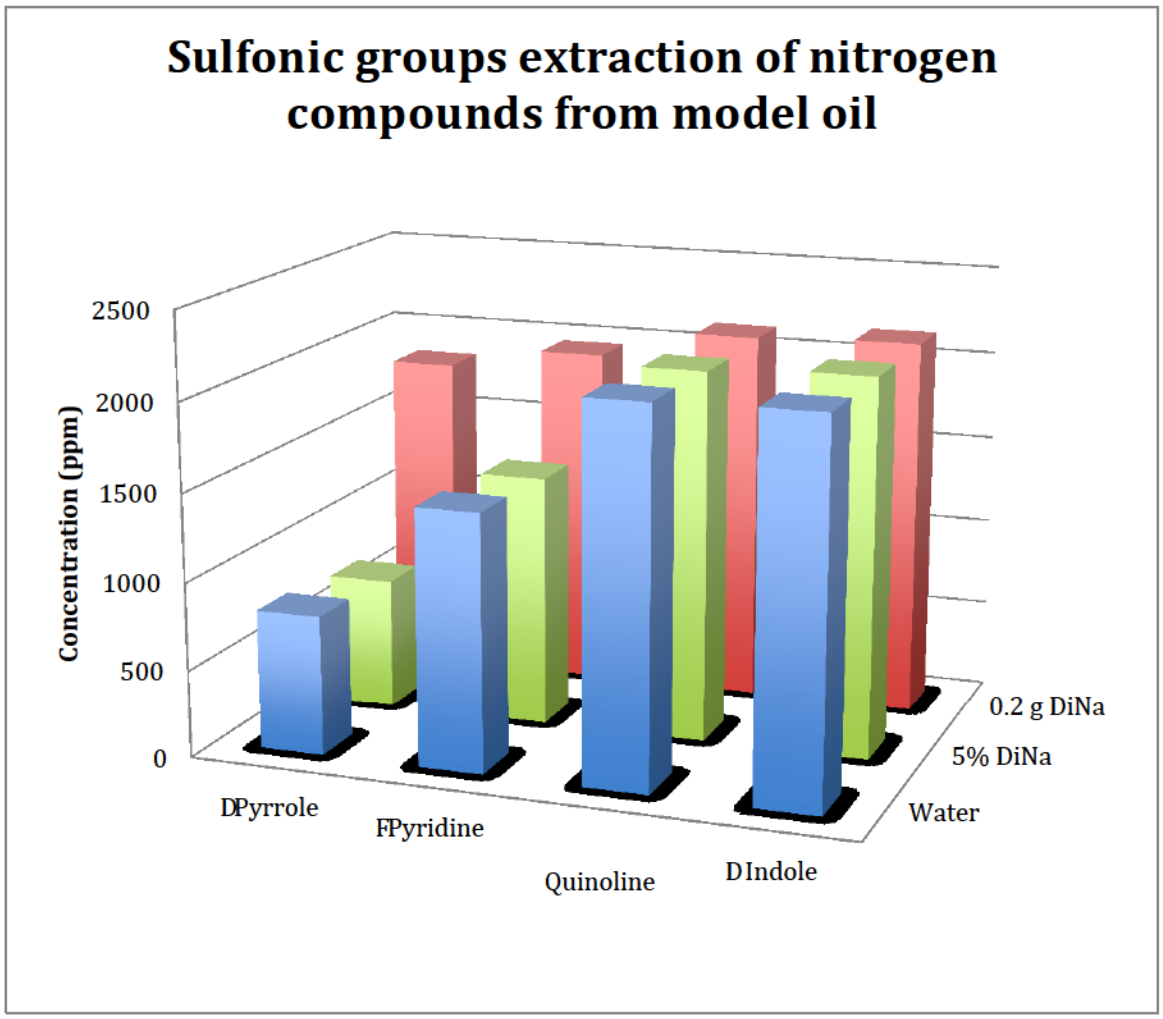

Figure 4-11. 2,6-naphthalenedisulfonic acid disodium salt extraction of nitrogen compounds from model oil.

Influences of extraction parameter on water-alcohol mixed solvent liquid-liquid extractions

Knowing liquid-liquid extraction with water plays a role in removing small nitrogen compounds like pyrrole and pyridine from model oil, it is interesting to further explore whether altering solubility parameter of mixed solvent would affect the extraction outcomes.

In general, chemicals with similar solubility parameter are miscible to each other. Therefore, choosing suitable co-solvent that is miscible with water is based on their solubility parameter. Alcohols are polar solvents that are miscible with water. Mixing certain amount of alcohols with water would create a mixed solvent that has its own solubility parameter. This solubility parameter of binary solvent was calculated with the following equation (3).[7] In the equation (3), the Hildebrand solubility parameters of single solvent were obtained from literatures,[17-18] and were listed in Table 4-3.

In this study, 20 Vol. % of alcohols including methanol, ethanol and n-propanol were mixed respectively with distilled water. The solubility parameter of this mixed binary solvent were calculated and listed in Table 4-3. As the result of addition of alcohols into water, solubility parameters of mixed solvents all have smaller value than water. The values of solubility parameter of the mixed solvents are descending in order of methanol-water, ethanol-water and n-propanol-water, although the differences between them are not dramatic.

