

USING CARBON NANOTUBES IN SEPARATING MIDDLE DISTILLATE FUELS

by

Katharine A. Boni  
A Thesis  
Submitted to the  
Graduate Faculty  
of  
George Mason University  
in Partial Fulfillment of  
The Requirements for the Degree  
of  
Master of Science  
Chemistry

Committee:

\_\_\_\_\_ Dr. Paul Cooper, Thesis Director

\_\_\_\_\_ Dr. John Schreifels, Committee Member

\_\_\_\_\_ Dr. Kimi Hatton, Committee Member

\_\_\_\_\_ Dr. Gerald Weatherspoon, Department  
Chairperson

\_\_\_\_\_ Dr. Donna M. Fox, Associate Dean, Office  
of Student Affairs & Special Programs,  
College of Science

\_\_\_\_\_ Dr. Peggy Agouris, Dean, College of  
Science

Date: \_\_\_\_\_ Spring Semester 2018  
George Mason University  
Fairfax, VA

Using Carbon Nanotubes in Separating Middle Distillate Fuels

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

by

Katharine A. Boni  
Bachelor of Science  
George Mason University, May 2011

Director: Paul Cooper, Professor  
Department of Chemistry

Spring Semester 2018  
George Mason University  
Fairfax, VA

Copyright 2018 Katharine A. Boni  
All Rights Reserved

## **DEDICATION**

This is dedicated to my mother and grandmother, whom gave me support, and for my father, whose words have given me the motivation to prove him wrong.

## ACKNOWLEDGEMENTS

I would like to thank Dr. George Mushrush and Dr. Paul Cooper for guiding me throughout my undergraduate and graduate schooling. They have been a great help throughout this journey and I appreciate all the knowledge he has given me.

I would also like to thank Dr. Thomas Huff for allowing me use the shared research lab and helping me perform the GC/MS analysis. I would also like to thank Dr. Joy Bauserman for their previous research in the field which was indispensable to me.

I would again like to thank my mother and grandmother for their continued support both emotionally and financially during these times. I would like to thank Ken Grimm who over the years has become my surrogate father and pushed to achieve lofty goals. And lastly, my cat George, who acted as the best paperweight/stress reducer during the whole process.

## TABLE OF CONTENTS

|   | Page |
|---|------|
| List of Tables .....  | vi   |
| List of Figures .....   | vii  |
| List of Equations .....   | viii |
| List of Abbreviations and Symbols.....  | ix   |
| Abstract .....  | x    |
| Introduction.....   | 1    |
| Composition and Characteristics of Diesel .....                                   | 4    |
| Hydrocarbon Compounds.....  | 7    |
| Non-Hydrocarbon Compounds.....  | 9    |
| Nitrogen Compounds and Fuel Stability and Incompatibility .....                   | 11   |
| Types of Nitrogen Heteroatoms and Implications to Instability and Incompatibility | 12   |
| Experimental.....   | 18   |
| Materials.....  | 18   |
| Extraction .....  | 18   |
| Instrumental Setup.....   | 19   |
| results and discussion.....   | 20   |
| DCM Extract Analysis .....  | 21   |
| MeOH Extract Analysis .....   | 26   |
| Overall Extract Analysis and Discussion .....                                     | 30   |
| Conclusions.....  | 35   |
| Appendix.....   | 38   |
| References.....   | 41   |

## LIST OF TABLES

| Table   | Page  |
|---|-------|
| Table 1 Characteristics of Crude Oil Fractions in Arabian Light ..... | 3     |
| Table 2 Cetane Number Standards .....                                 | 5     |
| Table 3 Examination of Nitrogen Compounds in DCM Extract .....        | 21-22 |
| Table 4 Examination of Hydrocarbon Compounds in DCM Extract .....     | 23-25 |
| Table 5 Examination of Nitrogen Compounds in MeOH Extract .....       | 26-27 |
| Table 6 Examination of Hydrocarbon Compounds in MeOH Extract .....    | 27-29 |

## LIST OF FIGURES

| Figure  | Page |
|---|------|
| Figure 1 Types of Nitrogen Compounds .....  | 12   |
| Figure 2 Possible Reaction Mechanism for DMP.....   | 15   |
| Figure 3 Gas Chromatogram of DCM Extract with Baseline Smoothing .....                                | 38   |
| Figure 4 Gas Chromatogram of DCM Extract without Baseline Smoothing .....                             | 38   |
| Figure 5 Gas Chromatogram of MeOH Extract with Baseline Smoothing .....                               | 39   |
| Figure 6 Gas Chromatogram of MeOH Extract without Baseline Smoothing .....                            | 39   |
| Figure 7 Mass Spectrum from MeOH extract at 11.142 identified as 2-ethenyl-1,4-dimethyl-benzene ..... | 40   |
| Figure 8 Mass Spectrum obtained from NIST Chemistry WebBook of 2-ethenyl-1,4-dimethyl-benzene .....   | 40   |

## LIST OF EQUATIONS

| Equation                                  | Page |
|---|------|
| Cetane Number Determination Equation..... | 5    |

## LIST OF ABBREVIATIONS AND SYMBOLS

|  |        |
|--|--------|
| Carbon Nanotubes.....                      | CNTs   |
| Dichloromethane.....                       | DCM    |
| Methanol.....                              | MeOH   |
| Dimethyl-pyrrole.....                      | DMP    |
| Gas Chromatography- Mass Spectroscopy..... | GC/MS  |
| Pi.....                                    | $\pi$  |
| Iron Carbon Nanotubes.....                 | FeCNTs |

## **ABSTRACT**

### **USING CARBON NANOTUBES IN SEPARATING MIDDLE DISTILLATE FUELS**

Katharine A. Boni, M.S.

George Mason University, 2018

Thesis Director: Dr. Paul Cooper

This thesis describes a novel purification technique using carbon nanotubes (CNTs) as a filtering medium for a middle distillate fuel, Spanish fuel No. 2, for the removal of nitrogen-containing compounds. Two extracts were used, dichloromethane (DCM) and methanol (MeOH), after filtering the fuel through the CNTs, to determine the compounds that were captured. The compounds from the extracts were identified via gas chromatography-mass spectrum analysis (GC/MS). The extracts were compared for both their nitrogen content distribution and their hydrocarbon content distribution. In the DCM extract, the major nitrogen constituents were other cyclic nitrogen compounds such as piperidine and the most common type of hydrocarbon was alkanes with heptadecane and its isomers being the most prevalent type of alkane. In the MeOH extract, the most common nitrogen class was quinolines and the most common hydrocarbon class was benzenes. Overall, there was only a single pyrrole present in the study in the DCM

extract that could be identified from the chromatogram, however there may be more present in the background noise of the chromatogram without any baseline smoothing operations (see Appendix). The MeOH extract had the lowest nitrogen content with only eleven nitrogen compounds identifiable by the CNTs compared to the twenty-nine nitrogen compounds present in the MeOH extract, however more nitrogen compounds may be present if the ability to separate all the compounds present in the chromatograms.

## INTRODUCTION

Since the inception of petroleum products, they have shaped the landscape of modern living through transportation, heating oils, asphalts, and as feedstocks for various industries that produce plastics, chemicals, and other minutiae. In the 21<sup>st</sup> century, the demand for petroleum products has stayed consistent, even with recent advancements in eco-friendly alternatives such biofuels, solar power, and hybrid or electric vehicles, despite the dwindling natural sources. These alternative fuel sources have been utilized: shale oil, tar sands, and coal; however, these sources for gasification into liquid fuel products has unique issues themselves when compared to natural sources. For example, coal that undergoes gasification will contain more oxygen- and nitrogen-containing compounds, which are implicated in environmental pollutants and sediment formation, when compared to crude oil-based liquid fuels.<sup>31, 39</sup>

With all petroleum products, stability and compatibility between fuels and their feedstocks is of high priority. Stability is necessary for long-term storage applications or in the case of thermal stability, the ability to withstand high temperatures for short periods of time, whereas compatibility is necessary for the blending of feedstocks to form fuel blends. When petroleum products have instability or incompatibility, the formation of insoluble materials, gums, sludge, and sediment, will occur thus causing fuel

degradation<sup>31</sup>. Fuel degradation in refined fuels is based upon sediment and gum formation which is measured in terms of milligrams of solids per 100 mL of fuel.<sup>3,31</sup>

Instability, which is defined as the formation of sediments, sludges, and gums over a period time, and/or color changes, is of high priority if large volumes of fuels are purchased and stored for long periods of time. This issue is not just confined to the finished petroleum product, but could also be observed in crude oil throughout its process of refining. With regards to crude oil sediment, it can provide details into the method of the formation of sediment products. In liquid fuel products, the sludge can range from being solid to a gel-like consistency. The sludge can be further broken down into various categories: filterability, peroxide levels, and color body changes in the fuel itself.<sup>31,40</sup>

Incompatibility, defined as the sediment/precipitate formation or a phase separation when two liquid fuels are mixed, is an important determinate when blending fuel feedstocks together. Incompatibility can be a complex issue, with utmost care needed in determining what additives and feedstocks to use, since the presence of polar moieties such sulfur, nitrogen, and oxygen can cause sediment or gum formation after blending. For example, a feedstock that is moderate in oxygen moieties will have some antioxidant properties which when added to a feedstock with antioxidant additives can cause sediment formation by interactions between the oxygen moieties and the antioxidant additives.<sup>31,40</sup>

The distillate fraction, or petroleum fraction, corresponds to the groups that crude oil is separated into: natural gas, gasoline, diesel, kerosene, vacuum gas oils, and vacuum residue. Each group has unique characteristics that include boiling point temperature

range, carbon number, density, and different amounts of heteroatoms (sulfur, oxygen, and nitrogen) that enables it to be separated into the different fraction types through atmospheric and vacuum distillation. The actual proportions of the fractions and heteroatoms are wholly dependent on the geographic origin of the crude oil; an example being that crude oils from the North Sea tend to have higher portions of the lighter fractions when compared to other regions. <sup>26, 29, 43</sup>

