Summer 2015

Artificial Maturation Studies of Polymethylenic Plant Biopolymers: Investigating the Chemical Alterations from Plant Material to Coal

Blaine Elizabeth Hartman
Old Dominion University

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ARTIFICIAL MATURATION STUDIES OF POLYMETHYLENIC PLANT

BIOPOLYMERS: INVESTIGATING THE CHEMICAL ALTERATIONS FROM

PLANT MATERIAL TO COAL

by

Blaine Elizabeth Hartman
B.S. Environmental Chemistry, May 2010, Florida State University

A Dissertation Submitted to the Faculty of
Old Dominion University in Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY

CHEMISTRY

OLD DOMINION UNIVERSITY
August 2015

Approved by:

Patrick G. Hatcher (Director)

James W. Lee (Member)

Bala Ramjee (Member)

Sandeep Kumar (Member)
ABSTRACT

ARTIFICIAL MATURATION STUDIES OF POLYMETHYLENIC PLANT BIOPOLYMERS: INVESTIGATING THE CHEMICAL ALTERATIONS FROM PLANT MATERIAL TO COAL

Blaine Elizabeth Hartman
Old Dominion University, 2015
Director: Dr. Patrick G. Hatcher

The thermal maturation and alternation of vascular plant material into coals and as expelled petroleum-like compounds is the main focus of this dissertation. Utilizing artificial maturation studies, like hydrothermal liquefaction, yields useful information regarding how plant material is preserved in coals and the potential certain plant biopolymers possess to generate liquid fuels is acquired. The studies within this dissertation focus on utilizing the aliphatic biopolymers, cutin, cutan, and suberan, found in the epidermis of certain plants. These biopolymers contain minimal amounts of heteroatoms and are comprised of long polymethylenic chains, which are desirable characteristics in generating bio-oils. Additionally, understanding the chemical alterations that occur to these biopolymers during maturation is essential in evaluating their geochemical preservation in coals.

To evaluate the potential suberan has to become incorporated into coals and generate expelled oils, hydrothermal liquefaction experiments were conducted on modern, *Betula alleghaniensis* bark, and ancient, a lignite rich in crypto-eugelinite, samples. Both the bark and the coal display characteristic crystalline and amorphous peaks in solid-state $^{13}$C NMR, which is indicative of the presence of suberan. The expelled oil products of both feedstocks were mainly comprised of saturated hydrocarbons. These results suggest that suberan can
readily explain the existence of waxy crude oils typically associated with coals and Type III source rocks.

The oil generating potential of cutan and cutin were evaluated using skins collected from *Agave americana* and *Capsicum annumm*. Both cuticular materials resulted in approximately 35% wt.% bio-oil yields and exhibited heating values of 40.5 MJ kg$^{-1}$, comparable to those of typical crude petroleum. Furthermore, a two-step hydrothermal liquefaction experiment was successfully employed to reduce the heteroatom content of the produced *Agave americana* bio-oil.

Another focus of this dissertation is understanding the fate of plant materials during peatification and coalification. Humic acids were isolated from several peat swamps across the U.S. as well as a low rank collected from the Yallourn Open Cut in Australia, and analyzed using high resolution mass spectrometry and solid-state $^{13}$C NMR. From these analyses photochemically produced particulate organic matter was observed in all the samples. The presence of this material in peats and coals can likely explain the origin of ubiquitously occurring fusinite, macrinite, micrinite, and related inertinite macerals in coal.
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This dissertation is dedicated to patience and perseverance.
ACKNOWLEDGMENTS

There are several people that I would like to acknowledge and thank for their encouragement and support throughout these past five years at ODU. First and foremost I am most grateful for my advisor Patrick Hatcher. Thanks to his guidance, patience, and ongoing motivation throughout my dissertation research I was able to accomplish my goal of obtaining my Ph.D. in Chemistry. Additionally, he has taught me valuable critical thinking skills and has improved my scientific writing, for which I am most appreciative. I would also like to thank the other members of my committee, Dr. Lee, Dr. Ramjee, and Dr. Kumar, for our valuable discussions.

It is also necessary to thank all the members of the Hatcher group. The camaraderie of this research group is unique and I am fortunate to have been a part of this team. I would like to especially mention several Hatcher group members who have been particularly influential during my time at ODU. Sarah Gurganus, Albert Kamga, Wassim Obeid, Derek Waggoner, and Amanda Willoughby all have made my experience at ODU more positive and I look forward to our lifelong friendships.

I would like to thank my amazing family and friends for their unwavering support and encouragement. Although they may rarely understand my research, they continue to stay engaged and interested in my progress and accomplishments. I am especially grateful for the reassurance my parents have provided for all of my academic endeavors. It is thanks to them that I have had the confidence to pursue my academic goals. Lastly, I would like to acknowledge Rob. Throughout my time at ODU he has been my breath of fresh air, giving me a needed escape from the hectic life of graduate school. He has been there for me every day and for this I will always be grateful.
# TABLE OF CONTENTS

| LIST OF TABLES | ix |
| LIST OF FIGURES | xi |

## Chapter

### I. INTRODUCTION

#### II. ARTIFICIAL MATURATION OF SUBERAN FROM BARK AS DETERMINED BY HYDROTHERMAL LIQUEFACTION: POSSIBLE HYDROCARBON SOURCE FROM COAL

1. INTRODUCTION
2. MATERIALS AND METHODS
3. RESULTS AND DISCUSSION
4. CONCLUSIONS

#### III. HYDROTHERMAL LIQUEFACTION OF ISOLATED CUTICLE OF *AGAVE AMERICANA* AND *CAPSICUM ANNUUM*: CHEMICAL CHARACTERIZATION OF PETROLEUM-LIKE PRODUCTS

1. INTRODUCTION
2. MATERIALS AND METHODS
3. RESULTS AND DISCUSSION
4. CONCLUSIONS

#### IV. A NON-THERMOGENIC SOURCE OF BLACK CARBON IN PEAT AND COAL

1. INTRODUCTION
2. MATERIALS AND METHODS
3. RESULTS AND DISCUSSION
4. CONCLUSIONS

#### V. VALUABLE CRUDE OIL FROM HYDROTHERMAL LIQUEFACTION OF AN ALIPHATIC COAL

1. INTRODUCTION
2. MATERIALS AND METHODS
3. RESULTS AND DISCUSSION
4. CONCLUSIONS

#### VI. CONCLUSIONS AND FUTURE WORK

1. CONCLUSIONS
2. FUTURE WORK
REFERENCES .................................................................................................................... 136

