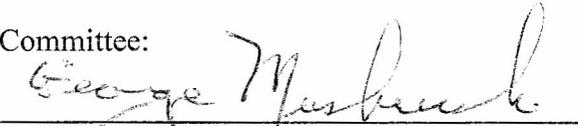
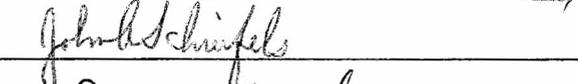
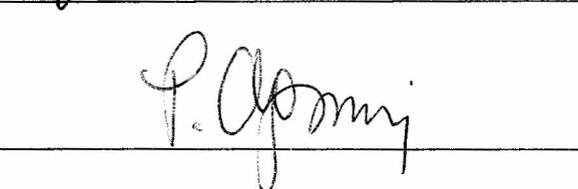


THE DETERMINATION, QUANTIFICATION AND ANALYSIS OF ORGANIC  
NITROGEN COMPOUNDS IN ALASKAN NORTH SLOPE DIESEL

by

Hien Le  
A Thesis  
Submitted to the  
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of  
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in Partial Fulfillment of  
The Requirements for the Degree  
of  
Master of Science  
Chemistry

Committee:

	Dr. George Mushrush, Thesis Director
	Dr. Gerald L. Weatherspoon, Committee Member
	Dr. Paul D. Cooper, Committee Member
	Dr. Douglas G. Mose, Committee Member
	Dr. John A. Schreifels, Department Chairperson
	Dr. Donna Fox, Associate Dean, Office of Student Affairs & Special Programs, College of Science
	Dr. Peggy Agouris, Dean, College of Science

Date:

April 29, 2014

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George Mason University  
Fairfax, Virginia

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Alaskan North Slope Diesel

A thesis submitted in partial fulfillment of the requirements for the degree of Master of  
Science at George Mason University.

By

Hien Le  
Bachelor of Science  
George Mason University, 2012

Director: George W. Mushrush, Professor  
Department of Chemistry

Spring Semester 2014  
George Mason University  
Fairfax, Virginia

## DEDICATION

This thesis is dedicated to my parents, Duc Le H. and My Nguyen T., who love and support me through my school years. I also dedicate this thesis to my loving brothers for always being by my side. All of you have been my best cheerleaders.

## ACKNOWLEDGEMENTS

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## TABLE OF CONTENTS

	Page
List of Tables -----	v
List of Figures -----	vi
List of Abbreviations -----	vii
Abstract -----	viii
Introduction -----	1
Experimental -----	11
Scheme of Extraction -----	13
Instrumental Methods -----	14
Chromatogram of Extracts -----	15
Results and Discussion -----	18
Conclusion -----	33
List of References -----	34

## LIST OF TABLES

Table	Page
1. Typical Basic and Neutral Nitrogen Compounds Present in Liquid Hydrocarbon Streams .....	9
2. BNC of Alaskan Diesel in methylene chloride.....	19
3. NBNC of Alaskan Diesel in methylene chloride .....	22
4. NBNC of Alaskan Diesel in methanol .....	24
5. Summary of area percentage of BNC and NBNC extracts .....	26

## LIST OF FIGURES

Figure	Page
1. U.S motor gasoline and diesel fuel consumption, 2000-2040 -----	2
2. 2012 World Oil Production -----	3
3. World petroleum consumption by region, 1980-2010 -----	4
4. Structure of asphaltenes -----	6
5. Nitrogen compound extract scheme -----	13
6. MS of BNC in methylene chloride -----	15
7. MS of NBNC in methylene chloride -----	16
8. MS of NBNC in methanol -----	17

## LIST OF ABBREVIATIONS

BNC – Basic Nitrogen Extract

bbl/d – Barrels per day

Da – Dalton

EIA – U.S. Energy Information Administration

GC/MS – Gas Chromatography/Mass Spectrometry

NBNC – Non Basic Nitrogen Extract

OPEC – Organization of the Petroleum Exporting Countries

PAH – Polynuclear Aromatic Hydrocarbons

THQ – Tetrahydroquinoline

UFAME – Unsaturated Fatty Acid Methyl Ester

## ABSTRACT

### THE DETERMINATION, QUANTIFICATION, AND ANALYSIS OF ORGANIC NITROGEN COMPOUNDS IN ALASKAN NORTH SLOPE DIESEL

Hien Le, M.S.

George Mason University, 2014

Thesis Director: Dr. George W. Mushrush

This study investigated a high nitrogen diesel fuel, which was derived from Alaskan North Slope oil. The purpose was to quantify the organonitrogen component distribution by using two methods: mild acid extraction and silica gel adsorption. The organonitrogen compounds of the Alaskan diesel fuel were isolated and analyzed. After the isolation process, three extracts were produced: a basic nitrogen extract (BNC) in methylene chloride, a nonbasic nitrogen extract (NBNC) in methylene chloride, and a NBNC in methanol. These extracts were studied by identifying the major constituents in each extract, which affect the fuel stability, using the GC/MS. Results from our laboratory indicated that alkyl substituted quinolines were the dominant class of compounds in all three extracts. In the BNC extract, there were two major functional groups present: pyrazines at 22.37%, and indole at 7.74%. In the NBNC/CH<sub>3</sub>Cl extract, alkylated pyrroles and carbazoles dominated with 37.25% and 15.8%, respectively.

Lastly, in the NBNC/ CH<sub>3</sub>OH extract, carbazoles at 8.23% and pyrroles at 29.6% prevailed.

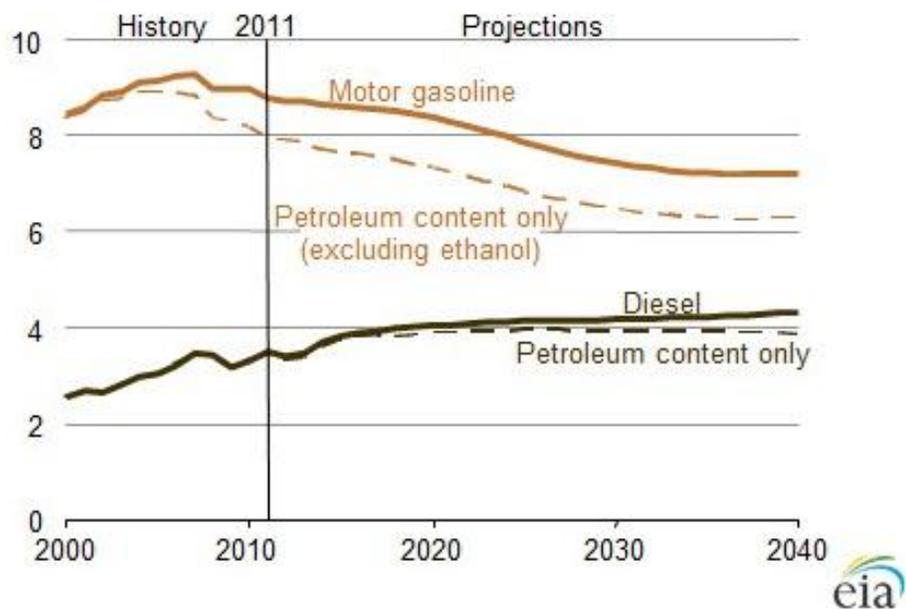
## INTRODUCTION

In the late nineteenth century, the development of petroleum diesel fuel refining began when Rudolf Diesel invented a compression ignition reciprocating engine to replace the inefficient (about 10% to 12%) steam engines. However, unfortunately, at that time, he used coal dust as a fuel for his original design, and was unsuccessful. In the process of finding another type of energy source, Diesel encountered crude oil. Obviously, this discovery had a big impact to Diesel's invention as well as automobile technology since there are several types of fuel that can be refined from crude oil, such as gasoline, kerosene, and heating oil. Among them, Diesel recognized a liquid petroleum byproduct that could be a better fuel for his engine than coal dust. Therefore, he started exploring possibilities, and by 1895, a successful prototype engine was born. The liquid fuel was later referred to as diesel fuel.