**Table 1: Characteristics of Crude Oil Fractions in Arabian light <sup>43</sup>**

| <b>Fraction</b> | <b>Temperature Range, °C</b> | <b>Carbon Number Range</b>        | <b>Percentage in Crude Oil</b> |
|-----------------|------------------------------|-----------------------------------|--------------------------------|
| Natural Gas     | < 0                          | C <sub>1</sub> – C <sub>4</sub>   | 1.37                           |
| Gasoline        | 0 – 180                      | C <sub>4</sub> – C <sub>10</sub>  | 17.72                          |
| Kerosene        | 180 – 230                    | C <sub>10</sub> – C <sub>14</sub> | 6.74                           |
| Diesel          | 230 – 375                    | C <sub>14</sub> – C <sub>25</sub> | 24.37                          |
| Vacuum Gas Oil  | 375 – 600                    | C <sub>25</sub> - C <sub>55</sub> | 23.50                          |
| Vacuum Residue  | ≥ 600                        | > C <sub>55</sub>                 | 26.30                          |

Diesel, a middle distillate fuel, is considered to be one of the three most important fuels, which also include gasoline and jet fuel, because of their widespread usage throughout the world. This is in part to the diesel engine being more thermally efficient

when compared to gasoline engines, which could increase its demand in the future not only in the United States but throughout the world. In the United States, it accounts for twenty-one percent of all transport fuels and energy in 2015, with 3.995 million barrels a day consumed.<sup>42, 43</sup>

The demand for diesel is also turning attention to its production and its impact on the environment, that calls for tightening regulations and lower emission standards. The U.S. Clean Air Act Amendments of 1990 and the 2004 U.S. Environmental Protection Agency's new regulations target lowering the amount of aromatics and sulfur components in diesel, as well as new emission standards that include the reduction of particulates and nitrogen oxides in diesel exhaust.<sup>39</sup>

### **Composition and Characteristics of Diesel**

Diesel is a petroleum-based product in majority of the world, except in South Africa where the diesel is derived from coal and gasified into liquid fuel. There are standards in each category of fuel (gasoline, diesel, and jet), which include different distillate fraction, boiling range, sulfur weight percentage, and different quality indicators, that are standardized in the United States by American Society for Testing and Materials (ASTM).<sup>26</sup>

In diesel, the cetane number is the quality indicator; it measures the ignition quality or ignition delay of the fuel and relates to the time it takes the fuel to ignite in the compression engine. A higher cetane number corresponds to a shorter ignition delay. To measure the cetane number, three standards are currently used: cetane (n-hexadecane), 1-methylnaphthalene, and heptamethylnonane (2,2,4,4,6,8,8-heptamethylnonane), which

corresponded cetane number values of one hundred, zero, and fifteen, respectively. By definition, the cetane number is the volume amount of cetane mixed with 1-methylnaphthalene to give the same engine ignition performance of the representative diesel being tested. It should be of note that with 1-methylnaphthalene's propensity to degradation, the third standard of heptamethylnonane has taken over the role of 1-methylnaphthalene in the determination of cetane number in the following equation.

$$\text{Cetane No.} = \text{vol. \% of cetane} + 0.15(\text{vol. \% of heptamethylnonane}) \quad (\text{Eq. 1})$$

The cetane number is directly related to the auto-ignition of the fuel in the diesel engine, which is needed for spontaneous combustion without a spark or flame. The correlation between auto-ignition temperature and cetane number becomes apparent when looking at the three standards, where the higher the cetane number equals a lower auto-ignition temperature in most cases.<sup>11, 39</sup>

**Table 2: Cetane Number Standards**

| <b>Standard</b>     | <b>Cetane Number</b> | <b>Auto-Ignition Temperature, °C</b> |
|---------------------|----------------------|--------------------------------------|
| n-Hexadecane/Cetane | 100                  | 202                                  |
| 1-Methylnaphthalene | 0                    | 529                                  |
| Heptamethylnonane   | 15                   | 472                                  |

If other common hydrocarbon compounds in diesel are included into the table, another pattern emerges that is related to its structure and cetane number, where the cetane value decreases from n-alkanes to n-alkyl aromatics in this order: n-alkanes > alkenes > cycloalkanes > hydroaromatics > n-alkyl aromatics. In the order of n-alkanes, an increase in cetane number is related to an increase in chain length, which means that n-decane will have a lower cetane number when compared to n-hexadecane.<sup>39</sup>

The boiling range for refined diesel fuel is approximately between 150°C to 400°C and a government regulated sulfur weight percentage value of 0.05.<sup>31, 39</sup> There is variance in the density of diesel fuels, which is dependent on the type of refining the fuel went through, but an upper limit of the density was set forth to avoid smoke formation. Viscosity is another property of diesel that is regulated in the industry due in part to its function of the diesel engine; at both ends of the spectrum, too viscous of fuel will lead to poor performance whereas a less viscous fuel will result in leakage or injector pump wear.<sup>39</sup>

Diesel fuels also have low temperature characteristics that can affect the performance of the fuel. In lower temperatures, the higher chained hydrocarbons (the paraffinic compounds) of the diesel fuel will crystallize and precipitate out. The wax crystals will block the fuel lines and filters, which can cause engine problems such as stalling or malfunction. There are three tests that are used to characterize its low temperature properties: cloud point, pour point, and low-temperature filterability. The cloud point is a visual based test where an observer records the temperature at which they see wax crystals precipitating in the diesel fuel; the average cloud point temperature has a

range between  $-10^{\circ}\text{C}$  to  $20^{\circ}\text{C}$ , but is dependent on the location and season due the difference in climate between various places such a temperate winter environment versus alpine winter environment. The different geolocations will call for different additives to be added to the diesel to account for the temperatures faced. The pour point is defined as the lowest temperature that a measured amount of fuel will not flow for 5 seconds when tilted horizontally; the pour point in diesel has a range of  $-15^{\circ}\text{C}$  to  $-35^{\circ}\text{C}$ . The third test for low-temperature filterability and is defined as the lowest temperature that a fixed volume of diesel will pass through a filter during a certain time interval; in the US, it is the ability of 180 mL of diesel to pass through a  $17\ \mu\text{m}$  mesh screen in under 60 seconds.

These characteristics of diesel are due to the composition of the fuel itself, which despite the variance between two diesel fuels, can be broken down into two categories hydrocarbon compounds and non-hydrocarbon compounds.

### **Hydrocarbon Compounds**

Hydrocarbon compounds are the primary constituent of crude oil and refined middle distillate fuels. In middle distillate fuels, there are several common types: alkanes, alkenes, aromatics, and cyclic (mono-, bi-, and tri-). In both crude oil and diesel fuel there are several overlapping terms where saturated hydrocarbons without a ring structure is termed paraffin hydrocarbons and saturated ring compounds are termed naphthene/cycloparaffin hydrocarbons.

Alkanes are a series of saturated hydrocarbons with the general formula of  $\text{C}_n\text{H}_{2n+2}$  and tend to be the more stable compounds in petroleum. In a crude oil, the range of alkanes goes from  $\text{C}_1$  to  $\text{C}_{40}$ , whereas in a middle distillate fuel the range is between

C<sub>10</sub> to C<sub>24</sub>. With increasing chain length, the number of structural isomers increases as well. The stability of the alkane is reliant on the structure with branched alkanes being less stable when compared to straight chain alkanes.

Alkenes, also known as olefins, are an unsaturated hydrocarbon compounds which are hardly found in crude oils, but n-hexene, n-heptene, and n-octene have been found in small quantities. However, through the refining process of steam cracking, olefins can be produced<sup>26</sup>, which are more reactive when compared to other paraffinic hydrocarbons. This feature of olefins makes it highly desirable in the polymer industry.

Naphthenes, which include cycloparaffins and alicyclic compounds, have the formula of C<sub>n</sub>H<sub>2n</sub>. The majority of the naphthenes in crude oil will contain anywhere from three- to eight-membered rings, with five- to six-member rings being the norm due to their stability.<sup>26,40</sup> In lower boiling point fractions of crude, monocyclic and bicyclic compounds are the common naphthenes, with an increasing boiling point and molecular weight when alkyl chains are added to the naphthenes. In higher boiling fractions, two to six ringed compounds can be found in addition to mono- or bicyclic compounds.<sup>40</sup>

Aromatic hydrocarbons are common through all fractions of petroleum the differences in prevalence based upon the origin of the crude oil. With increasing molecular weight within the crude oil there is a proportional increase of aromatics. In lower boiling point fractions, benzene homologues such as toluene or xylene are more common when compared to benzene. Naphthalene compounds are also common in crude oil, such as 1-methylnaphthalene and 2-methylnaphthalene, but in heavier fractions naphthalene aromatics are more common than aromatics without naphthalene rings. In

heavier fractions the aromatic rings conjugate into naphthalene and derivatives, which contain two aromatic rings, or phenanthrene and its derivatives, which contain three aromatic rings. Tetralin and derivatives are bicyclic compounds, with one ring being naphthenic and the other being aromatic; these compounds tend to be found in heavier crude oils.<sup>40</sup>

### **Non-Hydrocarbon Compounds**

In addition to hydrocarbons, other compounds are present with different atoms such as sulfur, oxygen, and nitrogen (which will be described in detail in the section), along with inorganic salts and organometallic compounds. While the fraction of those atoms is small when compared to the hydrocarbon fraction, it can still play a key role in the storage and stability of the fuel.

Sulfur in crude oil accounts for 0.05 to 6.00 wt/wt% which makes it one of the most abundant heteroatoms. The geographic location of the crude as well as the type of crude oil (light crude versus heavy crude, for example) will cause a variance in the sulfur content. Sulfur is also present in the finished refined product, with a value of 0.05 wt/wt% that is regulated in the US by EPA regulations. The presence of sulfur in a finished fuel can cause erosion of the engine and exhaust systems, increased deposition of the carbon materials in the pistons/cylinders, color body changes and, in the interest of public health, SO<sub>x</sub> and particle emissions. Organosulfur compounds present can be further broken down into acidic or non-acidic; depending on which sulfur compounds predominate in the crude oil will determine how the petroleum is further refined. Acidic organosulfur compounds require more treating during the refining process, so high sulfur

content crude oils are less desirable due to the increase in production costs for the refinery.<sup>26, 31, 39, 40</sup>

Oxygen is another heteroatom present in petroleum compounds; it often accounts for around two wt/wt% of the crude oil with some variance based upon the source and how it was processed.<sup>40</sup> There are two classifications of oxygen containing compounds in petroleum: acidic and non-acidic. The acidic oxygen compounds are hydroperoxides, carboxylic acids, and phenols, which are more common than the non-acidic oxygen compounds of esters, ethers, ketones, and amides.<sup>26, 31</sup> Non-acidic oxygen compounds are of little concern because they can offer an antioxidant effect on the refined fuel without the use of antioxidant additives.<sup>31</sup> Acidic oxygen in fuels however can be detrimental which can undergo reaction mechanisms with itself, such as the case of phenols, or with other heteroatoms to form sediment. Hydroperoxides are of great concern to fuel stability because of their instability and ability to undergo chain reactions even at low concentrations.<sup>31</sup>

Nitrogen compounds in the crude oil are rather low when compared to the sulfur and oxygen moieties present, accounting for under one wt/wt% (although in some crude oil it can contain up to two wt/wt%).<sup>26, 31, 40</sup> The next section will go into further detail about the nitrogen heteroatom's role in petroleum products.