APPENDICES .................................................................................................................. 153
A. COPYRIGHT PERMISSIONS ..................................................................................... 153
B. ABBREVIATIONS AND ACRONYMS ........................................................................ 156

VITA .................................................................................................................................. 159
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>II.1.</td>
<td>Proportions of C, H, and N present in the untreated YB bark and WA coal, and the spent residues and oil products produced after subjecting the YB bark and WA coal to HTL</td>
</tr>
<tr>
<td>II.2.</td>
<td>Distribution (%) of carbon atoms in untreated YB bark and WA coal, and YB bark and WA coal that has been subjected to HTL</td>
</tr>
<tr>
<td>III.1.</td>
<td>Percent distributions of C, H, N, O (based on ash-free dry weights) and HHVs of the cuticular materials and their expelled oils</td>
</tr>
<tr>
<td>III.2.</td>
<td>Percent distributions of carbon in the CPMAS-$^{13}$C NMR spectra of C. annuum cuticle and A. americana cuticle untreated and heated at 250 °C</td>
</tr>
<tr>
<td>III.3.</td>
<td>GC X GC-MS compound classes’ classification codes, total area percentage and peak count percentages corresponding to Figure III.3</td>
</tr>
<tr>
<td>III.4.</td>
<td>FTICR-MS heteroatom content and compound classes’ relative peak magnitudes and peak count percentages of the A. americana bio-oil and C. annuum bio-oil</td>
</tr>
<tr>
<td>IV.1.</td>
<td>Proportions of C, H and N present in the Okefenokee Swamp Peat HA, Pahokee Peat HA, Dismal Swamp Peat HA, Mt. Rainier wood HA, and YOC coal HA</td>
</tr>
<tr>
<td>IV.2.</td>
<td>Distribution (%) of carbon atoms in Okefenokee Swamp Peat HA, Pahokee Peat HA, Dismal Swamp Peat HA, Mt. Rainier wood HA, and YOC coal HA</td>
</tr>
<tr>
<td>IV.3.</td>
<td>Distribution (%) of biochemical classes in humic acids of the Okefenokee Swamp Peat, Pahokee Peat, Dismal Swamp, Mt. Rainier wood, and YOC coal</td>
</tr>
<tr>
<td>V.1.</td>
<td>Solid-state CPMAS-$^{13}$C NMR experimental parameters</td>
</tr>
<tr>
<td>V.2.</td>
<td>Percent abundance of macerals and sub-macerals observed in the untreated WA coal</td>
</tr>
</tbody>
</table>
Table

V.3. Proportions of C, H, N, O, S and ash present in the untreated WA coal, the spent WA coal and expelled oil product produced after subjecting the WA coal to HTL

V.4. Carbon balance of the starting dried untreated WA coal and recovered dried products and the carbon percent distributions (TC%) of the recovered products

V.5. Estimates of carbon masses of various types of carbon observed in the untreated and spent WA coal as well as the corresponding total carbon percent (TC %)

V.6. Distribution (%) of carbon atoms in untreated WA coal and WA coal that has been subjected to HTL

V.7. GC X GC-MS compound classes’ classification codes, total area percentage and peak count percentages as shown in Figure V.4A-G

V.8. GC X GC-MS sub-compound classes’ classification codes, total area percentage and peak count percentages as shown in Figure V.4A-G

V.9. FTICR-MS heteroatom content and compound classes’ relative peak magnitudes and peak count percentages
**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.1.</td>
<td>Hydrothermal liquefaction product separation procedure</td>
<td>3</td>
</tr>
<tr>
<td>II.1.</td>
<td>CPMAS-$^{13}$C NMR spectra of A) milled but chemically untreated YB bark and B) WA coal</td>
<td>21</td>
</tr>
<tr>
<td>II.2.</td>
<td>CPMAS-$^{13}$C NMR spectra of thermally altered spent residues of A) YB bark and B) WA coal</td>
<td>22</td>
</tr>
<tr>
<td>II.3.</td>
<td>py-GC-MS chromatograms of the untreated YB bark and WA coal; A) TIC of YB bark, B) EIC ($m/z$ 57) of YB bark; C) TIC of WA coal, D) EIC ($m/z$ 57) of WA coal</td>
<td>25</td>
</tr>
<tr>
<td>II.4.</td>
<td>py-GC-MS chromatograms of the YB bark and WA coal thermally altered spent residues; A) TIC of spent YB bark, B) EIC ($m/z$ 57) of spent YB bark; C) TIC of spent WA coal, D) EIC ($m/z$ 57) of spent WA coal</td>
<td>26</td>
</tr>
<tr>
<td>II.5.</td>
<td>GC-MS chromatograms of expelled oil after subjecting the YB bark to HTL; A) TIC, B) EIC ($m/z$ 57)</td>
<td>27</td>
</tr>
<tr>
<td>II.6.</td>
<td>GC-MS chromatograms of expelled oil after subjecting the WA coal to HTL; A) TIC, B) EIC ($m/z$ 57)</td>
<td>29</td>
</tr>
<tr>
<td>III.1.</td>
<td>CPMAS-$^{13}$C NMR of A) untreated <em>A. americana</em> cuticle B) <em>A. americana</em> cuticle that has been heated at 250°C for 30 min and C) untreated <em>C. annuum</em> cuticle</td>
<td>43</td>
</tr>
<tr>
<td>III.2.</td>
<td>GC-FID chromatograms of A) <em>C. annuum</em> bio-oil and B) <em>A. americana</em> bio-oil</td>
<td>49</td>
</tr>
<tr>
<td>III.3.</td>
<td>GC X GC-MS total ion chromatograms of expelled oils after subjecting the A) <em>C. annuum</em> and B) <em>A. americana</em> cuticles to HTL</td>
<td>50</td>
</tr>
<tr>
<td>III.4.</td>
<td>van Krevlen diagrams using all assigned molecular formulas from the A) <em>C. annuum</em> bio-oil and B) <em>A. americana</em> bio-oil produced after HTL</td>
<td>56</td>
</tr>
<tr>
<td>III.5.</td>
<td>H/C ratio versus number of carbon atoms per molecule for A) <em>C. annuum</em> bio-oil molecular formulas and B) <em>A. americana</em> bio-oil molecular formulas</td>
<td>59</td>
</tr>
</tbody>
</table>
Figure