Nevertheless, for several reasons, diesel fuel and diesel engines had not been popular after they were first introduced. The first reason is because of the high cost of diesel fuel. In addition, the clattering noise, odor and smoke of diesel engines also made them less attractive in the automobile market. Diesel engines were also inconvenient to consumers because they required an extended warm-up time compared to gasoline engines. However, as time passed, diesel engines improved, and by the 1930s, the world recognized diesel engine's advantages including high combustion efficiency, high

reliability, high adaptability, and lower flammability.<sup>18</sup> As a result, diesel fuel eventually became more essential in transportation especially for heavy-duty engines. Nowadays, in the United States, 60% of transportation, primarily trucks, use diesel fuel. In fact, the consumption of diesel fuel is expected to increase from 3.0 million barrels per day in 2010 to over 4 million barrels per day in 2020.<sup>2</sup>

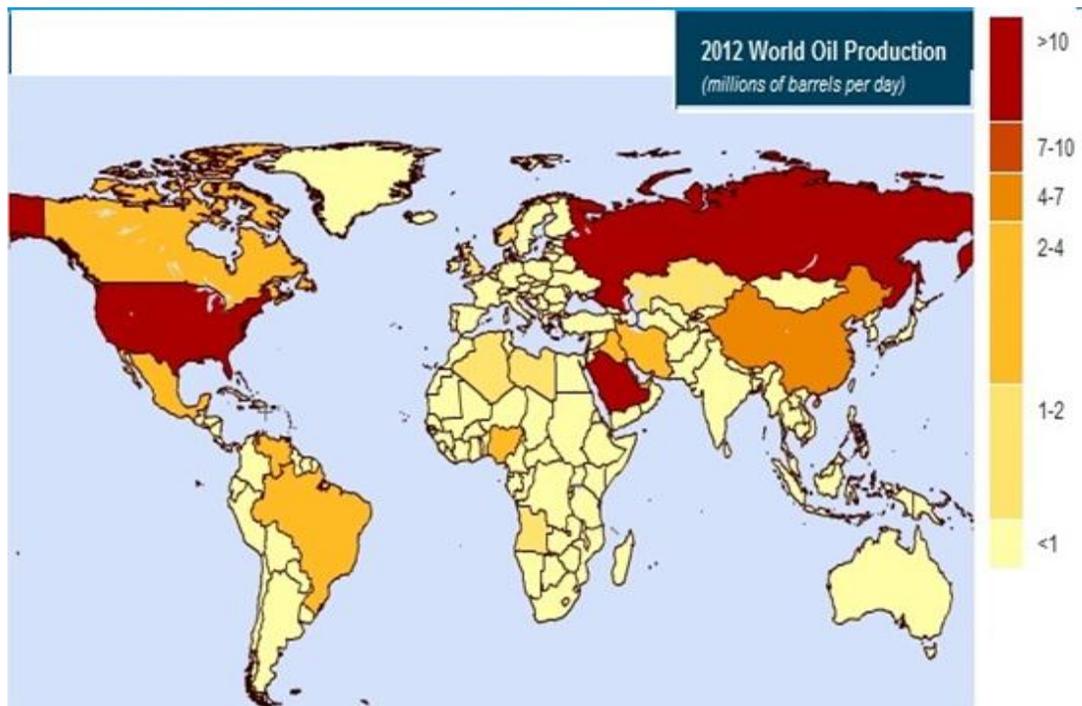
**U.S. motor gasoline and diesel fuel consumption, 2000-2040 (million barrels per day)**



**Figure 1: U.S Motor Gasoline and Diesel Fuel Consumption, 2000-2040.<sup>2</sup>**

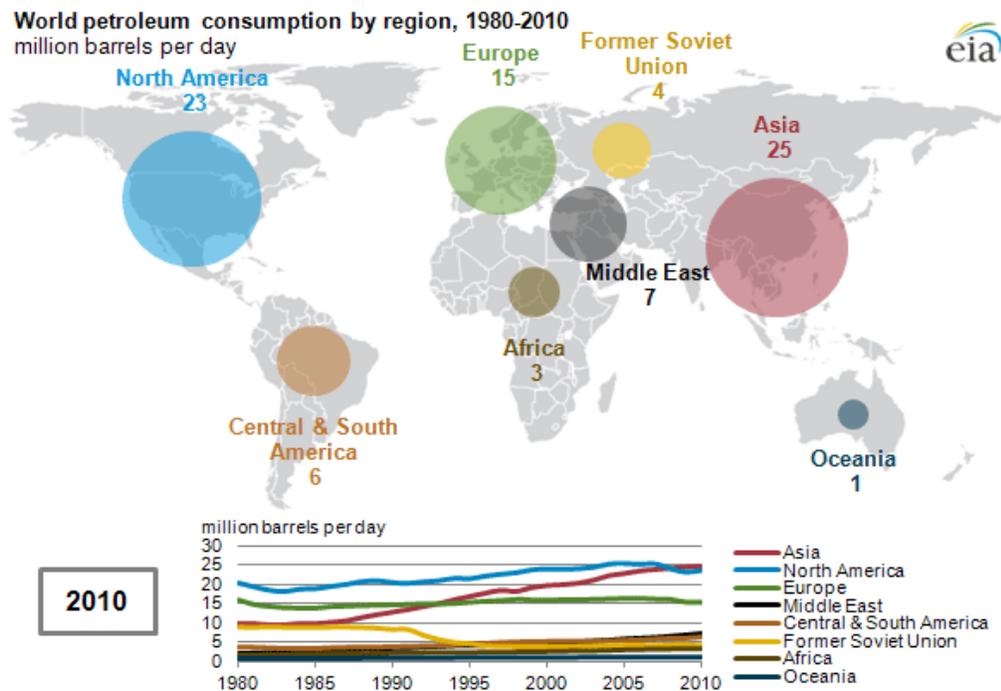
Consequently, the growth in diesel consumption led to an increase in diesel production. According to the U.S. Energy Information Administration (EIA), in 2014 and 2015, petroleum production will increase by 1.7 million barrels per day (bbl/d) and

1.4 million bbl/d respectively, with Saudi Arabia, the United States, Russia, China, and Canada being the top five largest oil producers worldwide.<sup>28</sup> In fact, based on data up through 2012 reported by the Organization of the Petroleum Exporting Countries (OPEC), Saudi Arabia remains the world's largest oil producer, with 11.7 million bbl/d, while the United States ranks second, with 11.4 million bbl/d. While the difference in oil production between Saudi Arabia and the United States is relatively small, the same thing is not necessarily true with the other three countries. In 2012, the oil production of Russia, China, and Canada was approximately 10.3 million bbl/d, 4.3 million bbl/d, and 3.8 million bbl/d respectively.<sup>28</sup>