Table 4-3. Solubility parameters of alcohol co-solvents and water

Solvents	Solubility parameter δ $(cal/cm^3)^{0.5}$
Water	23.40
Methanol	14.50
Ethanol	12.78
n-Propanol	12.18
20% Methanol + water	21.62
20% Ethanol + water	21.28
20% n-Propanol + water	21.16

Equation (3) was employed for calculation of the solubility parameter of co-solvents and water

The results of the extractions with these three types of alcohol-water mixed solvents are listed in Table 4-4. The numbers indicating the concentrations (ppm) of nitrogen compounds which were remaining in the model oil after the extractions with each mixed solvents. The original concentration of the nitrogen compounds in model oil was 2000 (ppm). Due to solvent evaporation, in certain experiments, the concentration of quinoline and indole were slightly higher than original concentration after extraction. The peak of pyrrole was found overlapping with the peak of ethanol, therefore, the remaining concentration of pyrrole after ethanol-water extraction was not record in the table 4-4 to avoid confusion. In general, pyrrole and pyridine were more likely to be extracted than quinoline and indole, which has been observed when water was used in the single solvent extraction. The addition of alcohols did not have significant effects on removing nitrogen compounds that are having large molecular structure. Moreover, having the additional 20% of alcohols in the water, extraction performances were not largely improved, and small amount of alcohols may dissolve into the organic model oil. However, change of solubility parameter of the solvent had some effects on the extraction. For example, in Figure 4-12, the extraction with n-propanol-water shown the mixed solvent that has the lowest solubility parameter had the highest ability to extract nitrogen compounds from model oil. Methanol-water has the highest solubility parameter, however, shown the lowest ability to extract nitrogen compounds from model oil. The binary solvent systems that lower solubility parameter of water could have better extraction performance because nitrogen compounds like pyridine and quinoline have relatively low solubility parameter at 10.6 cal/cm^3 and 10.8 cal/cm^3 respectively. The experimental observation confirmed that chemicals are more likely to be dissolved or extracted into a solvent that has similar solubility parameter. Theoretically, increase the ratio of alcohol to water would further reduce the value of mixed solvent, which will benefit for the extraction of nitrogen compounds

from model oil. Whereas, high percentage alcohol mixed solvent is not always practical because alcohol could also be dissolved into the organic phase model oil.

Table 4-4. Alcohol extractions of nitrogen compounds from model oil. (Ethanol extraction of pyrrole was not recorded in this table, because of its peak overlapping with ethanol)

Model Compounds	Retention time (mins)	20% Methanol (ppm)	20% Ethanol (ppm)	20% n-Propanol (ppm)
Pyrrole	1.403	953.1	NA	739.0
Pyridine	1.809	1331.3	1356.9	1389.0
Quinoline	7.905	2257.3	2217.8	1914.7
Indole	8.999	2287.9	2261.7	1962.5
Lepidine*	10.869	7085	7085	7085

*Lepidine was the internal standard for quantitative analysis with GC-FID.