IV.1. van Krevelen plots of CHO molecular formulas for humic acids isolated from the A) Okefenokee Swamp peat, B) Pahokee peat, C) Dismal Swamp peat, and D) brown-rotted wood sample (Hatcher, 1987) .................................................. 70

IV.2. A van Krevelen plot of CHO molecular formulas of photochemically produced particulate material from Dismal Swamp DOM (Chen et al., 2014) and a humic acid extract of a brown-rotted wood sample collected from Mt. Rainier, WA (Hatcher, 1987) ........................................................................................................ 73

IV.3. Percent distributions of CHO molecular formula of CCAM- (black), lignin-(dark gray), CCAM & lignin- (light gray), aromatic- (gray diagonal), and condensed aromatic like (black checkered) observed in Okefenokee Swamp peat humic acid, Pahokee peat humic acid, Dismal Swamp peat humic acid, and YOC coal humic acid........................................................................................................ 74

IV.4. Percent distributions of photoPOM CHO molecular formulas obtained from Chen et al., (2014) observed in Okefenokee Swamp peat humic acid, Pahokee peat humic acid, Dismal Swamp peat humic acid, and YOC coal humic acid........................................................................................................ 75

IV.5. A van Krevelen plot of CHO molecular formulas of humic acids isolated from a low-rank coal ........................................................................................................ 76

IV.6. MultiCPMAS-13C NMR spectra of humic acids from A) Okefenokee Swamp peat, B) Pahokee peat, C) Dismal Swamp peat, D) Mt. Rainier wood, and E) the YOC coal ........................................................................................................ 80

V.1. Photomicrograph of the untreated coal in blue light excitation, magnified 500x. A) cutinite, B) sporinite, C) mixture of cutinite and suberinite, D) amorphinite and E) inertodetrinite ........................................................................................................ 101

V.2. CPMAS-13C NMR spectra of the untreated WA coal and the thermally altered spent coal residue utilizing experimental parameters listed in Table V.1........................................................................................................ 104

V.3. GC-FID chromatograms of A) the expelled oil after subjecting the WA coal to HTL where n-alkanes have been labeled with a triangle and B) a 3:1 DCM:MeOH Soxhlet extract of the untreated WA coal ........................................................................................................ 109

V.4. TIC and EIC GC X GC-MS chromatograms of expelled oil ........................................................................................................ 110
Figure

V.5. Distribution of peak intensities of $n$-alkanes observed in GC X GC-MS chromatogram (Fig. V.4A) of the expelled oil from HTL treatment of WA coal .................................................................113

V.6. A van Krevlen diagram using all assigned molecular formulas from the expelled oil collected after HTL of the WA coal .................................................................119

V.7. H/C ratio versus number of carbon atoms per molecule for A) CHO compounds, B) CHOS compounds, C) CHON compounds and D) CHONS compounds .................................................................121

V.8. Distribution of peak magnitudes of saturated fatty mono-acids (blue) and saturated fatty di-acids (red) observed in FTICR-MS analysis of the expelled oil from HTL treatment of WA coal .................................................................123
CHAPTER I
INTRODUCTION

Energy has become an essential component of our everyday life that many have come to depend on. Currently, the primary sources of energy are non-renewable fossil fuels, encompassing petroleum, coal, and natural gas which represent approximately 80% of global energy consumption (USA EIA, 2012; Höök and Tang, 2013). Since 1980 consumption of fossil fuels has increased 70% globally and has risen 21% in the United States (USA EIA, 2012). The reality shows that fossil fuels are in limited quantities and are likely not able to meet our energy demands, additionally, the exploration, processing, and use of these energy types inflict serious damage to the environment. These concerns regarding energy security and impacts on the environment has triggered an increased interest in the development and utilization of renewable energy. While there are many established technologies relating to the production of alternative energy, in the case of alternative transportation fuels, hydrothermal liquefaction (HTL) of biomass materials is particularly promising.

HTL is a technique used for the reduction of organic material, such as biomass and biowaste, into crude oil. The technique has gained attention in the alternative fuel community due to its relatively low costs, ease of implementation, and lack of a need for catalysts and/or solvents therefore making it environmentally friendly. Furthermore, HTL is able to closely simulate the naturally-occurring thermal maturation of organic material, thus is often employed by Organic Geochemists to examine the formation of petroleum from various source rocks (Burnham and Braun, 1990; Lewan et al., 1985). Generally,

This dissertation is formatted based on the journal Organic Geochemistry.
maturation experiments require long contact times in order to simulate the C-C cracking that occurs during catagenesis, and are commonly referred to as hydrous pyrolysis experiments. Conversely, in the bio-fuel community short contact times are implemented in an effort to yield the maximum amount of bio-oils with minimal expended energy. These types of experiments are regarding as HTL. For the purpose of consistency with chapters within this dissertation that have been published in the literature, the term HTL will be used throughout this dissertation to describe maturation experiments; however, the focus of this dissertation is on both the production of bio-oils from biowaste materials and on examining the geochemical alternations that occur to plant biopolymers upon burial, thus also making it appropriate to refer to the maturation experiments as hydrous pyrolysis.

HTL is an approach that involves the use of water in contact with a sample at subcritical temperatures (200-370 °C), high pressures (4-20 MPa) (Behrendt et al., 2008; Tekin et al., 2014), and an oxygen free environment all within a closed system. A key advantage of HTL over other thermochemical methods, specifically fast pyrolysis, is that since water is the reaction medium there is no need for an energy consuming drying step (Bridgwater et al., 1999). The primary products that are generated from HTL are char, water-soluble compounds, expelled bio-oils, and gases. A schematic of the HTL product collection procedure is shown in Figure I.1.