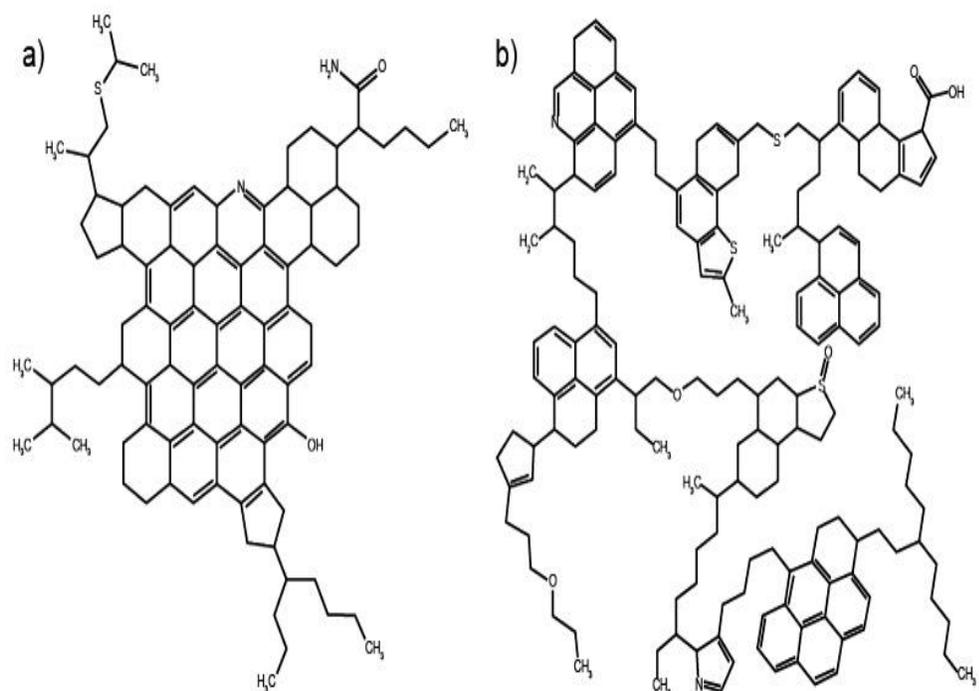
**Figure 2: 2012 World Oil Production.**

Although Saudi Arabia is the world largest oil producer, it is not the largest oil consumer. According to the EIA, in 2012, the United States was considered as the world's largest oil consumer (18.5 million bbl/d) followed by China (10.2 million bbl/d), Japan (4.7 million bbl/d), India (3.6 million bbl/d), and Russia (3.1 million bbl/d).<sup>27</sup> However, when taking regions into consideration, it is easy to realize that Asia will likely surpass North America in the future as the world largest oil consuming group since its demand keeps rising. For instance, from 1980 to 2010, Asia's demand for oil has increased by 146% while North America's demand has increased only by 16%.<sup>26</sup> With that being said, the demand in petroleum will continue to rise as human advance further into the age of modern technology.



**Figure 3: World Petroleum Consumption by Region, 1980-2010.**<sup>26</sup>

Nevertheless, the fact remains that our energy source is limited. As the petroleum based fuel is depleting and the energy demand keeps increasing, developing an alternative fuel becomes a very promising solution to our problem. The goal is to synthesize a fuel that rivals diesel in term of the chemical and physical properties. In order to achieve this, an understanding of conventional diesel fuel is necessary. First of all, diesel fuel is a product made from distillation of crude oil. Even though the chemical composition for each type is different depending on the sources, all petroleum crude oils are composed mainly of hydrocarbons. In general, there are four major molecular classes that make up the chemical composition of crude oils. They include saturates (alkanes and cycloparaffins), aromatics, resins, and asphaltenes.<sup>20</sup> Each class contains a very wide range of molecular weights as well as chemical and physical properties. For instance, in the saturates class, the molecular weight can range from C<sub>1</sub> to C<sub>60</sub> (methane to n-hexacontane, C<sub>60</sub>H<sub>122</sub>) while in the aromatic class, mono-, di-, and polynuclear aromatic hydrocarbons (PAHs) with and without alkyl side chains are the main building species.<sup>20</sup> On the other hand, the latter two classes, which are resins and asphaltenes, are much more complex and very difficult to analyze. Resins are created by aggregation of many building blocks such as sulfoxides, amides, thiophenes, pyridines, quinolines, and carbazoles. Asphaltenes, however, are created by aggregation of complex species such as extended polyaromatics, naphthenic acids, sulfides, polyhydric phenols, fatty acids, and metalloporphyrins.<sup>20</sup> Therefore, it is no surprise that the main components of diesel include a complex mixture of *n*-alkanes, isoalkanes, aromatics, other hydrocarbons, and non-hydrocarbons. Below is a figure which shows the structure of asphaltenes.



**Figure 4: Structure of Asphaltenes.<sup>6</sup>**

Despite the complexity in chemical composition of crude oil, science has advanced in its search of an alternative fuel. One of the best examples is biodiesel, which is perhaps the most common alternative diesel fuel used today.<sup>23</sup> Biodiesel is derived from a variety of vegetable oils or animal fats, which contain mainly unsaturated fatty acid methyl ester (UFAME). After synthesizing, the final product will consist primarily of methyl ester, which makes up the main chemical composition of biodiesel. When blended with conventional petroleum diesel, biodiesel possesses tremendous potential as the exhaust emissions are reduced, lubricity is improved, and the cetane number is increased.<sup>25</sup> In the United States, the cetane number for diesel is normally forty-five, and

it refers to the combustion quality of diesel fuel. A low cetane number will cause problems such as ignition difficulties and slow engine starts.

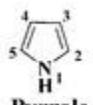
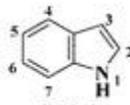
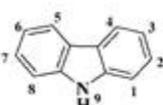
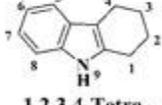
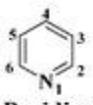
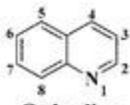
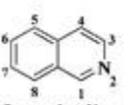
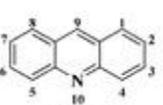
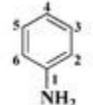
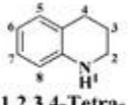
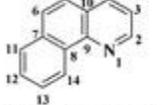
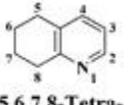
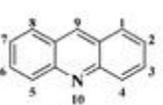
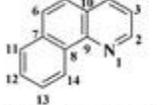
Unfortunately, there are also many cases where the mixed fuels are not compatible and result in sediment formation.<sup>15</sup> When that happens, the degradation reactions are triggered and it could ruin the entire contents of the storage tank. Therefore, biodiesel has some significant disadvantages which rely on its stability. There are three factors that affect biodiesel stability: oxidation stability, thermal stability, and storage stability.<sup>25</sup> The oxidation stability refers to the influence of oxygen on biodiesel degradation initiated by an auto-oxidation chain mechanism. Because of its nature, biodiesel is very easy to be oxidized or auto-oxidized. The thermal stability refers to the influence of temperature. For instance, at high temperature combined with air exposure, the rate of biodiesel degradation will increase. The last factor is storage stability, which refers to influence of time on biodiesel stability. Under a long period of time, which is normally about two or three years, biodiesel will likely form sediment and start the degradation process.

Therefore, whether it is biodiesel or conventional diesel fuel, when fuel stability is involved, there are typically two types of problems. The first type of problem involves short term oxidative instability.<sup>13</sup> Under both room temperature, as well as extremely cold weather, exposure to oxygen will likely cause the fuel to degrade faster. The reason is because oxygen is rather reactive and will interact with nitrogen containing compounds in fuel to initiate the degradation process. The second type of problem involves long term storage instability.<sup>13</sup> In this case, over a certain period of time, solid formation is

likely to occur, which will cause the entire tank of fuel to become unusable. Improving fuel stability is one of the biggest obstacles scientists have to overcome. With biodiesel, the factor that causes biodiesel instability is oxygen. In contrast, with conventional diesel fuel, the species that cause diesel degradation during transportation and long-term storage are the organosulfur and organonitrogen components. It is well known that the composition of nitrogen and sulfur in fuel control the rate of degradation in most crude oil reservoirs.<sup>16</sup> In addition, the presence of nitrogen compounds could also reduce the thermal stability of fuels and increase the emission of nitrogen oxides during combustion.<sup>31</sup> In other words, many undesirable effects of diesel oils, such as poisoning the catalysts, having poor storage stability, causing air pollution, and possessing mutagenic and carcinogenic activity are due to nitrogen containing compounds.<sup>4</sup> Therefore, one of the best ways to improve the quality of diesel is to remove nitrogen and sulfur compounds during the refining process. Consequently, a lot of research has been done during the past decade with one express goal being to determine the best method for denitrogenation. Currently, there are quite a few methods that have been studied including solvent extraction,<sup>3</sup> acid neutralization, hydrodenitrogenation,<sup>9</sup> liquid-phase adsorption using metal-organic material,<sup>1</sup> biodenitrogenation,<sup>5</sup> and complexation. Among them, hydrodenitrogenation is recognized as the most effective method as well as the most expensive one. No matter which method is used, in order to achieve the task of denitrogenation, an understanding of the identification, the quantification, and the distribution of various nitrogen compounds in diesel is essential. This knowledge will help to develop any novel process or efficient catalysts needed.