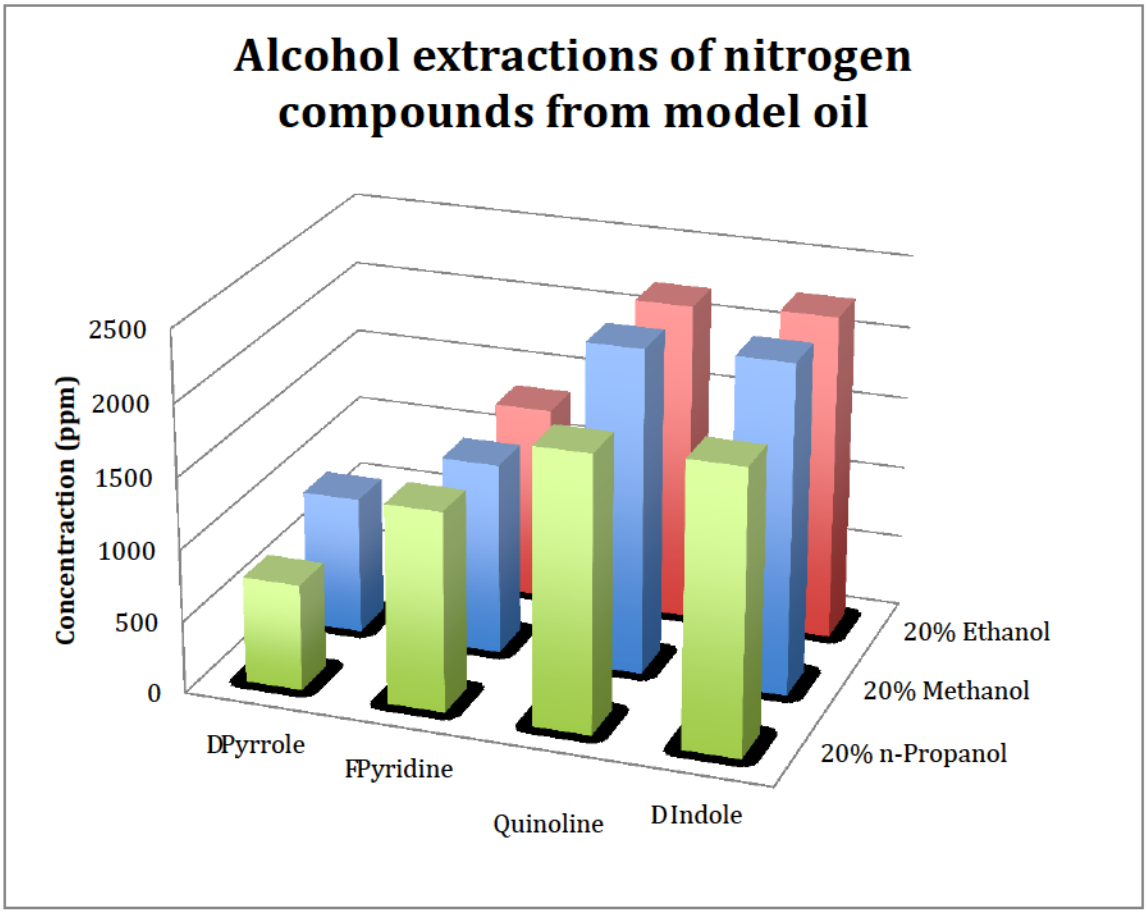

Figure 4-12. Alcohol extractions of nitrogen compounds from model oil. (Ethanol extraction of pyrrole was not recorded in this table, because of its peak overlapping with ethanol)

Water-acid mixed solvent liquid-liquid extractions

Water-acid mixed solvent extractions of the nitrogen compounds from model oil were performed with two organic acids (acetic acid and propionic acid) and one mineral acid (hydrochloric acid). In order of acidity, hydrochloric acid was the strongest acid in the test, followed by acetic acid and propionic acid. The results listed in Table 4-5 indicate the concentration of nitrogen compounds remaining in the model oil after the extraction. It is clear that the stronger the acid, the better the extraction outcome, although the reasons behind this observation is more complex than acidity change of mixed solvents.

In general, the extractions with organic acids, match up the extraction pattern of water extraction that smaller molecules were more vulnerable to the extraction. However, the extraction with hydrochloric acid has completely removed all the nitrogen compounds from model oil, regardless of molecular size. Interestingly, neutral nitrogen compounds pyrrole and indole were removed along with basic nitrogen compounds pyridine and quinoline. This excellent extraction to neutral nitrogen compounds seems against the fact that there is no acid-base reaction between neutral nitrogen compounds and hydrochloric acid. In fact, the chemical reaction unknown as polymerization occurred during the extraction, which was the main reason why neutral nitrogen compounds was removed from the model oil.

Table 4-5. Acid extractions of nitrogen compounds from model oil.

Model Compounds	Retention time (mins)	20% Acetic acid (ppm)	20% Propionic acid (ppm)	20% HCl (ppm)
Pyrrole	1.403	640.0	745.0	0
Pyridine	1.809	686.3	743.0	0
Quinoline	7.905	591.0	1200.0	0
Indole	8.999	1854.6	1662.2	0
Lepidine*	10.869	7085	7085	7085

*Lepidine was the internal standard for quantitative analysis with GC-FID.