Metal-containing compounds are found in all crude oil, with heavier crude oils having a higher chance of metallic elements, which must be reduced before refining because of their interactions with various catalysts and processes.<sup>31, 40</sup> Organometallic compounds typically fall into types: organometallic soaps or oil-soluble compounds. The

organometallic soaps have the ability to act as emulsion stabilizers and are found in the water-oil interfaces; the metals that are common to the organometallic soaps are zinc, titanium, calcium, and magnesium.<sup>40</sup> The oil-soluble group has vanadium, copper, nickel, and iron; they are able to interact with the pyrrole group from pigment compounds that were based on plant and animal sources.<sup>40</sup> The most common metallic constituents are vanadium (5.0 – 1500 ppm), nickel (3.0 – 120 ppm), calcium (1.0 – 2.5 ppm), and magnesium (1.0 – 2.5 ppm). High concentrations of metallic compounds tend to form sludge and sediment in crude oil.<sup>31</sup>

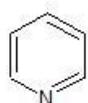
### **Nitrogen Compounds and Fuel Stability and Incompatibility**

Nitrogen compounds in the crude oil is rather low when compared to the sulfur and oxygen moieties present, accounting for under one wt/wt% (although in some crude oil it can contain up to two wt/wt%).<sup>26, 31, 40</sup> Nitrogen heteroatoms have been implicated in instability and incompatibility reaction in both crude oil and the finished product such as diesel.<sup>3, 31</sup> Nitrogen-based sediments have a definite structure consisting of partially oxidized dimers, trimers, tetramers of the parent nitrogen compound.<sup>18</sup> In previous studies at Exxon, nitrogen compounds were linked sediment and sludge formation at ambient temperatures in JP-5 jet fuel.<sup>18</sup> The storage conditions can also affect the amount of sediment produced in regards to if the fuel is stored in light or dark conditions.

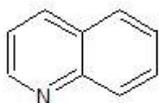
## Types of Nitrogen Heteroatoms and Implications to Instability and Incompatibility

Nitrogen compounds found in petroleum can be divided into two types: basic and non-basic. The nitrogen type can be determined by titrating the crude oil with a solution of perchloric acid in a 50:50 glacial acetic acid and benzene.<sup>40</sup> The basic nitrogen compounds mainly contain a pyridine ring whereas the non-basic contain a pyrrole group. Since both types contain an aromatic ring structure, they are stable compounds. The non-basic and basic nitrogen groups are often found in the high boiling point fractions and the vacuum residue portions of crude oil.

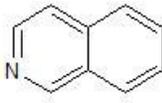
### Basic Nitrogen Compounds



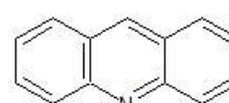
Pyridine



Quinoline

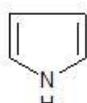


Isoquinoline

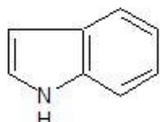


Acridine

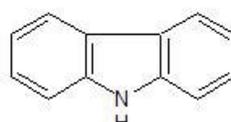
### Non-basic Nitrogen Compounds



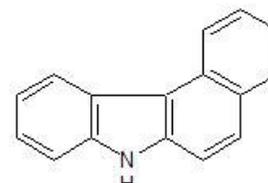
Pyrrole



Indole



Carbazole



Benzocarbazole

**Figure 1: Types of Nitrogen Compounds**

Pyridine is a thermally stable, generally unreactive compound that is able to be protonated.<sup>23</sup> In middle distillate fuels, there are multiple alkyl chain substitutions on the pyridine ring, with the alkyl chain length dependent on the distillation range. At ambient temperatures, pyridine compounds are unable to oxidized by oxygen or hydroperoxides to

form pyridine N-oxide, but at the increased temperature of the diesel engine, they would be able to oxidize the pyridine. The position of the alkyl substitution can influence the reactivity of the pyridine, with the 3-position being the most stable whereas the 2- and 4-positions are more acidic than the 3-position and will undergo normal condensation reaction.<sup>31</sup> The group that is substituted on the pyridine can have influence on the reaction of pyridine compounds; pyridines with an olefin substitution may be connected to polymerization reactions, since it homologous to olefin-substituted benzene compounds such as styrene, and the olefin-substituted pyridine shows a higher reactivity when compared to its benzene homologue. However, most olefin-substituted pyridines will react while undergoing thermal refining that will result in negligible concentrations in the final fuel. If a middle distillate fuel undergoes hydrotreatment, the alkyl-substituted pyridine compounds will result in alkyl-substituted piperidines.<sup>31</sup> Lower molecular weight pyridines can be removed by dilute mineral acids.

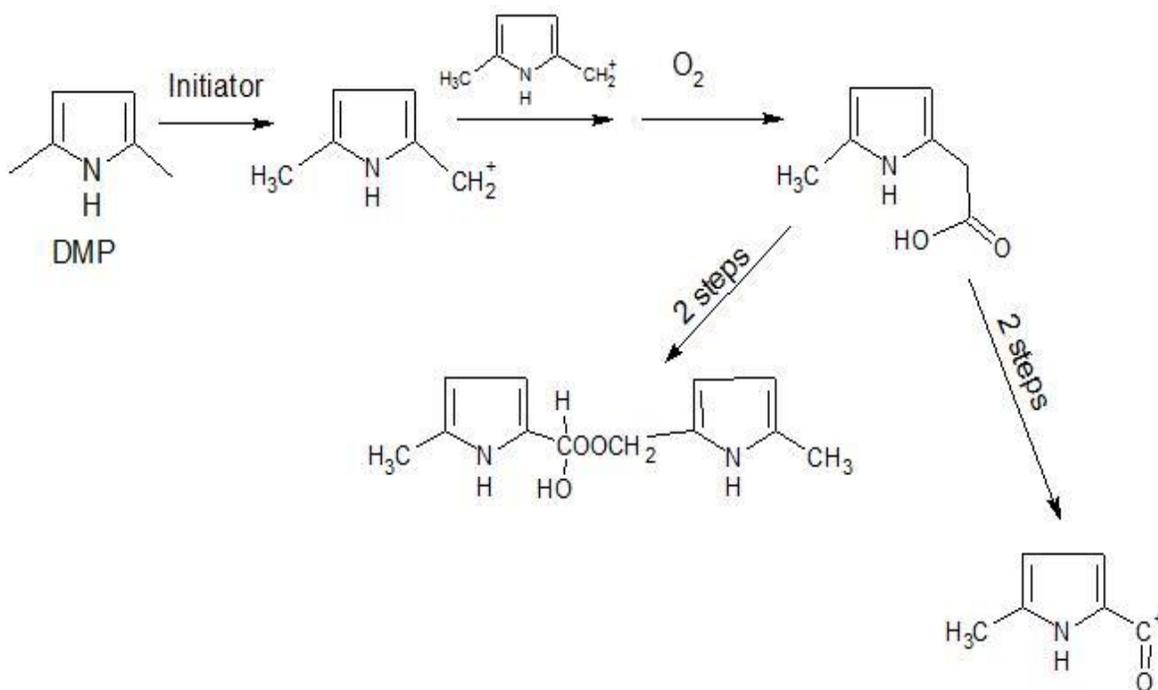
Quinoline and isoquinoline compounds behave similarly to the pyridine compounds. Both are not active in the sediment formation in models,<sup>31</sup> which is a characteristic of pyridine compounds. When quinoline and isoquinoline compounds in middle distillates undergo hydrotreatment, it results in the partial protonation of the compounds which include dihydroquinolines, tetrahydroquinolines, and decahydroquinolines. Dihydroquinolines are able to be oxidized by the air back into quinoline motif. Tetrahydroquinolines can be used to determine the severity of the hydrotreatment by comparing it to the ratio of quinoline. Quinoline compounds are able to undergo oxidation, however strong oxidants are needed to form the N-oxides.

Quinoline compounds will follow the same chemistry of pyridine. Quinoline is able to undergo electrophilic substitution due to the benzene ring. Electrophilic monosubstitution will occur at positions adjacent to the ring junction in quinolines, highlighting its similarities to naphthalene electrophilic substitutions.

Pyrrole compounds are thermally stable, much like quinolines, but differ in several regards to quinolines and other nitrogen groups. One of the major differences between pyrroles and other nitrogen groups is that pyrrole is easily oxidized, readily polymerizes, and readily reacts with electrophilic reagents. The only exception is that electron-withdrawing group substitutions on pyrrole will not readily react, often forming simple salts when mineral acids are present. In the case of substituted pyrroles, they can undergo acid-base reactions to form polymers. In the majority of fuels, pyrrole compounds have mono- or di-alkyl substitutions with the substitution chain length up to pentyl; multi-substituted short chain pyrroles react more readily with air to form peroxides which in turn are used in oxidation reactions for other volatile species found in fuel. A pyrrole's reactivity is depended on the position, with the C<sub>2</sub> position being the most reactive. Pyrrole compounds will also form high molecular weight polymers in the presence of ketones and aldehydes via a 1-,4- addition reaction. The ease of oxidation in pyrroles can be seen by the changes in the color body of the fuel; oxidized pyrroles darken the fuel much like straight distilled pyrrole will darken over a period time after distillation.<sup>31, 40</sup>

Pyrroles, such as 2,5-dimethyl pyrrole (DMP), are easily polymerized except in cases where the pyrrole contains an electron-withdrawing group. The reaction of DMP is

not a simple polymerization reaction, but rather an autoxidation process that happens in the fuel. In figure 2, it shows the possible reaction mechanisms of DMP with the two possible outcomes of the polymerization reaction. Dimethyl pyrrole, however, is not a good indicator of the sediment production in fuels due to the fact that it generates more sediment than any other nitrogen functional group in instability studies generating over 100 mg/100mL. Frankenfield and Taylor (1979) showed that DMP generates more sediment in light storage than darkness, with almost a hundred times more sediment generated when compared to pyrrole in dark storage.<sup>18</sup> The reasoning behind choosing DMP as a model for instability studies is because of how defined the reaction is in literature and it available commercially in high purity standards.<sup>3, 31</sup>