While the molecular nature of sulfur containing hydrocarbon compounds in petroleum is relatively well-known, the same is not true for nitrogen containing compounds. Due to their low concentrations, high boiling points, and increased molecular complexity, it is difficult to characterize the nitrogen content in crude oil.<sup>19</sup> In general, the main nitrogen compounds in petroleum are divided into two major groups: the nonbasic nitrogen group, which includes pyrrole, indole, carbazole, and their alkylated derivatives, and the basic nitrogen group, which includes amines, aniline, pyridine, quinoline, benzoquinoline, and their alkylated derivative.<sup>31</sup> Below is Table 1 which shows the general structures of these two groups.

**Table 1: Typical Basic and Neutral Nitrogen Compounds Present in Liquid Hydrocarbon Streams.<sup>31</sup>**

Nitrogen compound	One ring	Two rings	Three rings	
Neutral	 Pyrrole	 Indole	 Carbazole	 1,2,3,4-Tetrahydrocarbazole
	 Pyridine	 Quinoline	 Isoquinoline	 Acridine
	Basic	 Aniline	 1,2,3,4-Tetrahydroquinoline	 7,8-Benzoquinoline
		 5,6,7,8-Tetrahydroquinoline	 Acridine	 7,8-Benzoquinoline

Most of the nitrogen compounds are heteroatomic with multiple aromatic rings. The nonbasic groups, such as indole and pyrrole, contain mainly five-membered rings while the basic groups, such as aniline and acridine, contain mainly six-membered rings. These nitrogen compounds have a wide range of boiling points as well as different chemical properties. The basic groups tend to be less reactive than the nonbasic ones since most of the sediment formations, which would accelerate the fuel degradation, are caused by nonbasic nitrogen compounds. Therefore, it is extremely difficult to completely remove them during the refining. Since nitrogen compounds in diesel fuel is the problem we try to solve during refining, the identification and quantification of the exact substances that can affect catalysts have been focal points for research for quite some time. In this paper, the basic and nonbasic nitrogen containing compounds were isolated from Alaskan North Slope diesel, and characterized by GC/MS. The quality of the fuel, with respect to its stability, was then evaluated.

## EXPERIMENTAL

### **Extraction Procedure:**

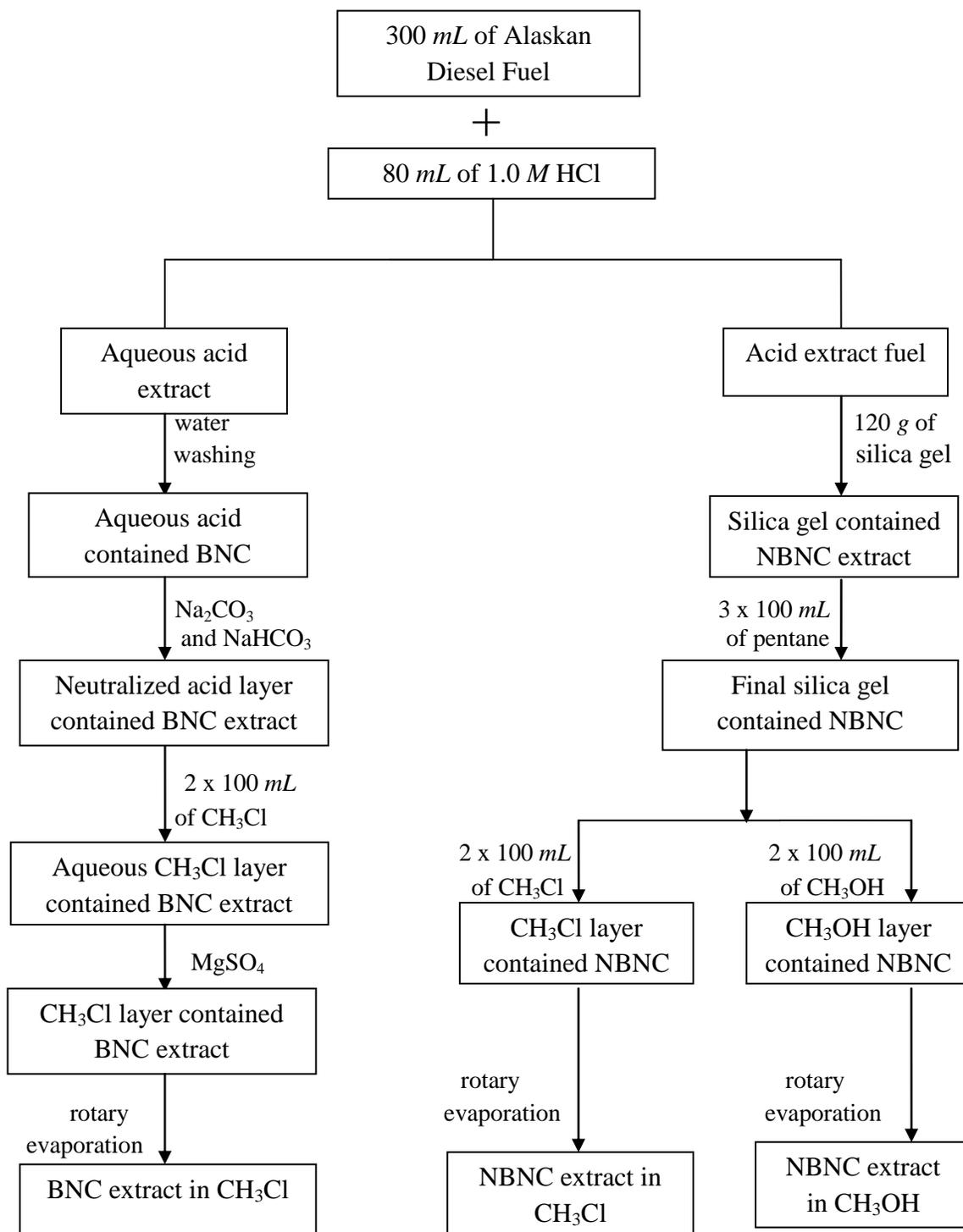
Unless otherwise stated, chemicals were obtained from the Aldrich-Sigma chemical company (Milwaukee, WI) and used without additional purification. The separation of nitrogen rich extracts from the Alaskan North Slope diesel involved several steps as depicted in Figure 5. The three extracts, which are basic nitrogen compounds in methylene chloride, nonbasic nitrogen compounds in methylene chloride, and the nonbasic nitrogen compounds in methanol, were examined by GC/MS to identify and quantitate the organonitrogen suite of compounds present.

The first step is called acid extraction, which gives the basic nitrogen extract in methylene chloride. In this step, 300 *mL* of Alaskan oil was placed in a 1 *L* separatory funnel. Next, it was treated by adding an excess (80 *mL*) of 1.0 *M* HCl. This mixture was vigorously swirled for five minutes using a magnetic bar. After a thorough mixing, it was allowed to stand for another five minutes, and then swirled gently again for an addition five minutes. Finally, after five minutes when the mixture settled down, the layers were separated. The top layer, which was the combined aqueous acid layer containing the “basic” nitrogen compounds, was extracted and treated with repeated water washing in order to remove traces of acid from the fuel. After the water washing step, this BNC extract was neutralized to pH 8-10 using Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>. The

organic layer was then extracted twice with methylene chloride (2 x 100 *mL*) and dried using anhydrous MgSO<sub>4</sub>. Finally, its solvent was gently removed by rotary evaporation to produce the final BNC extract.