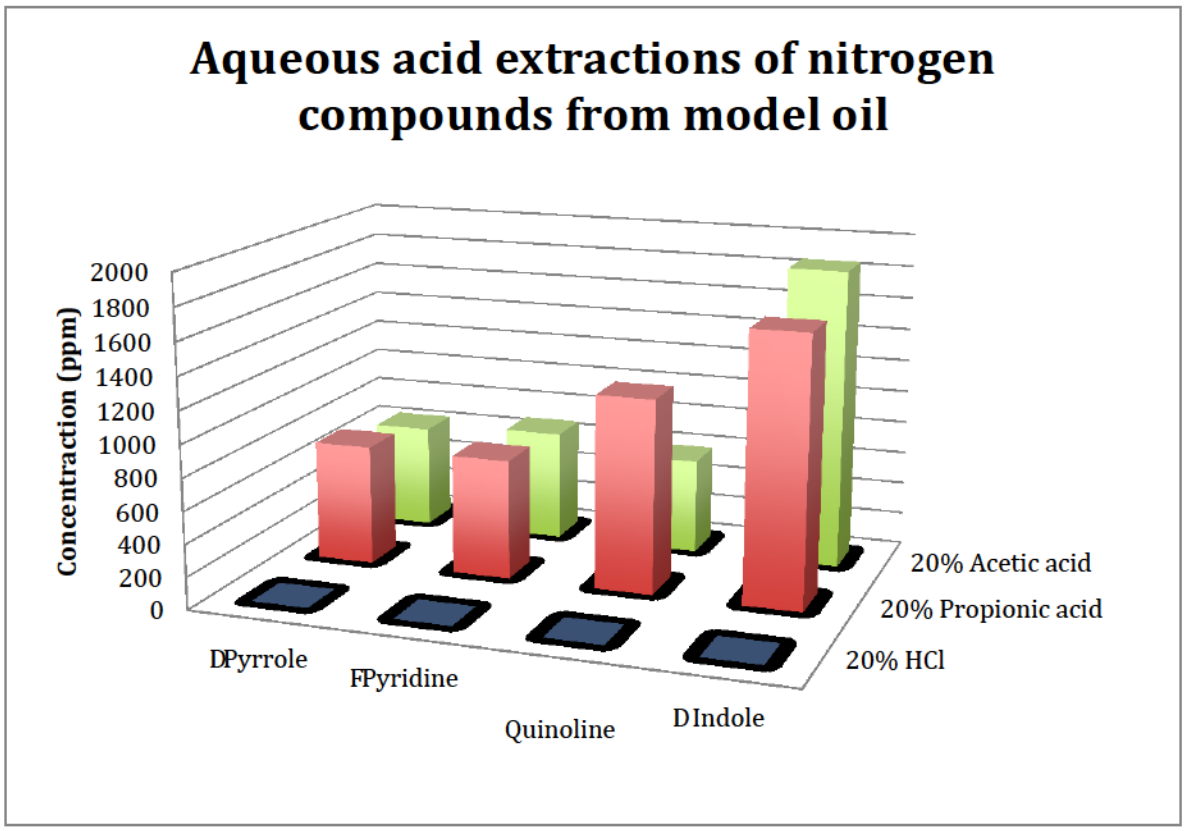

Figure 4-13. Aqueous acid extractions of nitrogen compounds from model oil.

There was brown precipitate that was insoluble in either toluene or water, after the extraction with 20% hydrochloric acid (HCl). In contrast to the 20% acetic acid and 20% propionic acid extractions, no such precipitate was found in the extraction solutions. The formation of this unique precipitate can explain HCl's excellent removal ability towards neutral nitrogen compounds (pyrrole and indole). The precipitate must be the product of pyrrole and indole polymerization. It is known that pyrrole is unstable in the strong acidic conditions so that pyrrole polymerization can occur when pKa of the acid is less than -4.[19] In the case of HCl extraction, the pKa of HCl is around -7, the condition of pyrrole polymerization was reached. The mechanism of pyrrole polymerization is shown in Figure 4-14, in the strong acidic condition, the lone pair electrons on the nitrogen atom delocalizes into the aromatic ring, the protonation occur on position 2, resulting the formation of a positive charged quaternary nitrogen intermediate. This positive charged intermediate is very reactive and available for the addition of the second pyrrole molecule, leading the formation of a positive charged pyrrole dimer. The same polymerization reaction can continue for more additional pyrrole molecules to be linked to form polymer.

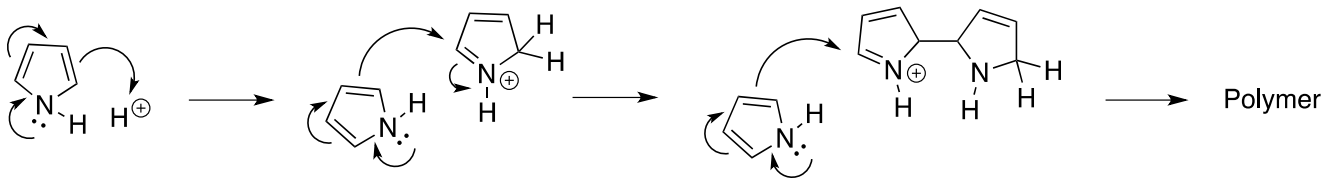

Figure 4-14. The mechanism of pyrrole polymerization.

The results in Figure 4-13. shows that indole was also completed removed by hydrochloric acid extraction. It is believed that the similar polymerization reaction has occurred during the extraction. However, the protonation position on the indole would be more likely on the position 3 (Figure 4-15), because the electrophilic substitution on the position 2 that requires a breaking of the adjacent aromatic system is not favorable (Figure 4-16).[20] The model oil contained both pyrrole and indole. It is not clear yet whether the generated polymers are single molecular polymers, bimolecular polymers, or a combination of both.