**Figure 2: Possible Reaction Mechanism for DMP (adapted from Mushrush 1995)**

Indoles and carbazoles, the latter which is essentially a substituted indole, share similar characteristics to pyrrole such as being slightly basic, readily reacts with electrophilic reagents, and resistant to substitutions. Indoles will also form dimers and trimers. In another similarity to pyrrole, indole's reactivity is based upon the position in the ring structure, with the C<sub>3</sub> position on indole being congruent to the C<sub>2</sub> position in pyrrole in terms of reactivity. Both indoles and carbazoles will form hydroperoxides, with saturated carbazoles easily forming a hydroperoxide.<sup>31</sup>

Indoles are also implicated in instability of diesel fuels, especially alkylindoles, which may play a greater role in gum formation than alkylpyrroles.<sup>3</sup> As previously stated, a substitution on certain positions of the indole ring will have a higher reactivity, much like substitutions on pyrrole. In the case of indole and sediment formation, a methyl substitution on the C<sub>2</sub> position will generate more sediment when compared to indole, generating about 15 times more sediment in light conditions. In dark conditions, indole will produce negligible sediment whereas 2-methylindole will produce approximately 1.4 g/500g of decane within the same sixty-day period.<sup>3</sup>

Given the importance of nitrogen compounds in diesel fuels, the purpose of this study is to determine if high purity CNTs are able to remove nitrogen compounds from a Spanish refined (No. 2) diesel. The diesel is filtered through the CNTs for a set period of time, followed by the removal of excess diesel fuel through a wash of cyclohexanol, and the filtrates removed from the CNTs by washes of DCM and MeOH. The compounds from the extraction processes were then determined through high-resolution gas chromatography-mass spectroscopy (GC/MS). The extracts were then compared in terms

of compounds, both nitrogen and hydrocarbons, present as well as concentration of the compounds.

## **EXPERIMENTAL**

### **Materials**

The high-purity carbon nanotubes were obtained from the Naval Research Laboratory in Washington, DC. The Spanish refined No. 2 diesel was from the collection at George Mason University. Cyclohexane, methylene chloride, and methanol were reagent grade and obtained from Aldrich Chemical Company, Milwaukee, Wisconsin and used without any further purification.

### **Extraction**

In a 100-mL beaker, 10.045 g CNTs and 45 mL of fuel were added with a magnetic stir bar and let to stir for 30 minutes. The CNT-fuel mixture was then vacuum filtered through a Buchner funnel until dry. Fifty milliliters of cyclohexane were used to rinse off the excess fuel from the CNTs and was discarded. Fifty milliliters of methylene chloride, and a final rinse of 50 mL methanol were collected in separate beakers. Both the methylene chloride and methanol extracts were reduced from 50 mL to approximately 5 mL via rotary evaporation. The temperature of the extraction was performed at ambient room temperature, approximately 20°C.

## **Instrumental Setup**

The DCM and MeOH extracts were analyzed by capillary GS-MS system. The GC-MS instrument was an Agilent 6890 gas chromatograph with a HP 5793 mass spectrum detector. The GC-MS was fitted with a 30.0 m x 0.25 mm HP-5 5% (phenyl)-methylpolysiloxane capillary column (model number Agilent 19091J-433, Agilent Technologies, Santa Clara, CA) that was operated using this program: 50°C start temperature, 5°C/min ramp, 300°C final temperature, with an eight-minute hold. The injection port was held at 290°C temperature with a splitless 1- $\mu$ L injection.

The mass spectrometer was operated in the electron impact mode at 70 eV with a continuous scan acquisition from 45 amu to 500 amu at a rate of 1 scan per second. The parameters were setup with the electron multiplier to be at 1050 V, a source temperature of 230°C, a transfer line temperature of 290°C, and the MS Quad temperature of 150°C. The mass spectrometer was calibrated with perfluorotributylamine before use. The Agilent ChemStation and OpenChrom programs were used to process mass spectral information.

## RESULTS AND DISCUSSION

The hydrocarbon and nitrogen compounds in the DMC and MeOH samples were analyzed and identified by using GC/MS. The parameters that were used were sufficient in both the separation of peaks and for the proper identification of the compounds. Peak identification was carried out through fragmentation pattern and in some cases, a comparison of mass spectra from NIST library was utilized. It should be of note that aromatic nitrogen compounds are one mass unit higher than the corresponding aromatic hydrocarbon compounds, coupled with aromatic hydrocarbon's propensity to have strong molecular ion peaks at odd mass numbers, can make identifying nitrogen compounds difficult to parse from the hydrocarbon fractions. Aromatic hydrocarbon compounds have greater intensities when compared to nitrogen compounds.<sup>14, 15</sup>

The peak identification while using fragmentation patterns and comparison from the NIST library's collection of mass spectra was carried out both by computer methods, such as OpenChrom and Agilent ChemStation, and by hand analysis. With hand analysis, fragmentation patterns were utilized, where a certain mass corresponds to a typical fragment. For example, if a peak has a value of 57 m/z it can be assumed to be butyl- ( $C_4H_9$ ) fragment. Since fuel is primarily hydrocarbons, it can be assumed that an addition of 14 m/z to the base of butyl fragment would be another methyl addition to the chain. To account for aromatics, a phenyl fragment would have a peak value of 77 m/z; a methyl

addition to the phenyl fragment (creating a benzyl fragment) would have a peak value of 91 m/z. With regards to nitrogen compounds, identification can be difficult due to hydrocarbons also having peaks at odd mass numbers. As stated previous, a phenyl fragment has a peak value of 77 m/z, but a pyridyl fragment, a comparable fragment, has a peak value of 79 m/z. It is only when there are two nitrogen atoms present in a compound that the peaks will have a even mass number; as an example, pyrimidine will have a peak value of 80 m/z. It through these fragmentation patterns that can aid in the identification of the compound.

The terms used in the GC/MS identification of the peaks was done in atomic composition along with a possible compound type; isomers of all types may be possible for any atomic composition due in part to polyaromatic nitrogen compounds' tendency to have very little fragmentation in electron impact mass spectroscopy which can limit the data available to interpret the structural information of that peak.

### **DCM Extract Analysis**

In the DCM extract, a total of 155 compounds were identified, of which 29 were nitrogen compounds. Nitrogen compounds accounted approximately 0.0930 percent of the total integrated area of the gas chromatogram. The other percentage was hydrocarbon compounds and a few sulfur- or oxygen-containing compounds.

**Table 3: Examination of Nitrogen Compounds in DCM Extract**

| <b>Organic Nitrogen Compounds</b> | <b>n</b> | <b>Area%*</b> |
|-----------------------------------|----------|---------------|
| <b>Total Nitrogen</b>             | 29       | 99.987        |

|   |    |        |
|---|----|--------|
| <b>Carbazoles</b>                       | 0  |        |
| <b>Indoles</b>                          | 1  | 5.705  |
| C <sub>2</sub>                          | 1  | 5.705  |
| <b>Pyridines</b>                        | 1  | 2.674  |
| C <sub>2</sub>                          | 1  | 2.674  |
| <b>Pyrroles</b>                         | 1  | 1.482  |
| C <sub>6</sub>                          | 1  | 1.482  |
| <b>Quinolines</b>                       | 2  | 5.476  |
| C <sub>3</sub>                          | 1  | 2.927  |
| C <sub>6</sub>                          | 1  | 2.548  |
| <b>Cyclic Nitrogen Compounds</b>        | 14 | 42.478 |
| C <sub>0</sub>                          | 1  | 10.314 |
| C <sub>6</sub>                          | 1  | 6.696  |
| C <sub>7</sub>                          | 1  | 1.525  |
| C <sub>8</sub>                          | 2  | 7.161  |
| C <sub>10</sub>                         | 4  | 7.200  |
| C <sub>13</sub>                         | 5  | 9.580  |
| <b>Total Cyclic Nitrogen Compounds</b>  | 19 | 57.815 |
| <b>Other Organic Nitrogen Compounds</b> | 10 | 42.173 |
| C <sub>11</sub>                         | 5  | 28.132 |
| C <sub>12</sub>                         | 2  | 6.750  |
| C <sub>13</sub>                         | 3  | 7.290  |

\*Area% is Nitrogen peak area not total area

Table 3 highlights that the most common nitrogen compound classes were cyclic in nature or were non-cyclic nitrogen compounds that composed about 57.8 percent and 42.2 percent of the total nitrogen content respectively. The cyclic nitrogen compounds did not fit the fragmentation patterns of the non-basic or basic nitrogen compounds

shown in Figure 1. The cyclic nitrogen compounds that were present were piperidines, triazoles, and benzoxazines. The non-cyclic nitrogen compounds were imines, amines, or amino- groups, which in Table 2, the number of carbons of the entire compound was given. There were no carbazoles present in the DCM extract.

The non-cyclic nitrogen compounds such as amines, amides, and nitrates are also used as diesel fuel additives. Secondary amines are one of the additives that can used to hinder gum formation to improve storage stability. Polyamides and amides additives are used for pre-combustion for cold flow improvements, such as preventing wax settlement, and as a dispersant to restrict the size of the particles in the diesel. Amines, amides, and imidazole are also used as detergent additive to removes carbonaceous and gum deposits from the fuel injector. Nitrates, such as iso-octyl nitrate, are used as cetane improvers; the additives increase the number of free radicals, which in turn makes auto-ignition easier. The concentration of the additives can range from 10 ppm to 500 ppm.<sup>39</sup> The capture of the non-cyclic nitrogen compounds might indicate that a portion of the diesel additives may have been captured by the CNTs.