Next, the nonbasic nitrogen compounds (NBNC extracts in methylene chloride and methanol) were extracted by using silica gel adsorption. First, the 300 *mL* of acid extracted fuel was placed into a 1 *L* beaker which contained 120 *g* of fully activated grade 9233 silica gel (100-200 mesh, W.R. Grace). Then, this mixture was stirred for 1.5 hour using the magnetic bar. After the silica gel adsorbed all of the remaining polar material in the fuel, it was separated from the fuel by vacuum filtration. The silica gel was then washed with three 100 *mL* aliquots of pentane to desorb all of the excess fuel. Finally, the first NBNC extract was made by washing the silica gel with methylene chloride (2 x 100 *mL*) to remove the slightly polar NBNC's. Then, these extracts were combined and retained through filtration. This step produced the NBNC extracts in methylene chloride. In order to make the NBNC extracts in methanol, the same procedures were applied. After washing the silica gel with methanol (2 x 100 *mL*) to remove the polar NBNC, the extracts were collected and retained through filtration. The solvents for both NBNC extracts were then removed by gentle rotary evaporation.

### SCHEME OF EXTRACTION



**Figure 5: Nitrogen Compound Extraction Scheme.**

### **Instrumental Methods:**

The organonitrogen compounds in all three extracts were quantified and analyzed by combined capillary GC/MS. This system consisted of two parts: a Hewlett-Packard 5890 gas chromatograph configured for splitless injection ( $1\mu\text{L}$ ), and a Finnegan INCOS 50B mass spectrometer operating in electron ionization mode. The GC part was equipped with a  $30\text{ m}\times 0.25\text{ mm}$  DB-5 fused-silica capillary column (95% dimethyl, 5% diphenyl siloxane) (J&W Scientific, Folsom, CA). The GC temperature program was as follows: an initial temperature of  $60^\circ\text{C}$  with a three minutes hold, a ramp of  $8^\circ\text{C}/\text{min}$  to a final temperature of  $260^\circ\text{C}$ , with a hold of 3 minutes. The injection port on the GC was set up at  $250^\circ\text{C}$  with helium as the carrier gas. The detector temperature and source temperatures were  $320^\circ\text{C}$  and  $200^\circ\text{C}$ , respectively. The Finnegan INCOS 50B mass spectrometer was operated in the electron impact ionization mode ( $70\text{ eV}$ ) with continuous scan acquisition from 50 to  $350\text{ amu}$  at a cycling rate of approximately 1 scan/s.<sup>13</sup> Based on the GC/MS setup, an excellent analysis of the organonitrogen compounds (Figure 6, 7, and 8) was provided.



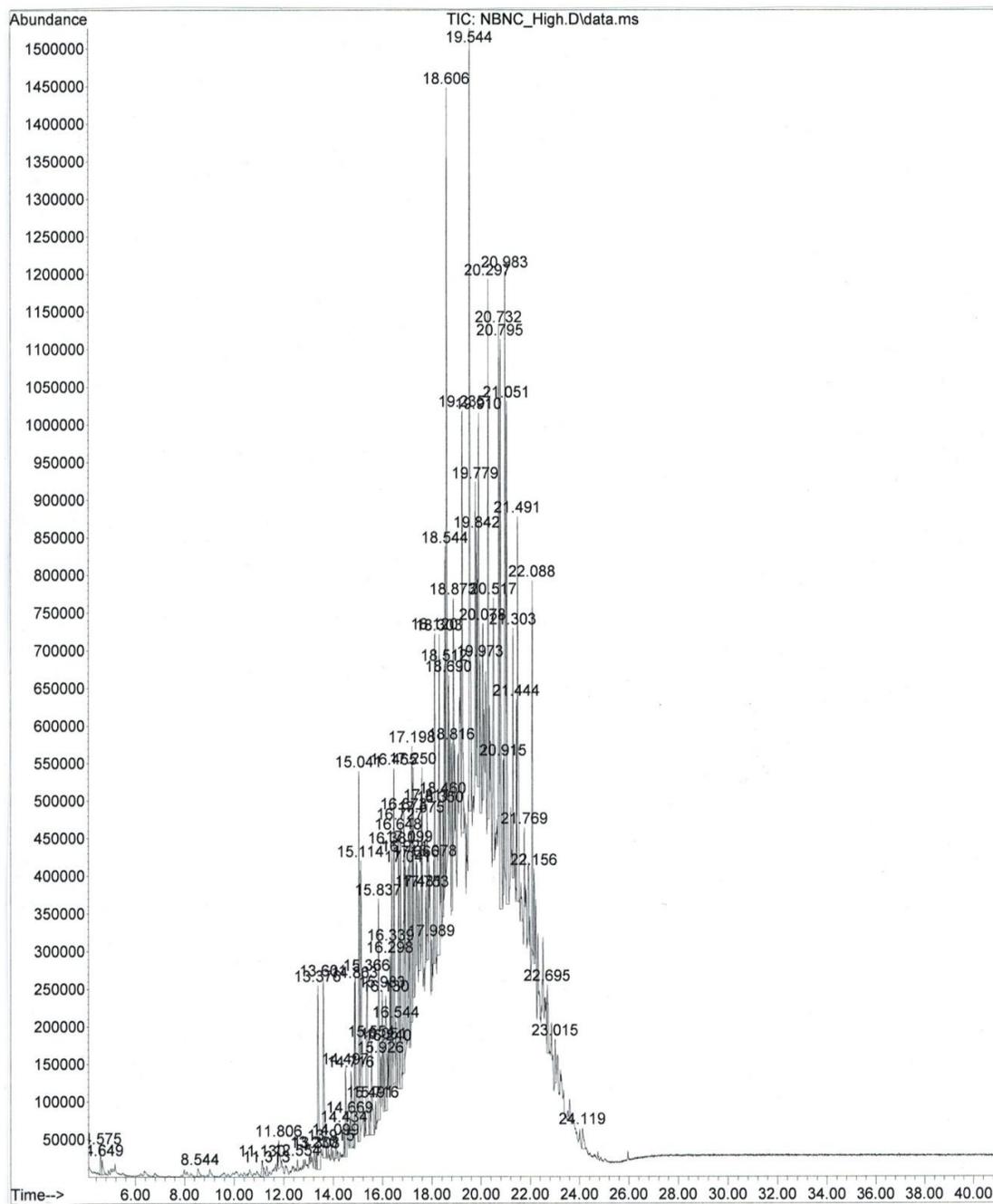


Figure 7: MS of NBNC in Methylene Chloride.



## RESULTS AND DISCUSSION

Diesel fuel is a liquid product obtained by distillation of crude oil over the range of 150–400°C (300–750 °F).<sup>13</sup> The chain length usually varies from C<sub>13</sub> to C<sub>21</sub>.<sup>13</sup> In this paper, the nitrogen heterocyclic compounds in Alaskan North Slope diesel were characterized by GC/MS. However, since GC/MS has low volatility, the instrument is not capable of analyzing any nitrogen samples with a molecular mass of over 300 Da.<sup>11</sup> Therefore, all of the nitrogen compounds, whose molecular weights are greater than 300 Da, were not identified in this study. As depicted in Figures 6, 7, and 8, the nitrogen heteroaromatic compounds present in the BNC, NBNC in methylene chloride (NBNC/CH<sub>2</sub>Cl<sub>2</sub>), and NBNC in methanol (NBNC/CH<sub>3</sub>OH) extracts were analyzed. They included alkylated pyridines, pyrroles, quinolines, tetrahydroquinolines, indoles, and carbazoles, which commonly occur in heavy fuels. The concentration of these nitrogen species determined the fuel stability. For instance, carbazoles, indoles, and pyrroles play a key role in accelerating the process of fuel degradation compared to pyridines and other classes of polar nitrogen species. Therefore, they are considered to be much more deleterious.