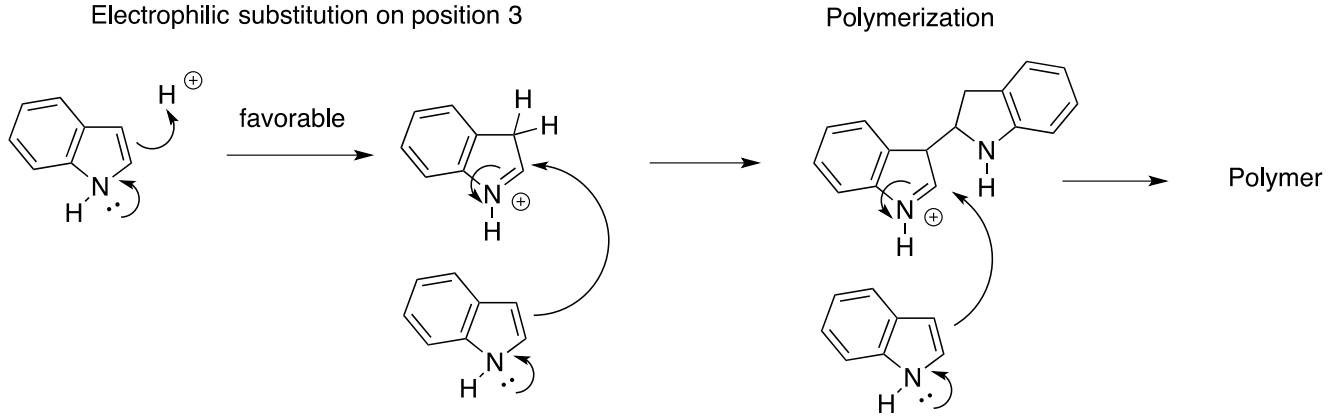

Figure 4-15. Polymerization mechanism of indole.

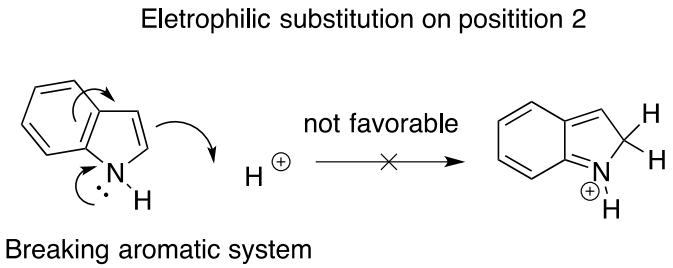

Figure 4-16. Mechanism of the electrophilic substation on position 2 of the indole molecule.

Oxidative acid extractions of nitrogen compounds from model oil

Hydrogen peroxide was mixed with formic acid to perform the peroxy acid extraction with the purpose of removing nitrogen compounds from the same model oil used in previous experiments. In addition, hydrogen peroxide and formic acid were also tested individually as single-solvent controls in the experiment, in order to compare the extraction outcomes with the mixed solvent. In table 4-6, the GC-FID quantitative analysis data of extracted model oil suggest that, the mixed solvent of hydrogen peroxide and formic acid had the best extraction results. In this case, pyrrole, pyridine and indole were completely removed by peroxy acid extraction. Exceptionally, there was a small amount of pyridine (105 ppm) remained in the model oil after this extraction. This means oxidation reactions might appear more accessible to quinoline (large basic molecule), instead of pyridine (small basic molecule), although the products of both reactions are N-oxides (Figure 4-6). In the case of neutral nitrogen compounds, indole (larger neutral molecule) and pyrrole (smaller neutral molecule) were both removed completely, which shows the products of oxidation reactions, oxidized dimer of pyrrole (Figure 4-5) and indole, are readily extracted from model oil.

In order to further confirm the effects of peroxy acid extraction towards nitrogen compounds are exclusively from peroxy acid, but not from hydrogen peroxide or formic acid, results were compared against two control experiments. In comparison with the single-solvent controls, the peroxy acid extraction clearly provided the best extraction outcome. In the control experiment of hydrogen peroxide extraction, high concentration of quinoline (1908.2 ppm) and indole (1934.7 ppm) remained in the model oil, although less pyrrole (508 ppm) and pyridine (932.6 ppm) were remained. The second control experiment was conducted with formic acid. It was expected to have slight stronger nitrogen-compounds removal capability than the acetic acid and propionic acid extraction. However, interesting results were obtained in this experiment as quinoline was completely removed while pyridine (742 ppm) still remained in the model oil. Apparently, the results suggest that the reaction selectively occurred between formic acid and quinoline while pyridine also was present in the solution. The observation is against the simple rule of acid-base reaction, because quinoline (pKa: 4.85),[21] is less basic than pyridine (pKa: 5.25)[22]. In contrast to the previously performed acetic acid and propionic acid extraction, the remaining concentration of quinoline in model oil after formic acid extraction is inconsistent with the results from those two organic acid extraction. Therefore, there must be other type of reaction or interaction occurred between quinoline and formic acid during the extraction process.

According to Tao, L., formic acid can serve as a reducing agent and formylating reagent simultaneously, when quinoline is present (Figure 4-17).[23] This reaction was carried out in 130 ℃ with metal catalyst, which is a significantly different reaction condition comparing to the formic acid extraction. Furthermore, there were no any additional peaks appearing in the GC-FID chromatography after the extraction, which proves the products of reductive formylation were not generated during the formic acid extraction. Therefore, the powerful interaction responsible of removing quinoline during the extraction remains unknown.

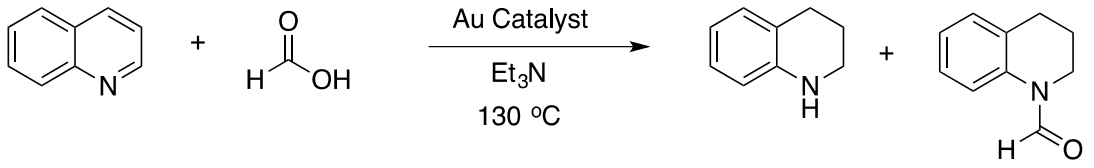

Figure 4-17. Catalytic reductive formylation of quinoline with formic acid [23].