**Table 4: Examination of Hydrocarbon Compounds in DCM**

| Hydrocarbon Compound Class | n  | Area%  |
|----------------------------|----|--------|
| <b>A. Alkanes</b>          | 38 | 70.451 |
| C10                        | 1  | 1.096  |
| C11                        | 1  | 3.858  |
| C12                        | 1  | 6.551  |
| C13                        | 3  | 9.837  |
| C14                        | 6  | 9.518  |
| C15                        | 3  | 7.618  |
| C16                        | 5  | 8.053  |

|                          |    |        |
|--------------------------|----|--------|
| C17                      | 6  | 6.333  |
| C18                      | 2  | 4.542  |
| C19                      | 4  | 5.311  |
| C20                      | 2  | 2.468  |
| C21                      | 1  | 2.049  |
| C22                      | 1  | 1.505  |
| C23                      | 1  | 1.036  |
| C24                      | 1  | 0.677  |
| <b>B. Alkenes</b>        | 4  | 0.387  |
| C6                       | 1  | 0.016  |
| C15                      | 1  | 0.100  |
| C17                      | 1  | 0.218  |
| C18                      | 1  | 0.052  |
| <b>C. Cycloalkanes</b>   | 10 | 2.926  |
| C4                       | 3  | 0.654  |
| C5                       | 3  | 0.795  |
| C6                       | 2  | 0.755  |
| C9                       | 1  | 0.244  |
| C11                      | 1  | 0.477  |
| <b>D. Dicycloalkanes</b> | 2  | 1.492  |
| C1                       | 1  | 0.345  |
| C4                       | 1  | 1.146  |
| <b>E. Benzenes</b>       | 27 | 10.332 |
| C2                       | 1  | 1.021  |
| C3                       | 4  | 0.398  |
| C4                       | 10 | 2.091  |
| C5                       | 4  | 2.074  |
| C6                       | 5  | 1.824  |
| C7                       | 2  | 0.782  |
| C8                       | 1  | 2.143  |
| <b>F. Biphenyls</b>      | 8  | 0.935  |
| C1                       | 1  | 0.316  |
| C2                       | 3  | 0.268  |
| C3                       | 2  | 0.136  |
| C4                       | 1  | 0.122  |
| C5                       | 1  | 0.093  |
| <b>G. Naphthalenes</b>   | 16 | 5.151  |

|                     |    |       |
|---------------------|----|-------|
| <b>C1</b>           | 1  | 0.948 |
| <b>C2</b>           | 1  | 1.042 |
| <b>C3</b>           | 9  | 2.376 |
| <b>C4</b>           | 3  | 0.538 |
| <b>C5</b>           | 2  | 0.248 |
| <b>H. Tetralins</b> | 14 | 6.609 |
| <b>C1</b>           | 5  | 2.555 |
| <b>C2</b>           | 5  | 2.333 |
| <b>C3</b>           | 3  | 1.485 |
| <b>C4</b>           | 1  | 0.235 |
| <b>I. Acenaps</b>   | 1  | 0.323 |
| <b>C1</b>           | 1  | 0.323 |
| <b>J. Fluorene</b>  | 2  | 0.301 |
| <b>C1</b>           | 2  | 0.301 |

The hydrocarbon fraction was largely composed of alkanes and benzene compounds, with the both of them accounting for almost 81 percent of the total hydrocarbon fraction. There were smaller amounts of other cyclic hydrocarbons, such as tetralins, cycloalkanes, and dicycloalkanes, which could be indicative of hydrotreatment. The alkane range that was captured by the CNTs were C<sub>10</sub> to C<sub>24</sub>, with C<sub>13</sub> and C<sub>14</sub> alkanes being the most prevalent in terms of area that accounts for 19.355 percent of the total hydrocarbon area, but C<sub>14</sub> and C<sub>17</sub> having the most compounds present in the fuel at six a piece.

## MeOH Extract Analysis

In the MeOH extract, a total of 172 compounds were identified, of which 11 were nitrogen compounds. Nitrogen compounds accounted for 0.0476 percent of the total integrated area of the gas chromatogram. The other percentage was hydrocarbon compounds and a few sulfur- or oxygen-containing compounds.

**Table 5: Examination of Nitrogen Compounds from MeOH extract**

| Organic Nitrogen Compounds              | n  | Area% |
|---|----|-------|
| <b>Total Nitrogen</b>                   | 11 | 99.38 |
| <b>Carbzaoles</b>                       | 1  | 1.494 |
| C3                                      | 1  | 1.494 |
| <b>Indoles</b>                          | 0  | 0.000 |
| <b>Pyridines</b>                        | 2  | 11.96 |
| C4                                      | 1  | 5.197 |
| C5                                      | 1  | 6.760 |
| <b>Quinolines</b>                       | 4  | 58.30 |
| C2                                      | 1  | 13.20 |
| C3                                      | 1  | 34.11 |
| C4                                      | 1  | 5.197 |
| C5                                      | 1  | 5.793 |
| <b>Acridine</b>                         | 1  | 4.845 |
| C3                                      | 1  | 4.845 |
| <b>Other Cyclic Nitrogen</b>            | 2  | 5.295 |
| C6                                      | 2  | 5.295 |
| <b>Other Organic Nitrogen Compounds</b> | 3  | 24.27 |
| C11                                     | 1  | 18.62 |

|     |   |       |
|-----|---|-------|
| C15 | 2 | 5.646 |
|-----|---|-------|

\*Area% is Nitrogen peak area not total area

Quinolines accounted for 58.301 percent of the nitrogen compounds present in the MeOH extract, of which one C<sub>3</sub> quinoline accounts for 34.110 percent. Other organic nitrogen compounds were composed of an aniline and two amides, with the carbon number in Table 4 being representative of the total number of carbons in the compound. There were indoles present in the MeOH extract.

**Table 6: Examination of Hydrocarbons in MeOH extract**

| Hydrocarbon Compound Class | n  | Area%  |
|----------------------------|----|--------|
| <b>A. Alkanes</b>          | 15 | 10.63  |
| C10                        | 2  | 0.3900 |
| C11                        | 3  | 1.425  |
| C12                        | 1  | 2.127  |
| C13                        | 2  | 3.633  |
| C14                        | 1  | 0.8105 |
| C15                        | 1  | 1.031  |
| C16                        | 1  | 0.3152 |
| C17                        | 1  | 0.3253 |
| C18                        | 1  | 0.2449 |
| C19                        | 1  | 0.1762 |
| C20                        | 1  | 0.1540 |
| <b>B. Cycloalkanes</b>     | 3  | 2.598  |
| C5                         | 1  | 0.5922 |
| C7                         | 1  | 0.7409 |
| C8                         | 1  | 1.265  |

|                        |    |         |
|------------------------|----|---------|
| <b>C. Benzenes</b>     | 43 | 13.33   |
| C3                     | 11 | 1.431   |
| C4                     | 13 | 6.161   |
| C5                     | 4  | 1.896   |
| C6                     | 5  | 1.056   |
| C7                     | 1  | 0.2018  |
| C8                     | 6  | 2.085   |
| C9                     | 1  | 0.3185  |
| C11                    | 1  | 0.1584  |
| C12                    | 1  | 0.02341 |
| <b>D. Biphenyls</b>    | 19 | 4.462   |
| C1                     | 4  | 2.647   |
| C2                     | 4  | 0.6692  |
| C3                     | 4  | 0.4743  |
| C4                     | 6  | 0.6005  |
| C5                     | 1  | 0.07104 |
| <b>E. Naphthalenes</b> | 35 | 45.63   |
| C0                     | 1  | 0.8299  |
| C1                     | 1  | 4.003   |
| C2                     | 12 | 25.41   |
| C3                     | 12 | 12.65   |
| C4                     | 7  | 2.620   |
| C5                     | 1  | 0.1231  |
| C6                     | 1  | 0.05755 |
| <b>F. Tetralins</b>    | 15 | 7.301   |
| C1                     | 3  | 2.814   |
| C2                     | 1  | 1.038   |
| C3                     | 5  | 1.425   |
| C4                     | 4  | 1.323   |
| C6                     | 1  | 0.2156  |
| C8                     | 1  | 0.4853  |
| <b>G. Decalins</b>     | 3  | 0.6476  |
| C4                     | 2  | 0.4385  |
| C5                     | 1  | 0.2091  |
| <b>H. Indenes</b>      | 7  | 3.389   |

|                                     |    |         |
|-------------------------------------|----|---------|
| <b>C<sub>0</sub></b>                | 1  | 0.1154  |
| <b>C<sub>2</sub></b>                | 2  | 1.412   |
| <b>C<sub>3</sub></b>                | 2  | 0.9759  |
| <b>C<sub>4</sub></b>                | 1  | 0.7812  |
| <b>C<sub>7</sub></b>                | 1  | 0.1042  |
| <b>I. Acenaps</b>                   |    |         |
| <b>C<sub>3</sub></b>                | 1  | 0.1727  |
| <b>C<sub>4</sub></b>                | 1  | 0.03582 |
| <b>J. Phenanthrenes/Anthracenes</b> |    |         |
|                                     | 10 | 2.162   |
| <b>C<sub>1</sub></b>                | 4  | 1.045   |
| <b>C<sub>2</sub></b>                | 4  | 0.5704  |
| <b>C<sub>3</sub></b>                | 1  | 0.5037  |
| <b>C<sub>4</sub></b>                | 1  | 0.04304 |
| <b>K. Fluorenes</b>                 |    |         |
|                                     | 8  | 1.314   |
| <b>C<sub>0</sub></b>                | 1  | 0.5256  |
| <b>C<sub>1</sub></b>                | 2  | 0.3283  |
| <b>C<sub>2</sub></b>                | 4  | 0.4319  |
| <b>C<sub>3</sub></b>                | 1  | 0.02791 |

The hydrocarbon fraction was predominately polycyclic aromatic hydrocarbons, comprising 49.314 percent of the total area. Naphthalenes were the most common polycyclic hydrocarbon in the MeOH fraction, C<sub>2</sub> naphthalenes being the most in terms of peak area percentage at 25.407%. Benzenes were also frequently found, with 43 compounds identified, but overall had a smaller total area when compared to the naphthalenes. There were also cycloalkanes, tetralins, and decalins (decahydronaphthalene) present, which is also another indicator of hydrotreatment. The

alkane range capture by the CNTs were from C<sub>10</sub> to C<sub>20</sub>, but accounted for approximately 11 percent of the total peak area.

### **Overall Extract Analysis and Discussion**

In both DCM and MeOH extracts, hydrocarbons predominated when compared to nitrogen compounds. In both extracts a total of 40 nitrogen compounds were captured by the CNTs of which were a small percentage in the total peak area of the gas chromatogram when compared to the hydrocarbon fraction. Of the nitrogen compounds captured, the most common were other cyclic nitrogen compounds, such as piperidine or triazoles, in the DCM extract or quinolines in the MeOH extract. There is little literature on other cyclic nitrogen compounds like piperidine having any detrimental qualities to fuel stability and compatibility, however it could be inferred that hydrogenated cyclic nitrogen compounds would follow a similar route as their aromatic homologue.