The chromatograms of all three extracts indicated a good separation of the nitrogen compounds. Each chromatogram contained hundreds of peaks which represented all nitrogen containing compounds in the Alaskan North Slope diesel. Each

peak represents two or more nitrogen compounds, whose percentages were estimated by using fragmentation patterns and ion counting techniques. Basically, the relative amount of each nitrogen compound in each peak was calculated by approximating the magnitude of the total ion count (area of the peak) for a given fragmentation pattern. Finally, by integrating the total ion count over the entire peak, the peak areas were determined.<sup>8</sup>

**Table 2: BNC of Alaskan Diesel in Methylene Chloride.**

<b>Compound Class</b>	<b>BNC/ CH<sub>2</sub>Cl<sub>2</sub></b>	
<b>Nitrogen compounds</b>	<b>n</b>	<b>Area %</b>
a. Pyrroles	19	7.50
C <sub>7</sub>	2	0.58
C <sub>8</sub>	4	0.61
C <sub>9</sub>	5	1.20
C <sub>10</sub>	6	4.92
C <sub>11</sub>	2	0.19
b. Pyridines	114	22.37
C <sub>1</sub>	1	0.01
C <sub>2</sub>	9	0.36
C <sub>3</sub>	30	6.56
C <sub>4</sub>	33	4.08
C <sub>5</sub>	25	7.70
C <sub>6</sub>	14	2.65
C <sub>7</sub>	1	0.87
C <sub>8</sub>	1	0.16
c. Pyrazines	2	0.14
C <sub>3</sub>	1	0.07
C <sub>4</sub>	1	0.08
d. Carbazoles	29	5.55

C <sub>2</sub>	10	1.05
C <sub>3</sub>	11	2.96
C <sub>4</sub>	7	1.32
C <sub>5</sub>	1	0.22
e. Indoles	48	7.74
C <sub>0</sub>	3	0.21
C <sub>1</sub>	2	0.14
C <sub>2</sub>	8	0.74
C <sub>3</sub>	12	1.13
C <sub>4</sub>	14	3.70
C <sub>5</sub>	8	1.77
C <sub>6</sub>	1	0.05
f. Quinolines	187	68.20
C <sub>0</sub>	3	1.18
C <sub>1</sub>	8	1.09
C <sub>2</sub>	28	4.38
C <sub>3</sub>	43	13.00
C <sub>4</sub>	44	18.71
C <sub>5</sub>	33	17.40
C <sub>6</sub>	21	10.52
C <sub>7</sub>	7	1.91
g. THQ	62	5.64
C <sub>0</sub>	8	0.46
C <sub>1</sub>	18	2.79
C <sub>2</sub>	17	1.49
C <sub>3</sub>	14	0.74
C <sub>4</sub>	4	0.13
C <sub>5</sub>	1	0.03
h. Indenes	2	0.11
C <sub>4</sub>	1	0.07
C <sub>5</sub>	1	0.04
i. Naphthal	3	1.53

C <sub>3</sub>	1	0.51
C <sub>4</sub>	1	0.51
C <sub>5</sub>	1	0.51
j. Alkenes	5	0.52
C <sub>16</sub>	2	0.24
C <sub>17</sub>	2	0.24
C <sub>18</sub>	1	0.04

Note- in the preceding table, C<sub>x</sub> denotes the number of carbon atoms in substituents on the heterocyclic ring, “*n*” is the number of isomers observed. “Area %” is based on the total ion count from mass of 45 through 450.

In the BNC/CH<sub>3</sub>Cl extract, Table 2, there were seven major classes of nitrogen compounds detected. The mole percentage of those compounds were as follows: 19 pyrrole isomers totaling 7.5% of the total nitrogen in this fraction; 114 pyridine isomers totaling 22.37%; 2 pyrazine isomers totaling 0.14%; 29 carbazole isomers totaling 5.55%; 48 indole isomers totaling 7.74%; 187 quinoline isomers totaling 68.20%; 62 tetrahydroquinoline isomers totaling 5.64%.

**Table 3: NBNC of Alaskan Diesel in Methylene Chloride.**

<b>Compound Class</b>	<b>NBNC/ CH<sub>2</sub>Cl<sub>2</sub></b>	
<b>Nitrogen compounds</b>	<b>n</b>	<b>Area %</b>
a. Pyrroles	75	37.25
C <sub>5</sub>	1	0.26
C <sub>6</sub>	9	1.76
C <sub>7</sub>	19	9.11
C <sub>8</sub>	19	12.95
C <sub>9</sub>	18	11.06
C <sub>10</sub>	9	2.12
b. Pyridines	20	4.64
C <sub>1</sub>	1	0.14
C <sub>2</sub>	2	0.08
C <sub>3</sub>	2	0.03
C <sub>4</sub>	2	0.04
C <sub>5</sub>	2	0.05
C <sub>6</sub>	5	0.99
C <sub>7</sub>	2	0.21
C <sub>8</sub>	3	2.76
C <sub>9</sub>	1	0.35
c. Pyrimidines	2	0.90
C <sub>5</sub>	1	0.32
C <sub>7</sub>	1	0.59
d. Carbazoles	98	15.80
C <sub>0</sub>	27	5.41
C <sub>1</sub>	23	4.40
C <sub>2</sub>	28	3.47
C <sub>3</sub>	15	2.05
C <sub>4</sub>	4	0.40
C <sub>5</sub>	1	0.08
e. Indoles	25	1.29

C <sub>0</sub>	12	0.96
C <sub>1</sub>	4	0.09
C <sub>2</sub>	3	0.09
C <sub>3</sub>	3	0.10
C <sub>4</sub>	3	0.06
f. Quinolines	133	41.33
C <sub>0</sub>	26	2.54
C <sub>1</sub>	28	7.38
C <sub>2</sub>	30	11.88
C <sub>3</sub>	24	9.11
C <sub>4</sub>	12	5.16
C <sub>5</sub>	10	4.64
C <sub>6</sub>	3	0.61
g. THQ	22	0.49
C <sub>0</sub>	7	0.20
C <sub>1</sub>	7	0.19
C <sub>2</sub>	7	0.10
C <sub>3</sub>	1	0.01
h. Acridines	10	4.29
C <sub>1</sub>	5	1.44
C <sub>2</sub>	5	2.85
i. Naphthal	3	0.66
C <sub>0</sub>	1	0.07
C <sub>1</sub>	1	0.07
C <sub>2</sub>	1	0.52
j. Acenaps	2	0.09
C <sub>0</sub>	1	0.03
C <sub>1</sub>	1	0.06

Note- in the preceding table, C<sub>x</sub> denotes the number of carbon atoms in substituents on the heterocyclic ring, “n” is the number of isomers observed. “Area %” is based on the total ion count from mass of 45 through 450.

In the NBNC/CH<sub>3</sub>Cl extract, Table 3, there were seven major classes of nitrogen compounds detected. The mole percentage of those compounds were as follows: 75 pyrrole isomers totaling 37.25% of the total nitrogen in this fraction; 20 pyridine isomers totaling 4.64%; 2 pyrazine isomers totaling 0.90%; 98 carbazole isomers totaling 15.80%; 25 indole isomers totaling 1.29%; 133 quinoline isomers totaling 41.33%; 22 tetrahydroquinoline isomers totaling 0.489%.