Numerous studies, such as those conducted by Lewan et al. (1979), Lewan (1983), and Winters et al. (1983), have demonstrated the ability of HTL to simulate the natural, thermal maturation of organic material. In the study conducted by Lewan et al. (1979), crushed organic rich Woodford Shale were heated at 330 °C for 3-4 days and the produced pyrolyzates were chemically similar to natural crude oil. Although the temperatures
utilized in HTL may be 200-250 °C higher than natural petroleum generation conditions to offset the longer time requirements (10^6 to 10^8 years), it was observed from Lewan et al. (1979) and Winters et al. (1983) that the higher temperatures used during HTL increases the reaction rate, but results in negligible differences on the gross properties between the expelled petroleum HTL products and a natural crude oil. Additionally, it was observed that the oils produced through other retorting and pyrolysis methods, such as anhydrous pyrolysis and hydrogasification, did not yield pyrolyzates that were chemically similar to natural crude oils (Lewan et al. 1979).

**Figure I.1.** Hydrothermal liquefaction product separation procedure.
The chemical reactions that occur during HTL are highly dependent on the feedstock materials and their substrates, i.e., carbohydrates, proteins, lignin, etc.; however a brief explanation can be provided. When organic material is heated to subcritical temperatures (360 °C) homolytic cleavage of weak bonds occurs resulting in free-radicals which, in the presence of water, can be capped by hydrogen abstraction from water (Hoering, 1984; Lewan, 1997). This results in the formation of low molecular weight hydrocarbons, mainly alkanes (Lewan, 1997). In order for these reactions to occur it is crucial that liquid water, not vapor or subcritical fluid, be in contact with the organic matter. To ensure that enough water will be present in the liquid form at the desired temperature equation I.1 is used.

\[ V_w^T = \frac{M_w - V_R \rho_v^T}{\rho_w^T - \rho_v^T} \quad (I.1) \]

\( V_w^T \) is the volume of water at the experimental temperature, \( M_w \) is the mass of the water added to the reaction autoclave at room temperature, \( V_R \) is the reaction autoclave volume, \( \rho_v^T \) and \( \rho_w^T \) are the specific volumes of the vapor phase and liquid phase, respectively, at the experimental temperature.

Water at ambient conditions (25 °C, 0.1 MPa) is a polar solvent dominated by a network of H-bonding and exhibits a high dielectric constant (78). As water is heated its chemical properties drastically change. The intricate network of H-bonding begins to weaken resulting in water dissociating into hydronium (H₃O⁺) and hydroxide (OH⁻) ions. When temperatures reach the critical point (374 °C, 22.1 MPa), the dielectric constant of water decreases dramatically, from 78 to 20 (Tester et al., 1993; Uematsu and Frank, 1980), resulting in water behaving more similarly to an organic solvent, such as acetone and isopropyl alcohol. Additionally, at near critical point temperatures water’s ionization constant increases approximately three orders of magnitude resulting in higher
concentrations of $H^+$ and $OH^-$ (Franck, 1987; Savage, 1999). Due to the unique properties water exhibits near the critical point, water is able to simultaneously act as the reactant and catalyst. This results in several reactions occurring at once, including hydrolysis, depolymerization, and repolymerization/self-condensation (Yin et al., 2010).

In organic geochemistry it is generally accepted that fossil fuels are the product of biomass materials buried in sediment and subjected to various degrees of maturation. Upon burial, organic matter undergoes several physicochemical transformations which are largely controlled by 1) biological activity, 2) temperature, and 3) pressure (Tissot and Welte, 1978). In general, labile compounds present in organic matter, such as carbohydrates and proteins, are destroyed by microbial activity during diagenesis. With the increasing temperature and pressure the remaining organic material evolves to invoke polycondensed structures, termed humin by soil scientists (Rice, 2001; Tegelaar et al., 1989; Tissot and Welte, 1978). Further burial results in the hydrolysable fraction of humin decreasing and ultimately leading to the formation of kerogen, which is defined as the sedimentary organic matter that is insoluble in organic solvents and a known precursor to petroleum (Durand, 1980; Tissot and Welte, 1984).

Kerogens are classified as Type I, Type II, Type III, and Type IV. It has been observed that kerogens with high H/C ratios (>1.2) have a high petroleum generating potential (Dow, 1977; Peters et al., 2005) which applies to Type I and Type II kerogens. Type I and II kerogen are dominated by aquatic plants; Type I kerogens are predominately lipid-rich algal debris and Type II kerogens originate from phytoplankton, zooplankton, and bacterial debris common to marine sediments (Peters et al., 2005; Tissot and Welte, 1978). The other two kerogen types are not known to demonstrate the same petroleum producing potential.
as Types I and II. Type III kerogen originates from land plants and typically yields gas products, and Type IV kerogen is inert and does not generate a significant amount of hydrocarbons (Peters et al., 2005). In the case of Type III kerogens, if the organic matter content is greater than 50% of the deposit, then the material is commonly referred to as coal.

It is believed that kerogens enriched in aliphatic biopolymers are more likely to be oil prone (Goth et al., 1988; Tegelaar et al., 1989). In Types I and II kerogens, marine and lacustrine sediments, primarily comprised of algal derived material, are the likely source of the aliphatic biopolymers (Dow, 1977; Pepper and Corvi, 1995). Algaenan has been identified in a number of microalgae and is characterized as a highly aliphatic, non-hydrolyzable, insoluble macromolecule (Berkaloff et al., 1983; Tegelaar et al., 1989). Numerous studies have demonstrated the selective perseveration of algaenan in kerogens (Derenne et al., 1991; Derenne et al., 1992; Goth et al., 1988) which is consistent with the high oil potential of Type I and II kerogens.

Similar to algae, terrestrial plants also contain aliphatic biopolymers, cutin, suberin, cutan, and suberan (Boom et al., 2005; Kolattukudy, 1980; McKinney et al., 1996; Tegelaar et al., 1995; Turner et al., 2013). Unfortunately, there is limited information regarding the thermal alteration of vascular plant material which is a known precursor of coal or Type III kerogen. Accordingly one of the overarching goals of this dissertation is to improve the chemical understanding regarding the geological preservation of terrestrial plant biopolymers within coals and kerogens and their ability to produce petroleum-like hydrocarbons using HTL. The aliphatic biopolymers, cutin, suberin, cutan, and suberan are thought to be resistant to biochemical degradation and have the potential to yield similar
hydrocarbon products with thermal maturation due to their highly aliphatic composition. In ancient deposits, effects of burial (time and temperature) are likely to transform part of these aliphatic materials to fossil fuels. While this has been suggested in the literature through analytical characterization studies, it is far from being established. Chapters II (suberan) and III (cutin and cutan) examine the alterations that occur to these terrestrial biopolymers when subjected to HTL. Advance analytical techniques are utilized to provide an enhanced characterization of both the feedstock materials and their expelled oil products, which is necessary in accessing their application as an alternative fuel.