When comparing to previous studies<sup>9,10,29</sup> using CNTs for petroleum purification the results were similar with regards to the number of organic nitrogen compounds captured and the type of compounds, but performed overall worse than the conventional silica gel, or activated clay for separating out nitrogen compounds when compared to Bauserman et al (2014).<sup>9</sup> In that research, FeCNTs were used as a filtering media, which yielded better results in the removal of nitrogen compounds when compared to the high purity CNTs; the FeCNTs removed a total of 61 nitrogen compounds compared to the CNTs' 40 nitrogen compounds, which is a 34.4 percent decrease in the total nitrogen compounds captured.

Mesoporous carbon molecular sieves, with large specific surface areas and large specific pore volumes coupled with electrical conductivity, might have some potential in filtering nitrogenous compounds from diesel fuel. The relative ease of using silica templates with sucrose, phenol-formaldehyde resins, or divinyl-benzene as the carbon makes it easier to synthesize than higher purity CNTs in house. The adsorption of nitrogen ( $N_2$ ) in mesoporous carbon molecular sieves is depended on the structure of molecular sieve and the relative pressure, which can cause the deformation and reduction of the pore volume. Similar results are to be found when using organic molecules, n-heptane and cyclohexane, however the organic molecules point to three things: the incomplete polymerization of the sucrose inside the template, ruptured C-C bonds during the pyrolysis of the template and carbon source, or changes in the structure during the treatment of hydrofluoric acid to dissolve the silica template.<sup>44</sup> Since mesoporous carbon materials that do not have arranged pores are already in use in adsorbents, it would be prudent to see if this material would be more suited as a filtering media for this application rather than CNTs.

The high purity carbon nanotubes, while can act as a molecular sieve, can also interact with and have hydrocarbons and aromatic compounds bind to the CNT surface via hydrophobic forces, van der Waals bonding between planar groups and the CNTs' wall, or  $\pi$ - $\pi$  interactions, such as  $\pi$ -stacking forces, which may inhibit the nitrogen compounds' ability to interact with CNTs directly, but rather through the progressive buildup of hydrocarbon compounds.<sup>19,20,25,38</sup> In another study performed by Srivastava et al, CNTs were quite efficient in removing heavier hydrocarbons in petroleum and in a

controlled experiment of a simpler solution of naphthalene and benzene when compared to conventional membrane filtration; in this study naphthalene was indicated to be absorbed within the first few minutes of the filtration process with saturation occurring around the ten-minute mark.<sup>2</sup> There are other factors that may have an effect on the bonding of nitrogen compounds and CNTs such as pore size, the internal diameter of the CNTs, single- or double-walled CNTs, the symmetry of the CNTs, defects in the lattice structure such as bending or rearrangements, and if there is a fracture in the sidewall from strain.<sup>20, 33</sup>

The  $\pi$ - $\pi$  interactions between CNTs and aromatic compounds can be increased by the number of rings on the compound itself or the addition of electron-withdrawing or electron-donating substituents to the aromatic compound. The addition of the polar -OH groups to the CNTs also increases the adsorption of aromatics which may be due in part of increasing strength in the  $\pi$ - $\pi$  interactions.<sup>19, 25, 38</sup> The  $\pi$ - $\pi$  stacking is not limited to neat sandwich stacking, but also can be arranged in the t-shaped or a parallel displacement, which could lend itself to a more complex shape which would make it more difficult for the nitrogen compounds to interact with the interstitial space or external grooves of the CNTs.<sup>36</sup>

In Sumanaskera *et al*, it was found that there is a correlation between single-walled CNTs and the adsorption of six-membered ring hydrocarbons, with the motif of  $C_6H_{2n}$  with  $n=3-6$ , which runs from being rich in  $\pi$ -electrons as in benzene to only  $\sigma$ -bonds remaining in the cyclohexane.<sup>41</sup> The thermoelectric power (S) of the nanotubes can be calculated for both the nanotube and the six-membered ring hydrocarbons by

using electrical resistivity, which shows a correlation between the number of  $\pi$ -electrons and  $\Delta S$  values, where the highest number of  $\pi$ -electrons in the benzene yielding the highest  $\Delta S$  value. The results indicate the creation of a new scattering channel for electrons in the CNTs' wall that is associated with molecular adsorption, with the  $\pi$ -electrons in the absorbed molecule causing an increase in the strength of the coupling.<sup>41</sup> This could in part explain the increased preference for aromatic and polyaromatic hydrocarbons over nitrogenous compounds in both the MeOH and DCM extracts.

Another force that influences the structure of CNTs is van der Waals interactions. The electrons in the CNTs could be semiconducting or metallic in nature which is depended on the diameter of the tube and the helicity of the CNTs (armchair, chiral, and zigzag configurations). The van der Waals interactions are responsible for the high binding energies between the CNTs and substrate in *Hertel et al.* Gains in binding energy, via the increases in contact area between the CNT and substrate, have the ability to warp the CNTs shape in the axial and radial directions which in turn ruin the ideal shape of the CNTs. However, as shown in *Hertel et al.*, the severity of the radial distortions in the cross-sectional portion of the CNTs can be predicted by the tube diameter and in the cases of MWCNTs, the number of shells present. SWCNTs with a larger tube diameter will have a larger distortion when compare to MWCNTs with a similar outer tube diameter; the atomic-force microscopy is limited in its ability to characterize minor differences in height in at such small scale, molecular mechanics calculations were used to determine the extent of cross-sectional distortions. The hydrocarbons, both aromatic and aliphatic, might be causing the deformation of the tube

shape in the CNTs, which in turn may impact the CNTs ability to absorb nitrogen containing compounds.

## CONCLUSIONS

The results of this study provided useful information on high purity CNTs as a novel purification technique for the removal nitrogen compounds from diesel fuel. The analysis of the two extracts, DCM and MeOH, provided insight into the ability of CNTs to remove nitrogen compounds from the Spanish Refined (No. 2) Diesel as well as other hydrocarbon compounds removed from the source fuel. These results are relevant for the studies of purification of petroleum and post-refining purification of fuels, especially with a special interest in fuel stability and incompatibility. Both extracts of the diesel fuel had both similarities and differences.

*Similarities:* In both extracts, the hydrocarbon fraction accounted for most of the peak area total. The type of hydrocarbon compounds present in both fractions were similar, which included alkanes and aromatic compounds. In the nitrogen compounds removed, cyclic nitrogen compounds and quinolines were both present in both extracts.

*Differences:* Between the two extracts, there were key differences. In the DCM extract, there were no carbazoles present, much like in the MeOH extract no indoles or pyrroles were detected. The peak percentage of the nitrogen compounds between the two extracts were different, with DCM being more than double than that of the MeOH. In the hydrocarbon fractions, there were minor differences in the composition of the two extracts; DCM had more alkanes present whereas in the MeOH had more benzenes

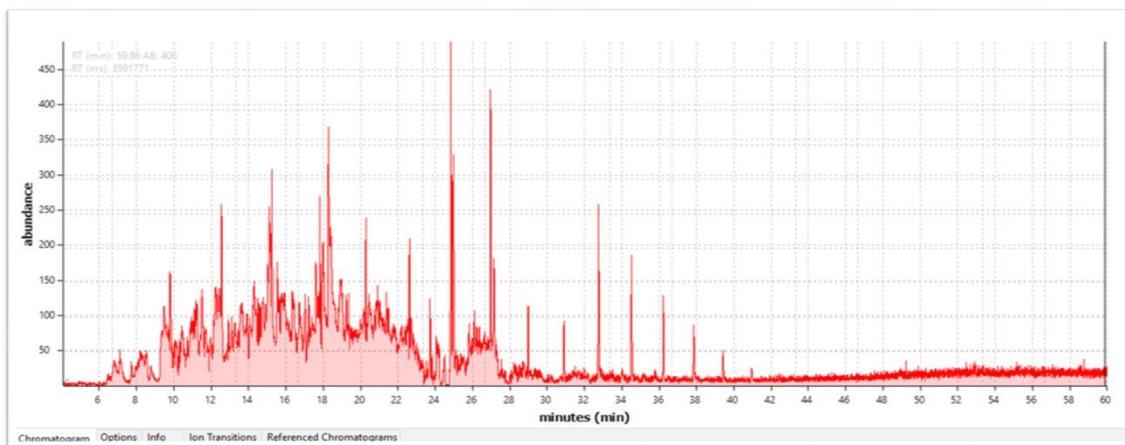
present. The MeOH extract also contained phenanthrenes and anthracenes, which were not present in the DCM extracts.

The extraction procedure of this study was successful in removing aromatic compounds but was moderate in the removal of nitrogen compounds. Both extracts were complex in the fact that hydrocarbon compounds, nitrogen compounds, and a small fraction sulfur- and oxygen-containing compounds were present. This made identification of the compounds difficult because of the fact that there were some overlapping peaks and small peaks that could be misconstrued for GC baseline noise. With the cost of CNTs being \$30-50/lb<sup>9</sup> and its moderate success at removing nitrogen compounds, it would not be economically feasible to utilize CNTs as filtering media at this point in time for post refining diesels.