In terms of reaction between pyridine and formic acid, it is believed to be the normal acid-base reaction forming a polar complex that is easily dissolved in water (Figure 4-18.).[24] In comparison to the previously performed organic acid extractions, the concentrations of pyridine in the model oil were similar (Table 4-5. and Table 4-6.), as they all shared the same removal mechanism, acid-base interaction.

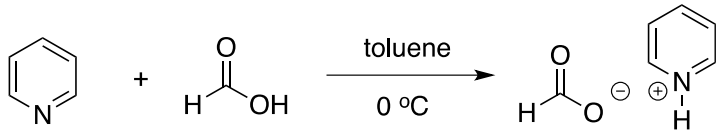

Figure 4-18. Acid-base reaction between pyridine and formic acid.[24]

Apart from the basic nitrogen compounds removed from the model oil, neutral nitrogen compounds were also removed by formic acid extraction (Table 4-6). It seems the influence of formic acid extraction to neutral nitrogen compounds was mainly from water, as the remained concentrations of neutral nitrogen compounds (pyrrole: 713.0 ppm and indole: 2073.3 ppm) in the model oil were similar to those in water extraction (Table 4-2.).

In general, the oxidation reactions between peroxy acid and both basic and neutral nitrogen compounds were very efficient when they were applied to remove nitrogen compounds from model oil. In the case of actual applications on removing nitrogen compounds from industrial oil, it is important to understand the limitation of this oxidative extraction, that oils with high olefin content are not compatible with this extraction method, as peroxy acids are reactive to olefins.

Table 4-6. Oxidative extractions of nitrogen compounds from model oil.

Model Compounds	Retention time (mins)	20% Hydrogen peroxide (ppm)	20% formic acid (ppm)	20% Hydrogen peroxide + 20% formic acid (ppm)
Pyrrole	1.403	508	713.0	0
Pyridine	1.809	932.6	742.4	105.0
Quinoline	7.905	1908.2	0	0
Indole	8.999	1934.7	2073.3	0
Lepidine*	10.869	7085	7085	7085

*Lepidine was the internal standard for quantitative analysis with GC-FID.