Cutin and suberin are saponifiable polymethylenic polyesters. Cutin is contained in the cuticular material of plants and fruits and its structure is primarily composed of C\textsubscript{16} and C\textsubscript{18} monomeric alkyl units along with alcohol and acid functionality (Kolattukudy, 1980; Deshmukh et al., 2003). Suberin is localized in the bark and roots of plants and is mainly comprised of C\textsubscript{16}, C\textsubscript{18}, C\textsubscript{22}, C\textsubscript{24} monomers, where the abundance of the monomers is dependent on the plant species (Holloway, 1984; Turner et al. 2013). Both cutan and suberan are polymethylenic biopolymers that are the non-extractable and non-hydrolyzable portion of leaf and bark material, respectively (Deshmukh et al., 2005; McKinney et al., 1996; Tegelaar et al., 1995; Turner et al., 2013). Both of these biopolymers act as protective layers that prevent desiccation and are resistant to microbial infections. Cutan’s structure has been found to be crystalline comprised of long chain C\textsubscript{7}-C\textsubscript{33} polymethylenic groups with alcohol, aromatic, epoxide, and acid functional groups (Boom et al., 2005; Deshmukh et al., 2005; McKinney et al., 1996; Schouten et al., 1998). Similarly, suberan’s structure is also crystalline with alkyl chain lengths C\textsubscript{18}, C\textsubscript{20}, and C\textsubscript{22} (the most abundant) with alcohol, acid, and a small amount of epoxide functional groups.
(Turner et al., 2013).

It is clear that aliphatic biopolymers found in the barks and leaves of terrestrial plants provide a source of organic matter for modern and ancient sedimentary systems, specifically in coal bearing strata. When terrestrial plants are buried in peats and other such organic environments they become the progenitors of coals or Type III kerogens in carbonaceous shales (Hatcher and Clifford, 1997; Scott, 2002; Teichmüller, 1989). While some of the terrestrial organic matter may settle to the surface layer of the peat unaltered, another fraction becomes dissolved organic matter (DOM) and is exposed to microbial and photochemical alterations in the water column (Chen et al., 2014; Obernosterer and Benner, 2004; Stach et al., 1982; Stubbins et al., 2010) ultimately chemically changing the dissolved and particulate material. Thus understanding the fate of DOM can yield crucial insight regarding precursor materials of coals and, in some cases, petrographically distinct submacerals. In Chapter IV the fate of photochemically altered DOM in peats and a low rank coal are investigated. Peat samples collected from several locations across the United States and a low rank coal collected from the Yallourn Open Cut in Australia are examined to determine the occurrence of photochemically produced organic material originally observed by Chen et al. (2014) and if these materials are geologically preserved.

While some coal macerals predecessor material is ambiguous, other macerals have a more clearly defined origin, as is the case of the coal maceral crypto-eugelinite. Crypto-eugelinite is often observed in location of cracks and crevices formally occupied by roots of plants or cell cavities (Taylor et al., 1998), and likely originated from root material. Coal macerals are often categorized based on their microscopy architecture (Stach et al., 1982; Taylor et al., 1998) as is the case of crypto-eugleinite. According to the International
Committee for Coal Organic Petrology, crypto-eugelinite is defined as precipitated, formless, humic gels of the huminite group that do not fluoresce (Taylor et al., 1998). However, the chemical composition of this maceral is not well defined, which could provide valuable information regarding its oil generating potential. Crypto-eugelinite is often observed in spaces previously occupied by roots, aliphatic moieties from the biopolymer suberan previously present in the roots may be abundant. In Chapter V examines the effectiveness a low rank coal containing crypto-eugelinite has to produce a high quality hydrocarbon-rich oil through HTL. The results of this chapter yield a detailed characterization of the starting coal material and the expelled oil products, and overall demonstrate application of HTL as an effective technique to generate petroleum-like products.

To summarize, the aim of this dissertation is to further the understanding of chemical alterations that occur to aliphatic biopolymers during peatification and coalification using the artificial maturation technique, HTL. I hypothesize that the aliphatic biopolymers found in vascular plant materials will yield high quality bio-fuels and contribute the aliphatic moieties necessary for coals to be oil producing. Through the use of advance analytical techniques, such as solid-state nuclear magnetic resonance, Fourier transform ion-cyclotron resonance mass spectrometry, and two dimensional gas chromatography-mass spectrometry, an in depth chemical characterization of the original and spent feedstock materials as well as their expelled oils is accomplished that will be essential in understanding geochemical transformations as well as the feedstocks’ applications as alternative fuels. From the studies outlined in this dissertation I will demonstrate and utilize HTL as a method to generate petroleum-like products from biomass materials and coal,
couple several data sets to accurately characterize the complex expelled oil samples as well as humic acids isolated from peats and coals, and finally I will reveal the ability of highly aliphatic biopolymers, specifically cutan, cutin, and suberan, to generate petroleum-like compounds.
CHAPTER II
ARTIFICIAL MATURATION OF SUBERAN FROM BARK AS DETERMINED
BY HYDROTHERMAL LIQUEFACTION: POSSIBLE HYDROCARBON
SOURCE FROM COAL

Preface

The majority of the material contained within this chapter was published in the 14th International Conference on Coal Science and Technology held in October 2013. Below is the full citation.