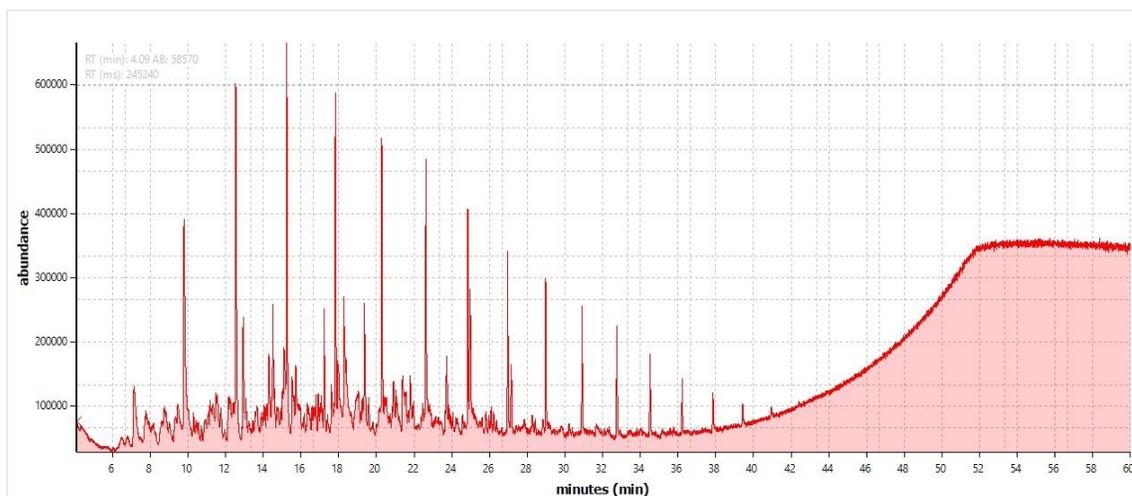
Future work is needed to determine if the high purity CNTs are a viable option in the filtration and purification of diesel fuels. One of the future studies could be the analysis of the CNTs surface after removal of excess fuel; it would be advantageous to understand the surface chemistry of the CNTs in regards to fuel and using near-infrared FTIR, x-ray crystallography, or Raman spectroscopy would be able to determine if the aromatic compounds are noncovalently bonding to the CNTs. Atomic-force microscopy could in turn also help visualize any critical deformations that occurred after the filtration process. Studies such as that could determine the exact mechanism of action that CNTs use when introduced to a fuel source and how to improve upon it in such a way that would increase the nitrogen compounds affinity for the CNTS, such as additions of side chains on the CNTs' sidewalls. By determining the surface chemistry of CNTs, it would

allow for a more tailored CNTs for purification and filtration based upon the composition of the fuel. This in turn would allow refineries and consumers, such as the US Military, the ability to remove detrimental compounds from the crude oil or fuel. The custom tailored CNTs could reduce costs by allowing the refinery an opportunity to utilize poorer quality crude oils by removing the nitrogen compounds and other detrimental compounds such as sulfur-containing compounds prior to the blending of the fuels. Another benefit of customizable side-chains on the CNTs would be the ability for crude oil refinement to be based upon the geographic region's composition rather than a generic "one size fits all" approach, which could be adding into either prior to or into the desalter. The ability to add some ability to remove nitrogen compounds prior to distillation of the crudes into the various cuts such a gasoline or diesel fuels, may increase the storability of the fuels prior to shipment, thus allowing a longer shelf life of the product.

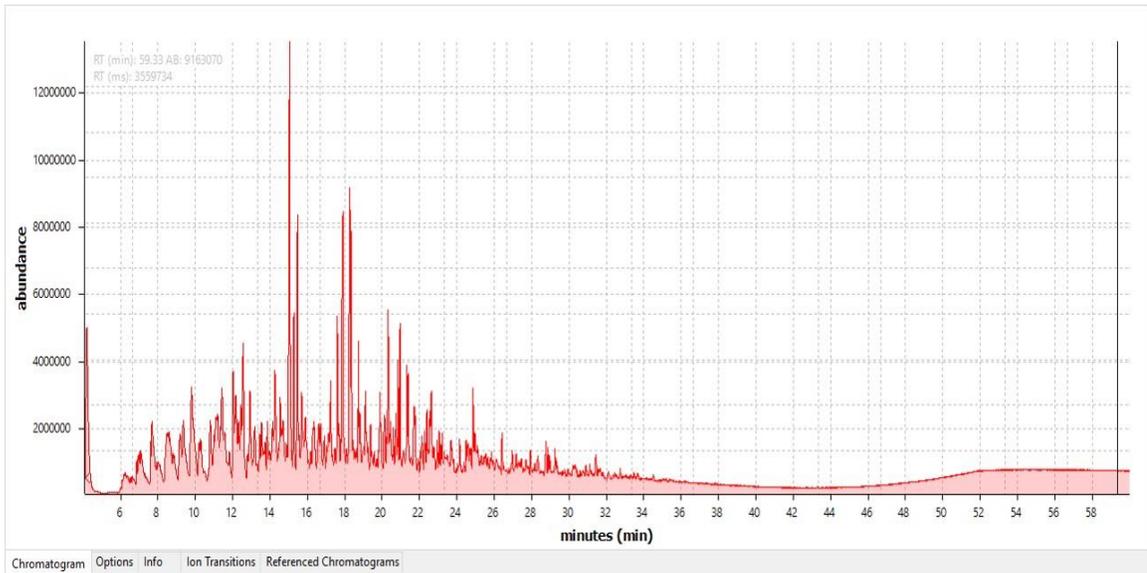
## APPENDIX



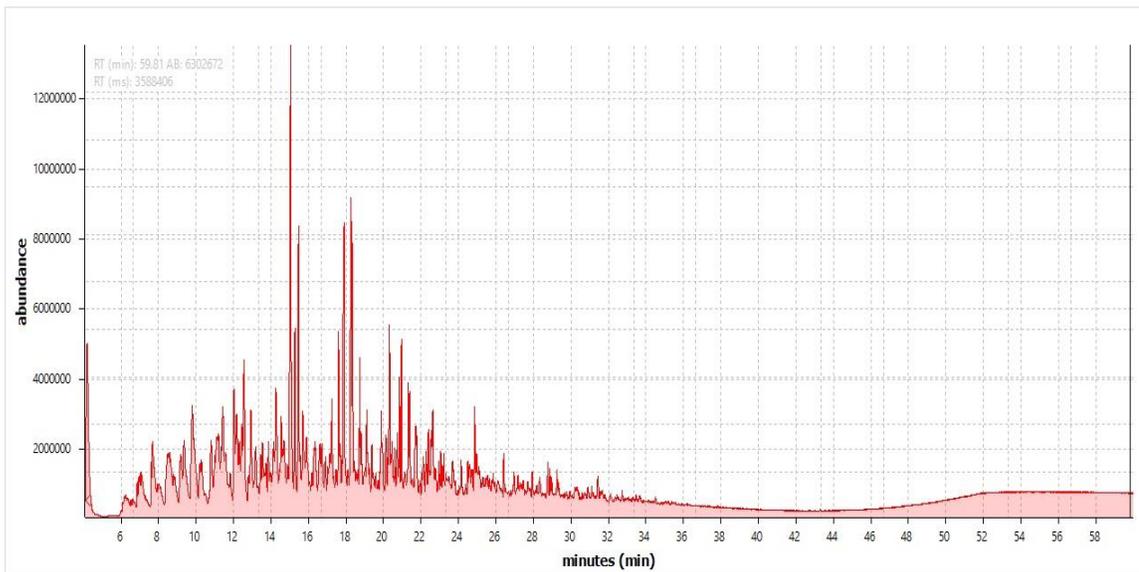
**Figure 3: Gas Chromatogram of DCM extract with baseline smoothing and noise reduction**



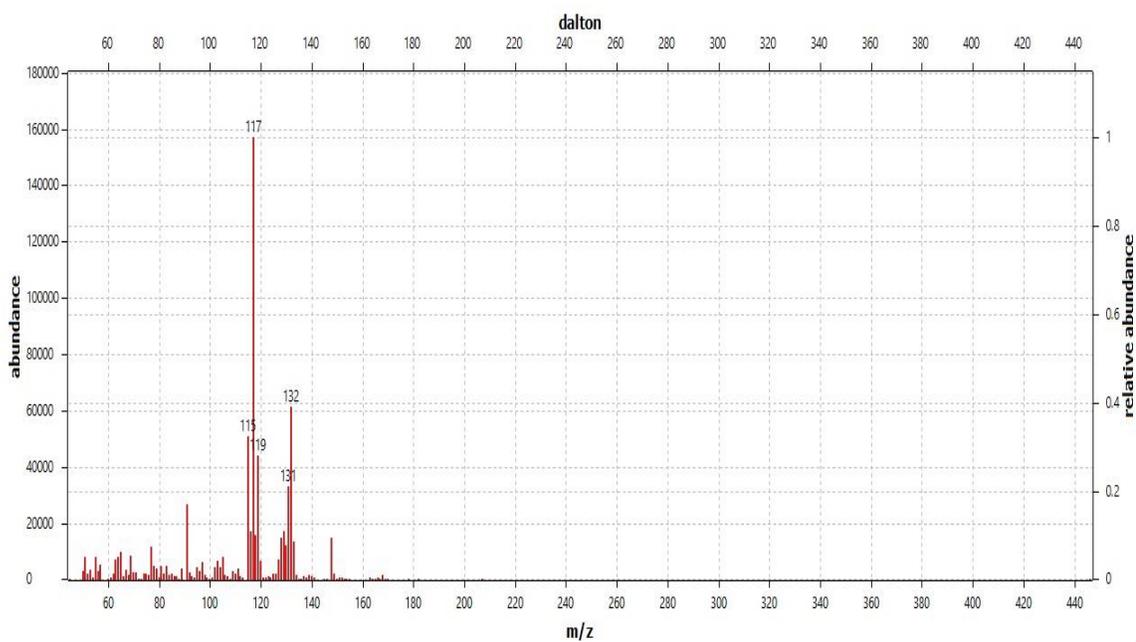
**Figure 4: Gas Chromatogram of DCM extract without baseline smoothing and noise reduction**



**Figure 5: Gas Chromatogram of MeOH extract with baseline smoothing**

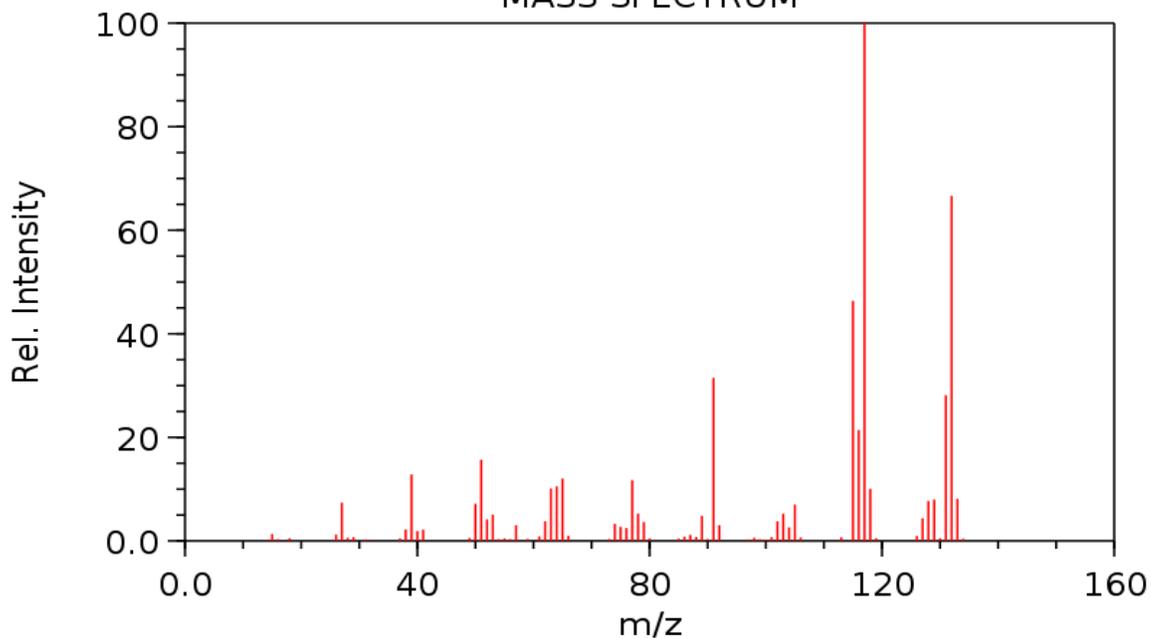


**Figure 6: Gas Chromatogram of MeOH extract without baseline smoothing**



**Figure 7: Mass Spectrum from MeOH extract at 11.142 identified as 2-ethenyl-1,4-dimethyl-benzene**

Benzene, 2-ethenyl-1,4-dimethyl-  
MASS SPECTRUM



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)  
**Figure 8: Mass Spectrum obtained from NIST Chemistry WebBook of 2-ethenyl-1,4-dimethyl-benzene**