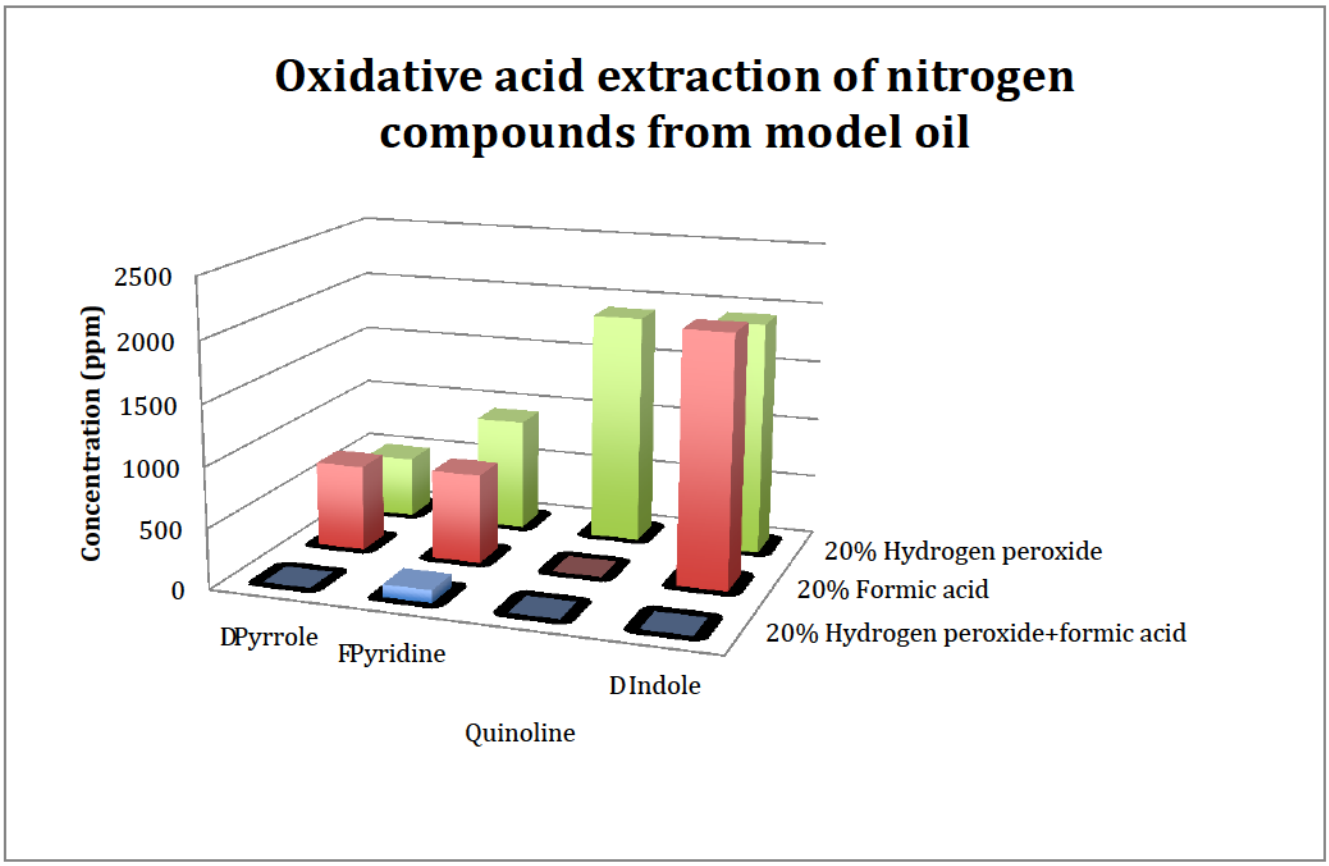

Figure 4-19. Oxidative acid extraction of nitrogen compounds from model oil.

4.4 Conclusion

This chapter started with the goal of exploring effective methods of removing neutral nitrogen compounds from oil. During our research, it was realized that selectivity of chemical reactions is the main problem that prevent a clear removal of neutral nitrogen compounds. Solid-liquid and liquid-liquid extractions of nitrogen compounds from model oil were studied with the purpose of understanding fundamental chemistry of several types of extractions, including sulfonic groups extractions, acid extractions and oxidative acid extractions.

The main outcomes of this study were:

(a) The two-phase reaction of bromoacetic acid in the present of sodium hydroxide has failed to remove both neutral and basic nitrogen compounds from thermally cracked naphtha. The products of reaction revealed that bromoacetic acid selectively reacted with thiols in the naphtha, instead of nitrogen compounds.

(b) 2,6-naphthalenedisulfonic acid disodium salt and sodium 2-naphthalenesulfonate salt were tested in the solid-liquid, liquid-liquid extractions of model oil. Experimental results revealed that sulfonic groups made no significant contributions to remove nitrogen compounds.

(c) The binary solvent system that combine alcohols and water were tested in the extraction of nitrogen compounds from model oil, with the purpose of understanding the effects from changing the solubility parameter of the extraction solvents. Extraction solvents with closer solubility parameter to the nitrogen compounds had slightly better extraction outcome. However, the nitrogen compounds removal effect from changing solubility parameter of the solvents was considered minor, as water was still the main reason that nitrogen compounds were removed.

(d) Acid extractions of nitrogen compounds from model oil have revealed many positive results on removing both neutral and basic nitrogen compounds. Hydrochloric acid extraction shown the best extraction outcome that both neutral and basic nitrogen compounds were completed removed. The fundamental chemistry was studied for explaining the removal of neutral nitrogen compounds in strong acidic environment. Polymerization was responsible for the neutral nitrogen compounds removal in strong acid liquid extraction.

(e) Oxidative peroxy acid extraction of nitrogen compounds from model oil was performed along with comparison of two separated control experiments, including formic acid and hydrogen peroxide extractions. The study has confirmed the positive effect was from peroxy acid extraction and this method was proven successful in removing all the neutral nitrogen compounds from the model oil. After peroxy acid extraction of the model oil (2000 ppm), 0 ppm of pyrrole and indole were remained in the model oil.

4.5 Reference

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5 Conclusions

5.1 Main achievements

With the goal of developing novel non-hydrotreating, denitrogenation methods that are applicable to solve catalyst deactivation problems in modern industrial oil refining, this thesis has described the study of three main topics related to denitrogenation of industrial naphtha. In the process of finding answers to questions that have been encountered in each topics, there were many problems have been conquered.

(a) Identification and quantification of nitrogen-containing compounds in thermally cracked naphtha.

In chapter 2, identification and quantification methods of thermally cracked naphtha were described. There were five main achievements from this topic including: (1) Development of a simple separation method to extract and concentrate nitrogen-containing compounds from thermally cracked naphtha. This separation method resolved the problem of low concentration of nitrogen-containing compounds in naphtha, which allowed the qualitative and quantitative analysis to be performed. (2) Oxygen-containing compounds like fatty acids that would affect the qualitative and quantitative analysis of nitrogen compounds, were removed by a newly developed base pretreatment method. This base pretreatment has overcome the problem of peaks overlapping. (3) Basic nitrogen-containing compounds were identified as pyridine and quinoline derivatives. This qualitative analysis provided crucial information of fundamental chemistry, which assisted the development of non-hydrotreating denitrogenation methods in chapter 3. (4) Total nitrogen-compound concentration in the thermally cracked naphtha was successfully quantified; (5) The investigation on the response of nitrogen phosphorus detector (NPD) to nitrogen-containing compounds were shown to be structure dependent. The data obtained can be used to correct the quantitative analysis with NPD, in order to achieve more accurate measurement.

(b) Non-hydrotreating denitrogenation of basic nitrogen-containing compounds from thermally cracked naphtha.