In the NBNC/CH<sub>3</sub>OH extract, Table 4 below, there were only five compound classes of nitrogen heterocyclic detected: alkylated pyrroles, carbazoles, indoles, quinolines, and tetrahydro quinolines. The mole percentage of those compounds were as follows: 188 pyrrole isomers totaling 29.68% of the total nitrogen in this fraction; 15 carbazole isomers totaling 8.23%; 9 indole isomers totaling 0.38%; 193 quinoline isomers totaling 65.71%; and 46 tetrahydroquinoline isomers totaling 5.45%.

**Table 4: NBNC of Alaskan Diesel in Methanol.**

<b>Compound Class</b>	<b>NBNC/ CH<sub>3</sub>OH</b>	
<b>Nitrogen compounds</b>	<b>n</b>	<b>Area %</b>
a. Pyrroles	188	29.68
C <sub>4</sub>	1	0.09
C <sub>6</sub>	12	1.29
C <sub>7</sub>	41	4.25
C <sub>8</sub>	35	5.07
C <sub>9</sub>	38	6.16
C <sub>10</sub>	42	9.72
C <sub>11</sub>	11	2.23

C <sub>12</sub>	8	0.87
<b>b. Carbazoles</b>	15	8.24
C <sub>0</sub>	1	2.46
C <sub>1</sub>	1	2.46
C <sub>2</sub>	6	0.53
C <sub>3</sub>	7	2.78
<b>c. Indoles</b>	9	0.38
C <sub>1</sub>	1	0.03
C <sub>2</sub>	1	0.05
C <sub>3</sub>	1	0.04
C <sub>4</sub>	1	0.05
C <sub>5</sub>	3	0.12
C <sub>6</sub>	2	0.09
<b>d. Quinolines</b>	193	65.71
C <sub>0</sub>	26	10.74
C <sub>1</sub>	42	14.68
C <sub>2</sub>	41	15.83
C <sub>3</sub>	37	12.78
C <sub>4</sub>	30	9.37
C <sub>5</sub>	12	1.55
C <sub>6</sub>	5	0.77
<b>e. THQ</b>	46	5.45
C <sub>0</sub>	16	2.37
C <sub>1</sub>	10	0.84
C <sub>2</sub>	10	1.46
C <sub>3</sub>	6	0.58
C <sub>4</sub>	4	0.20

Note- in the preceding table, C<sub>x</sub> denotes the number of carbon atoms in substituents on the heterocyclic ring, “n” is the number of isomers observed. “Area %” is based on the total ion count from mass of 45 through 450.

**Table 5: Summary of Area Percentage of BNC and NBNC Extracts.**

<b>Compound Class</b>	<b>BNC/ CH<sub>3</sub>Cl</b>	<b>NBNC/ CH<sub>3</sub>Cl</b>	<b>NBNC/ CH<sub>3</sub>OH</b>
Pyroles	7.50	37.25	29.60
Pyridines	22.37	4.64	
Pyrazines	0.14	0.90	
Carbazole	5.55	15.80	8.23
Indole	7.74	1.28	0.38
Quinolines	68.20	41.30	65.70
Tetrahydro-quinolines	5.64	0.49	5.45
Indenes	0.11		
Acridines		4.29	
Napthal	1.53	0.65	
Acenaps		0.08	
Alkenes	0.52		

## **Pyridines**

Pyridine compounds are quite stable under high temperature.<sup>12</sup> In addition, since they belong to the basic nitrogen groups, including pyridines, quinolines, and acridines, they are mainly weak bases.<sup>17</sup> In theory, this characteristic should provide them the ability to interact with other reactants or catalysts to induce instability reactions. Therefore, pyridine derivatives are good candidates that could cause diesel degradation. However, many literature reports have shown that most pyridine compounds, regardless of chain length, are rather inactive in sediment formation processes.<sup>12</sup> Therefore, their presence hardly has any effect on fuel stability. In this case, Alaskan North Slope diesel was found to contain a relatively large concentration of pyridine nitrogen compounds. In fact, according to Table 2, 114 pyridine isomers accounting for 22.37% of the total

nitrogen were found in the BNC extract. The number of carbons in the alkyl side chain ranged from C<sub>1</sub> to C<sub>8</sub>, with most in the C<sub>3</sub> to C<sub>6</sub> range. In contrast, in the NBNC/CH<sub>3</sub>Cl extract, Table 3, there were only 20 pyridine isomers totaling 4.64% of the total nitrogen presented in this extract. However, in terms of chain length, most of the pyridine compounds in this NBNC/CH<sub>3</sub>Cl extract were longer than the ones in the BNC extract. The carbon number of the alkyl side chains ranged from C<sub>1</sub> to C<sub>9</sub>, with most in the C<sub>6</sub> to C<sub>8</sub> range. There were no pyridine compounds present in the NBNC/CH<sub>3</sub>OH extract. This result was expected because methanol, which has a boiling point of 148.5°F, is much harder to evaporate compared to methylene chloride, which has a boiling point of 103.3°F. The difference in boiling point between these solvents results in a large percentage of nitrogen compounds unidentified in this particular extract.

Even though pyridine derivatives do not appear to decrease the quality of diesel fuel, they do have the ability to initiate oxidation as well as polymerization reactions due to the length of the alkyl side chain. Pyridine compounds with long alkyl side chains can undergo free radical reactions or be oxidized to the corresponding pyridine N-oxide.<sup>12</sup> However, in this Alaskan North Slope diesel, the alkyl substituted pyridine compounds contained side chains with short length (< C<sub>6</sub> range). As a result, their molecular weights as well as their boiling points were lower, thus they became very chemically stable. Consequently, this would make the oxidation reactions less likely to happen.

## Quinolines

Tables 2, 3 and 4 indicated that alkylated quinolines were the dominant class of nitrogen compounds in Alaskan North Slope diesel. In the BNC fraction, Table 2, 187 quinoline isomers representing 68.2% of the total nitrogen were found. The number of carbons in the alkyl side chains ranged from C<sub>1</sub> to C<sub>7</sub>, with most in the C<sub>3</sub> to C<sub>5</sub> range. Similarly, the NBNC/CH<sub>3</sub>Cl extract, Table 3, contained about 133 quinoline isomers accounting for 41.3% of the total nitrogen present. The last fraction, which is the NBNC/CH<sub>3</sub>OH extract, was found to contain approximately 193 quinoline isomers totaling 65.7% of the total nitrogen compound present.

Since alkylated quinolines and pyridines are both basic nitrogen compounds, their chemical reactivity is considered to be similar to each other. Due to their basic nature, they are both described as the strongest inhibitors of the catalysts during the hydrodenitrogenation process.<sup>30</sup> Substituted pyridines do not prohibit the catalysts or accelerate the sediment formation reactions. Compared to pyridine compounds, alkylated quinolines are not quite that harmless. It has been shown that quinoline compounds are poisonous to the catalysts, and are very difficult to remove. In the presence of substituted quinolines, the catalytic activity will decrease about 10%.<sup>29</sup> During the hydrotreating process, alkylated quinolines were converted into dihydroquinolines, and 1,2,3,4-tetrahydroquinoline (THQ). As the temperature increased, 1,2,3,4 THQ was hydrogenated to decahydroquinoline. The conversion rate of quinoline to tetrahydroquinolines was proportional to the severity of the hydrotreatment. The more hydrotreated the fuel is, the larger concentration of THQ present. In all three extracts, the

concentration of THQ was: 5.64% in BNC fraction, 0.49% in NBNC/ CH<sub>3</sub>Cl fraction, and 5.45% in NBNC/CH<sub>3</sub>OH fraction. Compared to the large percentage of alkylated quinoline, the small concentration of THQ indicated that this Alaskan North Slope diesel was not hydrotreated very well. This result implied that the diesel was likely an unstable fuel.