1. Introduction

In recent years there has been an increased interest in the artificial generation of liquid hydrocarbons for use in alternative fuels production. Certainly coals and biomass have been shown to produce oily liquids when subjected to artificial maturation; however there is limited information concerning the production of petroleum-like hydrocarbons from the thermal alteration of vascular plant material, a known precursor of coal or Type III kerogen. In organic geochemistry it is generally accepted that Type III kerogens and coals have low oil-generative potential (Durand, 1980; Peters et al., 2005); however this is a generalization that is not universal, especially when one considers that some terrestrially-derived plants
or plant tissues can have the potential to generate hydrocarbons during thermal treatment (Nip et al., 1986). Numerous studies, books, and reviews (Collinson et al., 1994; Difan et al., 1991; Hunt, 1991; Snowdon and Powell, 1982; Tissot et al., 1978; Wilkins and George, 2002) have evaluated the importance of coal as a petroleum source, yet the topic remains open for discussion.

It is believed that in order for coals to be oil producing they must contain a high hydrogen content (Collinson et al., 1994; Hunt, 1991; Wilkins and George, 2002). For example, coal containing 10% dry-ash-free weight of hydrogen can have an 80% oil yield (Saxby and Shibaoka, 1986). Early opinion was that the coal maceral liptinite, which is derived from lipid-rich components of plants (Peters et al., 2005a; Tissot and Welte, 1978), was the component of coal that contributed to the production of liquid hydrocarbons; whereas the other common non-liptinitic macerals were not prone to produce liquid hydrocarbons. The maceral huminite, found in brown coals, and vitrinite, found in bituminous hard coals, were considered to only generate hydrocarbon gases and inertinite was not prone to generating any type of hydrocarbon (Wilkins and George, 2002). Recently, there has been some dispute regarding these claims and it has been suggested that the oil-generating potential of coal is more dependent on the amount aliphatic moieties present in coals rather than a specific maceral (Isaksen et al., 1998; Petersen, 2006). In the case of huminite and vitrinite, which are derived from higher order plant material (Tissot et al., 1978), the aliphatic biopolymers cutan and suberan, which are present in the leaf and bark material of land plants (Deshmukh et al., 2005; McKinney et al., 1996; Tegelaar et al., 1995; Turner et al., 2013), could provide the aliphatic moieties necessary for oil production (Mukhopadhyay and Hatcher, 1993).
Suberan is an aliphatic biopolymer that is present in the bark and root material of terrestrial plants that acts as a protective layer to prevent desiccation and is resistant to microbial infections. Suberan differs from a similar bark and root biopolymer, suberin, in that suberan is the non-extractable and non-hydrolyzable portion of root and bark material (Nierop, 1998; Tegelaar et al., 1995; Turner et al., 2013). Suberan’s structure is predominately crystalline with alkyl chain lengths $C_{18}$, $C_{20}$, and $C_{22}$ (the most abundant) with alcohol, acid, and a small amount of epoxide functional groups (Turner et al., 2013).

In this particular study a low rank lignite rich in crypto-eugelinite, which is a submaceral of huminite, is examined. Crypto-eugelinite is observed in reflected light microscopy after etching of the submaceral levigelinite and is common in low rank coals (Sýkorová et al., 2005). Located in the cracks and crevices formally occupied by roots of plants or cell cavities (Taylor et al., 1998), crypto-eugelinite likely originated from root material. The chemical composition of crypto-eugelinite is not well defined; however, based on its presence in spaces previously occupied by roots, aliphatic moieties from suberan previously present in the roots may be abundant. Over 80% of the world’s coals are humic and contain the maceral huminite (Hunt, 1991). Being able to artificially generate liquid hydrocarbons from coal rich in aliphatic material would provide a beneficial and important source of liquid fuel resources.

A laboratory technique that has the ability to closely simulate the natural thermal maturation of fossil organic material is hydrothermal liquefaction (HTL). HTL is an approach that involves the use of subcritical liquid water in the absence of oxygen to artificially mature coal and kerogen samples. When organic material is heated to subcritical temperatures ($360 ^\circ C$) homolytic cleavage of weak bonds occurs resulting in free-radicals...
which, in the presence of water, can be capped by hydrogen abstraction from water (Hoering, 1984). The process generates low molecular weight hydrocarbons, mainly alkanes (Lewan, 1997).

In this study I employ and demonstrate the effectiveness of subcritical HTL for the artificial maturation of lignite coal and some potential precursor material, bark from an extant tree, to produce a hydrocarbon-rich oil dominated by $n$-alkanes. The bark of Yellow Birch (*Betula alleghaniensis*, YB) and a lignite rich in crypto-eugelite collected from the Wyodak-Anderson (WA) coal seam of the Powder River Basin of Wyoming are utilized for this study. It is important to mention that the YB bark is only examined here as an example of a plant tissue that contains suberan and it is not mean to imply that YB trees contributed to the organic matter in the WA coal. The assumption is made that bark of ancient trees may have contained suberan of the type found in YB and that the biopolymer suberan is likely to have contributed to the coal. As will be discussed below, both samples show great potential for oil production as demonstrated by flash pyrolysis-gas chromatography-mass spectrometry (py-GC-MS) and nuclear magnetic resonance (NMR). Samples of cleaned, milled YB bark and milled WA coal, collected from a zone that was predominately composed of crypto-eugelite (Warwick and Stanton, 1988b), were subject to HTL. Products collected after HTL included solid residues and expelled oils. The original samples and HTL residues (oils and spent solid residues) were subjected to py-GC-MS, GC-MS, NMR, and elemental analysis (EA).
2. Materials and methods

2.1. Materials

2.1.1. Yellow Birch bark

The bark of YB (*Betula alleghaniensis*) trees located in Blacksburg, VA was utilized for this study. YB trees naturally exfoliate their bark and therefore samples were collected by gently peeling the bark away from the tree without inflicting harm or damage to the tree. Prior to HTL treatment the bark was washed with DI water, lyophilized, and ground to 20 mesh using a Wiley mill.

2.1.2. Wyodak-Anderson coal

A low rank lignite collected from the Wyodak-Anderson coal seam of the Powder River Basin was used for this study. Additional details regarding the collection site can be found in Hartman and Hatcher (2014). The coal was lyophilized and milled (20 mesh) prior to HTL treatment.