## REFERENCES

1. Apul OG, Wang Q, Shao T, Rieck JR, Karanfil T. Predictive Model Development for Adsorption of Aromatic Contaminants by Multi-Walled Carbon Nanotubes. *Environ Sci Technol*. 2013 Mar 5;47(5):2295–303.
2. A. Srivastava, O. N. Srivastava, S. Talapatra, R. Vajtai, P. M. Ajayan. Carbon nanotube filters. 2004;3(9):610.
3. Batts BD, Fathoni AZ. A literature review on fuel stability studies with particular emphasis on diesel oil. *Energy & Fuels*. 1991;5(1):2–21.
4. Baugh PJ. *Gas chromatography : a practical approach*. 1993.
5. Bauserman JW, Nguyen KM, Mushrush GW. Nitrogen Compound Determination and Distribution in Three Source Fuels by GC/MS. 2004;22(11–12):1491–505.
6. Bauserman JW 1950-. Nitrogen compound determination & distribution in three source fuels by GC/MS. Thesis (M.S.)--George Mason University, 2001.; 2001.
7. Bauserman JW 1950-. The determination, distribution, and analysis of organic nitrogen compounds in refined fuels from a world-wide survey. Thesis (Ph.D.)--George Mason University, 2007.; 2007.
8. Bauserman JW, Castelly H, Mushrush GW. Analysis of Nitrogen Abundance in Treated Fuels by GC/MS. 2014;32(15):1824–32.
9. Bauserman JW, Mushrush GW, Hardy DR, Willauer HD, Laskoski M, Keller TM. The Removal of Organic Nitrogen Compounds from Unstable Diesel Fuels. 2014;32(6):638–45.
10. Bauserman JW, Mushrush GW, Willauer H, Wynne JH, Phillips JP, Buckley JL, et al. Removing Organic Nitrogen Compounds From Middle Distillate Fuels with a Catalyst Used as a Filtering Media. 2010;28(17):1761–9.
11. Bertocini F author, Courtiade-Tholance M author, Thiébaud D 1957- author. *Gas chromatography and 2D-gas chromatography for petroleum industry : the race for selectivity*. 2013.

12. Blagov EV, Klimchitskaya GL, Mostepanenko VM. van der Waals interaction between a microparticle and a single-walled carbon nanotube. *Phys Rev B*. 2007 Jun;75(23):235413.
13. Bozenko JS, Mushrush GW. Analytical Profile of Organo-nitrogen Compounds in Gulf Coast Refined Fuels by GC/MS. 2008;26(6):674–89.
14. Burchill P, Herod AA, Ernest P. Investigation of nitrogen compounds in coal tar products. 2. Basic fractions. *Fuel*. 1983 Jan 1;62(1):20–9.
15. Burchill P, Herod AA, Pritchard E. Investigation of nitrogen compounds in coal tar products. 1. Unfractionated materials. *Fuel*. 1983 Jan 1;62(1):11–9.
16. Comer J, Chen R, Poblete H, Vergara-Jaque A, Riviere JE. Predicting Adsorption Affinities of Small Molecules on Carbon Nanotubes Using Molecular Dynamics Simulation. *ACS Nano*. 2015 Dec 22;9(12):11761–74.
17. Ebert LB, American Chemical Society. Division of Petroleum Chemistry, American Chemical Society. Meeting 1986 : Anaheim C. Polynuclear aromatic compounds. 1988.
18. Frankenfield JW, Taylor WF. Continuation Study of Alternate Fuels Nitrogen Chemistry. DTIC Document; 1979.
19. Gotovac S, Yang C-M, Hattori Y, Takahashi K, Kanoh H, Kaneko K. Adsorption of polyaromatic hydrocarbons on single wall carbon nanotubes of different functionalities and diameters. *Journal of Colloid and Interface Science*. 2007 Oct 1;314(1):18–24.
20. Harris PJF (Peter JF 1957-. Carbon nanotube science : synthesis, properties and applications. Cambridge, UK: Cambridge, UK; 2009.
21. Hazlett RN. ACID BASE PHENOMENA IN DISTILLATE FUEL STABILITY. *Fuel Science and Technology International*. 1988 Jan 1;6(2):185–208.
22. Hughes JM, Mushrush GW, Hardy DR. BASE EXTRACTION TO REMOVE THE COMPONENTS CONTRIBUTING TO LUBRICITY IN A MIDDLE DISTILLATE FUEL. 2002;20(7–8):809–17.
23. Joule JA (John A. Heterocyclic chemistry. 4th ed. / J.A. Joule & K. Mills.. Oxford: Oxford; 2000.
24. Kinghorn RRF. An introduction to the physics and chemistry of petroleum. Chichester: Chichester; 1983.

25. Lin D, Xing B. Adsorption of Phenolic Compounds by Carbon Nanotubes: Role of Aromaticity and Substitution of Hydroxyl Groups. *Environ Sci Technol.* 2008 Oct 1;42(19):7254–9.
26. Matar S 1922-. *Chemistry of petrochemical processes.* Houston: Houston : Gulf Pub. Co.; 1994.
27. Mushrush GW, Beal EJ, Hardy DR, Hughes JM, Wynne JH. FUEL INSTABILITY STUDIES: THE CHEMICAL VALIDATION OF ASTM METHOD D5304. *Petroleum Science and Technology.* 2001 Jun 30;19(5–6):561–72.
28. Mushrush GW, Cooney JV, Beal EJ, Hazlett RN. CHARACTERIZATION AND STABILITY PROPERTIES OF POLAR EXTRACTS DERIVED FROM A RECENT SHALE LIQUID. *Fuel Science and Technology International.* 1986 Jan 1;4(1):103–25.
29. Mushrush G, Quintana M, Bauserman J, Willauer H. Post-refining removal of organic nitrogen compounds from diesel fuels to improve environmental quality. *Toxic/Hazardous Substances and Environmental Engineering.* 2011;46(2):176–80.
30. Mushrush GW, Spencer GO, Beal EJ, Wynne JH, Hughes JM, Hardy DR. THE SYNTHESIS OF A REACTIVE PYRIDINE INTERMEDIATE FOR FUEL INSTABILITY STUDIES. *Petroleum Science and Technology.* 2000 Aug 1;18(7–8):901–11.
31. Mushrush GW. *Petroleum products : instability and incompatibility.* Washington, D.C.: Washington, D.C. : Taylor & Francis; 1995.
32. Nguyen KM 1972-. Extraction & identification of nitrogen compounds in three middle distillate fuels by GC/MS. Thesis (M.S.)--George Mason University, 2001.; 2001.
33. Ottenhouse AP. *Carbon nanotubes : new research.* New York; 2009.
34. Parker MA, Mushrush GW. Nitrogen Compound Distribution of Refined Middle Distillate Fuels. *Petroleum Science and Technology.* 2006 Nov 1;24(11):1291–9.
35. Parker MA 1975-. Nitrogen compound distribution of refined middle distillate fuels. Thesis (M.S.)--George Mason University, 2004.; 2004.
36. Pasquale AJ, Bauserman JM, Mushrush GW. Nitrogen Compound Distribution in Refined Middle Distillate Fuels. *Petroleum Science and Technology.* 2009 Oct 22;27(18):2192–9.
37. Pasquale AJ 1966-. Refined middle distillate fuel nitrogen compound distribution. Thesis (M.S.)--George Mason University, 2007.; 2007.

38. Ren X, Chen C, Nagatsu M, Wang X. Carbon nanotubes as adsorbents in environmental pollution management: A review. *Chemical Engineering Journal*. 2011 Jun 1;170(2):395–410.
39. Song C, Hsu CS, Mochida I. *Chemistry of diesel fuels*. 2000.
40. Speight JG. *The chemistry and technology of petroleum*. 3rd ed., and expanded.. New York: New York : Marcel Dekker; 1999.
41. Sumanasekera GU, Pradhan BK, Romero HE, Adu KW, Eklund PC. Giant Thermopower Effects from Molecular Physisorption on Carbon Nanotubes. *Phys Rev Lett*. 2002 Sep;89(16):166801.
42. U.S. Energy Information Administration. *Energy Use for Transportation - Energy Explained, Your Guide To Understanding Energy - Energy Information Administration* [Internet]. U.S. Energy Information Administration. [cited 2017 Feb 8]. Available from: [http://www.eia.gov/energyexplained/?page=us\\_energy\\_transportation](http://www.eia.gov/energyexplained/?page=us_energy_transportation)
43. U.S. Energy Information Administration. *Product Supplied for Distillate Fuel Oil* [Internet]. U.S. Energy Information Administration. [cited 2017 Feb 8]. Available from: [http://www.eia.gov/dnav/pet/pet\\_cons\\_psup\\_a\\_EPD0\\_VPP\\_mbbldpd\\_a.htm](http://www.eia.gov/dnav/pet/pet_cons_psup_a_EPD0_VPP_mbbldpd_a.htm)
44. Vinu A, Hartmann M. Characterization and microporosity analysis of mesoporous carbon molecular sieves by nitrogen and organics adsorption. *Catalysis Today*. 2005 May 15;102:189–96.

## **BIOGRAPHY**

Katharine A. Boni graduated from Paul VI Catholic High School, Fairfax, Virginia, in 2005. She received her Bachelor of Science from George Mason University in 2011. She is employed as a substitute teacher in Fauquier County and received her Master of Science in Chemistry from George Mason University in 2018.