### **Pyrroles**

According to Tables 2, 3, and 4, alkylated pyrrole was found to be present at a relatively large concentration in this Alaskan North Slope diesel. In the BNC extract, refer to Table 2, 19 pyrrole isomers accounting for 7.5% of the total nitrogen present were found. The chain lengths for this sample were relatively long from C<sub>7</sub> to C<sub>11</sub> with most in the C<sub>8</sub> to C<sub>10</sub> range. Similarly, the NBNC/CH<sub>3</sub>Cl extract, Table 3, was found to contain a total of 75 pyrrole isomers comprising 37.25% of the total nitrogen present. The number of carbons in the alkyl side chains ranged from C<sub>5</sub> to C<sub>10</sub> with most in the C<sub>7</sub> to C<sub>9</sub> range. The last fraction, which is the NBNC/CH<sub>3</sub>OH extract, contained about 188 pyrrole isomers totaling 29.68% of the total nitrogen compound present. Their chain lengths varied widely from C<sub>4</sub> to C<sub>12</sub>, with most in the C<sub>7</sub> to C<sub>10</sub> range. The major difference between these extracts was that the alkyl side chains in the NBNC extracts were considerably longer than those in the BNC extract.

By far, among nitrogen heteroaromatic compounds, pyrrole derivatives are the most active compounds that increase the sludge formation rate.<sup>7</sup> The differences lie in its molecular structure. While pyridines and quinolines are basic in nature, pyrrole is neutral and readily polymerized via their unsaturated bonds. This will produce oligomer

products that are highly viscous, dark in color, and insoluble in dichloromethane.<sup>21</sup> In the early literature, it is called “pyrrole black”.<sup>12</sup> Based on this information, the amount of pyrrole present in fuel can be qualitatively estimated by simple observation.

In this experiment, during the evaporation process, the color of all three extracts changed from yellow to dark rapidly. The change in color proved that the Alaskan North Slope diesel contained a large amount of pyrrole compounds. The mechanism for the color change is explained as follows: when the pyrrole oligomer is heated, it will be converted back to pyrrole, indole, and ammonia. In addition, multi-substituted pyrroles with short chain lengths also undergo rapid oxidation to form peroxides in the presence of oxygen. These unstable peroxides then function as radical sources to initiate other oxidation reactions to take place. The chain of reactions rapidly turns the color of fuel from brown to near black. Besides the negative effect on color, pyrrole compounds also play a key role to initiate sediment formation reactions. In fact, thanks to their basic nature, alkylated pyrroles react readily with aldehydes and ketones by a 1,4-addition reaction to form insoluble oligomer product.<sup>12</sup> Subsequently, under long term storage, the concentration of these compounds can be greatly increased. Therefore, it is not wrong to consider substituted pyrroles as one of the most deleterious nitrogen heteroatoms that need to be removed during the denitrogenation process. It was found that the denitrogenation reactivities were as follows: for basic compounds, the ranking order is pyridine > aniline > acridine > quinoline,<sup>21</sup> and for nonbasic compounds, pyrrole > indole > carbazole is the order.<sup>22</sup>

## Indoles and carbazoles

Since the chemical reactivity and structure of indoles and carbazoles are relatively similar, they can be examined together. For the substituted indoles, the BNC extract (Table 2) contained approximately 48 indole isomers comprising 7.74% of the total nitrogen present. The chain lengths for this sample were relatively short from, C<sub>1</sub> to C<sub>6</sub>, with most in the C<sub>3</sub> to C<sub>5</sub> range. On the other hand, the NBNC/CH<sub>3</sub>Cl extract (Table 3) was found to contain a total of 25 indole isomers accounting for 1.28% of the total nitrogen present. The number of carbons in the alkyl side chains ranged from C<sub>1</sub> to C<sub>4</sub>, with most in the C<sub>1</sub> to C<sub>2</sub> range. The last fraction, which is the NBNC/CH<sub>3</sub>OH extract, contained 9 isomers totaling 0.38% of the total nitrogen compound present. The carbon number of the alkyl side chains present varied from C<sub>1</sub> to C<sub>6</sub>, with most in the C<sub>4</sub> to C<sub>6</sub> range.

In this study, the Alaskan North Slope diesel contained a relatively small concentration of carbazole nitrogen. For the BNC extract, a total of 29 carbazole isomers comprising 5.55% of the total nitrogen presented. The alkyl side chains for this sample were relatively short (< C<sub>6</sub> range). In contrast, the NBNC/CH<sub>3</sub>Cl extract (Table 3) was found to contain a total of 98 isomers accounting for 15.8% of the total nitrogen present. The carbon number of the alkyl side chains present varied from C<sub>1</sub> to a high of C<sub>5</sub>, with most in the C<sub>1</sub> to C<sub>3</sub> range. The last fraction, which is the NBNC/CH<sub>3</sub>OH extract, contained 15 isomers totaling 8.23% of the total nitrogen compound present. The chain length is very short (< C<sub>4</sub> range). In comparison, the results indicated that carbazoles were present in greater concentration than indoles in all three extracts.

At the molecular structure level, carbazoles and indoles are considered to be closely similar. In fact, they are both nonbasic nitrogen compounds containing a pyrrole ring fused together with a benzene ring in the 2,3-position.<sup>24</sup> Consequently, the similarities in structure lead to the similarities in chemical reactivity. Both carbazoles and indoles share some interesting characteristics. For instance, they are both basic with the ability to form dimers and trimers. They can also react readily with electrophilic reagents that are slightly acidic.<sup>12</sup> One of their special properties is their ability to induce autooxidative and polymerized reactions. These types of reactions usually lead to the formation of sediment, which in turn accelerates the fuel degradation process. In the case of indoles and carbazoles, upon the exposure of air, autooxidation reactions will take place with both 2,3-dialkyl and 3-alkyl substituted isomers, followed by polymerization reactions to produce hydroperoxides. However, comparing between indole and carbazole compounds, carbazoles are recognized as the ones that are more resistant to catalytic hydrodenitrogenation than indole, quinoline and the benzoquinoline.<sup>10</sup> That is why it has been known as a major constituent that causes fuel instability. In this study, Alaskan North Slope diesel was found to contain a significant amount of alkylated carbazoles. This result indicated that the fuel is unstable and is not fit for long term storage.

## CONCLUSION

The composition of nitrogen polycyclic aromatic compounds obviously plays a big role in the fuel stability since it controls the amount of sediment formed. In this study, the nitrogen composition in Alaskan North Slope diesel was isolated into three extracts, which were then analyzed by GC/MS. The first extract, the BNC, contained the most pyridines, 114 isomers accounting for 22.37%, as well as the most quinolines, 187 isomers totaling 68.2%. The second extract, NBNC/CH<sub>3</sub>Cl, contained three major functional groups: pyrroles at 37.25%, carbazoles at 15.8%, and quinolines at 41.3%. Since pyrrole and quinoline compounds are very reactive in the degradation reactions, the results indicated that, with a relatively large concentration of pyrrole and quinoline present in the fuel, the Alaskan North Slope diesel has low quality in regards to fuel stability. In addition, the NBNC/CH<sub>3</sub>OH extract consisted of 29.6% pyrroles and 65.7% quinolines, which caused the change in the fuel's color as well as its properties. Overall, the most deleterious organonitrogen containing compound appears to be alkyl substituted quinolines. Until now, scientists have not found a way to completely remove all the nitrogen containing compounds in fuel. One of the reasons is because these species are very persistent and reactive such that they deactivate the catalysts. However, with the advance of technology, there is hope for a future where economically and environmentally friendly fuel is possible.

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## BIOGRAPHY

Hien N Le grew up in Binh Duong, VIETNAM. In 2007, she moved to the United States of America and received her Bachelor of Science from George Mason University in 2012. Her fields of interest are analytical chemistry, petroleum industry with concentration on diesel and biodiesel analysis, as well as environmental science. She currently interns at Northern Virginia Soil & Water Conservation District, Fairfax.