2.2. Hydrothermal liquefaction

The HTL conditions employed in this study followed previously reported conditions (Hartman and Hatcher, 2014) and will be described briefly. Samples (approximately 1 g bark and 3 g coal) were packed into 22 mL stainless steel autoclaves in the presence of 7 g milli-Q water. The headspace was flushed with Ar gas for approximately 3 min to remove oxygen. The prepare autoclaves were then heated at 360 °C for 72 h. Upon completion of the HTL treatment, the autoclaves were immediately placed in an ice bath to halt all reactions. Analyses were conducted on the remaining spent residues and the expelled oil products.
2.3. **Elemental analysis**

The proportions of C, H, and N in the feedstock materials, spent solids, and expelled oils were determined using a Flash 1112 series Elemental Analyzer. The samples were run in triplicate and their response areas were fit to standard curves of nicotinamide (C and H) and L-aspartic acids (N). Ash content of the feedstock materials and the spent residues was determined from the dry sample weights before and after oxidation in a muffle furnace at 425 °C for 2 h followed by 725 °C for 2 h and cooling in a desiccator. Oxygen content was determined by difference.

2.4. **Flash pyrolysis (py)-GC-MS**

Py-GC-MS experiments were conducted on the YB bark and the WA coal using a Chemical Data Systems (CDS) Pyroprobe 2000 Plus pyrolysis system connected online to a LECO Pegasus II GC- Time of Flight Mass Spectrometer (TOFMS) system. Approximately 0.40 mg of sample was placed into a quartz capillary tube fitted with a quartz spacer and covered with quartz wool. Samples were dropped into the pyrolysis chamber (300 °C) using an auto sampler and flash pyrolysis occurred by rapidly heating (0.01 °C/ms) the chamber to 650 °C and held for 15 s. The gaseous products generated were transferred to the GC using a flow of He through a transfer line held at 300 °C.

The pyrolysis products were introduced into the GC using a 50:1 split. The GC separation was achieved using a non-polar Restek Rtx-5 column (30 m x 0.25 mm x 0.25 µm 5% phenyl-95% dimethyl polysiloxane). The carrier gas was He at a constant flow rate of 1.0 mL min⁻¹. The temperature program was as follows: initial temperature of 50 °C held for 1 min, followed by a 15 °C/min ramp to reach a final temperature of 300 °C and held for 10 min.
The TOF transfer line temperature was 280 °C, the electron ionization mode was set to 70 eV, and the MS ion source temperature was 200 °C. The MS detector voltage was set to 1950 V and the data acquisition rate was 20 spectra sec\(^{-1}\) over a mass range of 35-500 Da. The total ion chromatogram (TIC) was processed using LECO ChromaTOF optimized for Pegasus software implementing a signal to noise (S/N) of 10.

2.5. **Solid-state CPMAS-\(^{13}\)C NMR spectroscopy**

Solid-state \(^{13}\)C NMR analyses of the untreated bark and coal and spent solids were performed using a 400 MHz Bruker AVANCE II spectrometer equipped with a solid-state MAS probe. Experimental conditions follow previously reported procedures (Hartman and Hatcher 2015). Briefly, all samples employed the following experimental conditions: 11 kHz spinning speed, 0.7 ms contact time, and a 1 s recycle delay. The feedstock materials were run using 32,000 scans whereas the spent residues were run at 2,000 scans. Cross polarization \(^{13}\)C NMR spectra were obtained with the basic ramp cross polarization pulse program (cp.av) with a two pulse phase modulated decoupling. Chemical shift calibration was performed with a glycine secondary standard and referenced to the carboxyl signal at 176 ppm.

2.6. **GC-FID**

GC analyses were performed according to previously reported experimental conditions (Hartman and Hatcher, 2014), using an HP6890N GC-Flame Ionization Detector (FID) equipped with a Rtx-5 column (30 m x 0.25 mm x 0.25 µm of 5% phenyl-95% dimethyl polysiloxane) supplied by Restek (USA).

2.7. **GC-MS**

One dimensional GC-MS analyses of the expelled oils were performed using a
Hewlett-Packard HP 6890 GC system equipped with a split/splitless injector (HP 6890 Injector) coupled to a LECO Pegasus III Time of Flight Mass Spectrometer (TOFMS). Samples were injected in 1 µL volumes using the split mode at a split ratio of 50:1. The chromatographic column used was a Rtx-5 column (30 m x 0.25 mm x 0.25 µm of 5% phenyl-95% dimethyl polysiloxane) supplied by Restek (USA). He gas was the carrier gas with a constant flow rate of 1.0 mL min⁻¹. The temperature program was as follows: 50 °C for 2 min, 10 °C min⁻¹ to 300 °C and held at 300 °C for 10 min.

The TOF transfer line temperature was 280 °C, the electron ionization mode was set to 70 eV, and the MS ion source temperature was 200 °C. The MS detector voltage was set to 1400 V and the data acquisition rate was 20 spectra sec⁻¹ over a mass range of 45-500 Da. Chromatograms were produced using LECO ChromaTOF optimized for Pegasus 4D software implementing a signal to noise (S/N) of 1000.

3. Results and discussion

3.1. Feedstock composition

3.1.1. Elemental analysis

The percent compositions of C, H, N, and O present in the untreated YB bark, the spent solid, and the produced oil after subjecting the YB bark to HTL at 360 °C for 72 h are shown in Table II.1. Similar data for untreated WA coal, its spent solid, and the produced oil after subjecting the WA coal to HTL at 360 °C for 72 h are also shown in Table II.1. The C, H, and N composition of the untreated YB bark is similar to the composition observed for suberan from River Birch bark (Turner et al., 2013). The similarities observed between the elemental compositions of the bark and the biopolymer supports the hypothesis that the YB bark contains an abundance of suberan biopolymers. Both the
YB bark and the WA coal have elemental compositions that are predominantly carbon and have H/C ratios of 1.72 and 1.48, respectively. These high H/C ratios suggest that the untreated bark and the WA coal have substantial aliphatic character, which is supported by py-GC-MS discussed below.