In chapter 3, the effort of developing non-hydrotreating denitrogenation methods to remove basic nitrogen compounds from thermally cracked naphtha was described. There were several attempts to target and remove the basic nitrogen compounds from naphtha. The most successful achievement is that a bromoacetic acid denitrogenation method was developed to selectively remove basic-nitrogen containing compounds from the thermally cracked naphtha. Unlike the traditional acid-base interactions, the denitrogenation mechanism was based on N-alkylation reaction. During the investigation of bromoacetic acid denitrogenation, a cleavage method was discovered to break the quaternary ammonium carbon bond (N-C bond). This cleavage method can be used to recover the basic nitrogen-containing compounds from naphtha as an oil product, as well as benefit both the qualitative and quantitative analysis of nitrogen-containing compounds, because it can serve as a method to extract

nitrogen-containing compounds from naphtha. The quantitative measurement of the outcome from bromoacetic acid denitrogenation has confirmed more than 75% of basic nitrogen compounds were successfully removed by this method. For analytical purpose, denitrogenated naphtha was separated by column chromatography (silica extraction), acetone and dichloromethane were used to elute the column and separate basic and neutral nitrogen compounds. Utilizing the quantitative measurement data of both acetone and dichloromethane fractions after denitrogenation reaction, accurate concentrations of neutral and basic nitrogen compounds in the thermally cracked naphtha were calculated. Apart from the bromoacetic acid denitrogenation, a potential denitrogenation method that involves *p*-toluenesulfonyl chloride was found, which has a limitation of being only compatible with low alcohol content naphtha.

(c) Non-hydrotreating denitrogenation of neutral nitrogen-containing compounds from thermally cracked naphtha and model oil.

Having the positive experience of removing basic nitrogen compounds with bromoacetic acid reaction, the target was changed to neutral nitrogen compounds. Removal of neutral nitrogen compounds was considered more challenging than basic nitrogen compounds as "neutral" also means less reactive in general. In order to "activate" the neutral nitrogen compounds, more reactive chemical reagents are usually needed, however, this would lead to difficulties in controlling reaction selectivity. In chapter 4, the study mainly focused on investigating combining methods that involved chemical reactions and liquid-liquid extractions to remove neutral nitrogen compounds from model oil.

Although the first attempt, which involved a combination of sodium hydroxide and bromoacetic acid, have failed to remove neutral nitrogen compounds from thermally cracked naphtha, it was found that this method can potentially remove thiols from naphtha. Then the investigation was moved on to utilize sulfonic groups, in order to remove neutral nitrogen compounds by possible hydrogen-bonding interactions. However, this method was proven not so successful, as the most of N removal effects were from aqueous liquid-liquid extraction. Next, the influence of altering solubility parameter of binary extraction solvent, by adding certain amount of alcohols to water, was investigated. The results shown these methods were not effective when compared with normal water extraction.

Acid extractions and oxidative acid extractions were also studied from the perspective of fundamental chemistry. Both neutral and basic nitrogen compounds were completely removed by strong acid extraction. Polymerization was the reason why neutral nitrogen compounds formed precipitate in this strong acidic condition. Oxidative peroxy acid extraction was also found effective for removing both neutral and basic nitrogen compounds. The chemistry responsible for this extraction was explained in detail, as well as the limitation of this oxidative extraction was discussed. The study of fundamental chemistry behind oxidative extractions has provided valuable knowledge to benefit future research on developing selective oxidative denitrogenation methods.

5.2 Future research directions

Neutral nitrogen-containing compounds would continuously be the major target in the future research in the area of non-hydrotreating denitrogenation. In addition, there are several directions worth to be explored based on the results of our study in this thesis.

(1) The separation method that was used to extract basic nitrogen compounds and remove complex matrix of naphtha could not selectively extract neutral nitrogen compounds. The dichloromethane fraction contained neutral nitrogen compounds and some oxygen-containing compounds like alcohols and ketones. Effective separation and selective extraction methods will be investigated to assist the identification of neutral nitrogen-containing compounds in the thermally cracked naphtha. On the other hand, identification of alcohols in the naphtha worth to be further explored, as some alcohols are potential sources of esters and carboxylic acids.

(2) In the investigation of nitrogen phosphor detector (NPD) responses towards nitrogen compounds, a larger number of nitrogen compounds will be tested to further support the idea that the NPD responses are structural dependent. And the influence of changing concentration of the sample solution on the NPD responses will be studied, in order to build an acceptable mathematical model to assist quantitative analysis of nitrogen compounds in naphtha.

(3) The research on non-hydrotreating denitrogenation methods to selectively remove neutral nitrogen compounds from oil will be continued. The bromoacetic acid reaction in basic reaction condition to remove thiols would be further studied.

(4) In terms of liquid-liquid extractions, non-hydrogen bonding salt can be introduced to serve as a control, to further study hydrogen bonding interaction between neutral nitrogen compounds and sulfonic group. For acid extractions, various concentrations can be tested to seek the lowest practical concentration for extraction, therefore reduce the amount of acid used in the extraction. This will benefit to the industrial scale operation from financial point of view. Selective oxidative extraction would also be one important direction for our research in future.

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