Table II.1. Proportions of C, H, N, and O present in the untreated YB bark and WA coal, and the spent residues and oil products produced after subjecting the YB bark and WA coal to HTL. C, H, N, and O are reported on a dry, ash free basis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% Ash average</th>
<th>% O</th>
<th>molar H/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Yellow Birch bark</td>
<td>61.28 ± 0.51</td>
<td>8.78 ± 0.07</td>
<td>0.56 ± 0.01</td>
<td>0.52 ± 0.36</td>
<td>29.36 ± 0.51</td>
<td>1.71 ± 0.02</td>
</tr>
<tr>
<td>Spent Yellow Birch bark</td>
<td>76.58 ± 0.21</td>
<td>5.82 ± 0.14</td>
<td>1.01 ± 0.09</td>
<td>9.78 ± 2.44</td>
<td>7.53 ± 2.01</td>
<td>0.91 ± 0.04</td>
</tr>
<tr>
<td>Yellow Birch bark expelled oil (neat)</td>
<td>74.06 ± 1.31</td>
<td>10.47 ± 0.15</td>
<td>0.25 ± 0.12</td>
<td>0.34 ± 0.19</td>
<td>15.19 ± 1.34</td>
<td>1.69 ± 0.04</td>
</tr>
<tr>
<td>Untreated Wyodak-Anderson coal</td>
<td>57.64 ± 1.21</td>
<td>7.08 ± 0.16</td>
<td>0.39 ± 0.05</td>
<td>12.40 ± 2.00</td>
<td>34.67 ± 1.22</td>
<td>1.46 ± 0.03</td>
</tr>
<tr>
<td>Spent WA coal</td>
<td>81.53 ± 2.95</td>
<td>5.81 ± 0.38</td>
<td>0.59 ± 0.28</td>
<td>24.05 ± 1.40</td>
<td>12.07 ± 2.99</td>
<td>0.54 ± 0.01</td>
</tr>
<tr>
<td>WA coal expelled oil (neat)</td>
<td>73.44 ± 1.65</td>
<td>10.85 ± 0.21</td>
<td>0.39 ± 0.03</td>
<td>1.14 ± 0.17</td>
<td>15.31 ± 1.66</td>
<td>1.77 ± 0.05</td>
</tr>
</tbody>
</table>

The elemental compositions of both the untreated YB bark and WA coal change significantly after subjecting the materials to HTL, as is demonstrated by the drastic decrease in the H/C ratios for the spent solids. The YB bark H/C ratio decreases from 1.71 to 0.91 and the WA coal demonstrates a similar H/C ratio drop, decreasing from 1.46 to 0.54. Low H/C ratios of the solid materials that remain after the HTL treatment indicate that the remaining solids have a higher degree of aromaticity, which is expected with increased thermal maturation (Durand, 1980). The H/C ratios for the solid materials are
consistent with the NMR data discussed below. The expelled oils from the HTL treatments of the YB bark and the WA coal both display an H/C ratio that is consistent with what would be expected for oils rich in $n$-alkanes. The expelled oil associated with the YB bark has an H/C ratio of 1.69 and oil associated with the WA coal has an H/C ratio of 1.77.

### 3.1.2. Solid-state CPMAS-$^{13}\text{C}$ NMR spectroscopy

CPMAS-$^{13}\text{C}$ NMR spectra of the milled but chemically untreated bark and coal (Fig. II.1) along with the relative peak areas for the various functional groups listed in Table II.2, show that both samples contain a large fraction of aliphatic and aromatic functional groups. In Figure II.1, the aliphatic region for both the bark and the coal are dominated by two intense peaks at 30 ppm and 33 ppm. These peaks are characteristic of amorphous (30 ppm) and crystalline (33 ppm) polymethylenic chains that have previously been associated with the terrestrial biopolymers cutan and suberan (Hu et al., 2000; Turner et al., 2013). It is well known that certain biopolymers, such as cutan and suberan, are biologically and chemically resistant and able to survive early diagenetic transformations (Nip et al., 1986; Tegelaar et al., 1989; Tegelaar et al., 1995), thus enabling these biopolymers to be incorporated into coals (Hatcher and Clifford, 1997; Scott, 2002). Based the knowledge that crypto-eugelinite, which is the abundant submaceral in the WA
Figure II.1. CPMAS-$^{13}$C NMR spectra of A) milled but chemically untreated YB bark and B) WA coal.
Figure II.2. CPMAS-\textsuperscript{13}C NMR spectra of thermally altered spent residues of A) YB bark and B) WA coal.

Table II.2. Distribution (%) of carbon atoms in untreated YB bark and WA coal, and YB bark and WA coal that has been subjected to HTL. Distribution of samples determined from solid-state CPMAS-\textsuperscript{13}C NMR spectroscopy.

<table>
<thead>
<tr>
<th>Sample</th>
<th>\textsuperscript{13}C Chemical Shift (ppm)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aliphatic (0-45)</td>
<td>Methoxy (45-60)</td>
</tr>
<tr>
<td>Untreated Yellow Birch bark</td>
<td>63</td>
<td>6</td>
</tr>
<tr>
<td>Spent Yellow Birch bark</td>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>Untreated WA coal</td>
<td>66</td>
<td>5</td>
</tr>
<tr>
<td>Spent WA coal</td>
<td>41</td>
<td>3</td>
</tr>
</tbody>
</table>
coal sample, is found in peats and originates in the cracks and crevices formally occupied by roots (Taylor et al., 1998), it is likely that the 30 and 33 ppm signals for both the bark and the coal are associated with suberan. The abundant amounts of aliphatic functionality present in the bark and coal samples (Table II.2) indicate that these samples have the potential to generate petroleum products upon thermal maturation.

The aromatic components in both the bark and the coal are likely related to lignin. The peaks 56, 115, 130, and 150 ppm are attributed to methoxy, H-substituted aromatic, C-substituted aromatic, and O-substituted aromatic compounds, respectively. The presence of these classical lignin peaks in the coal spectrum confirm that the coal is made up of some lignin-derived components. The two peaks located at 143 ppm and 153 ppm in the coal spectrum represent catechol-like and phenolic structures. Hatcher and Clifford (1997) showed that these peaks are indicative of woody textinite components of the coal transitioning between lignite and subbituminous coal ranks. Additional characterization of the macerals found in the coal are described in Chapter V.

After subjecting the YB bark and the WA coal to HTL, the thermally altered spent residues are analyzed by solid-state CPMAS-$_{13}$C NMR and the spectra are displayed in Figure II.2 with relative peak areas shown in Table II.2. The most apparent changes observed between the untreated bark and coal and the remaining solid residues after HTL are the loss of aliphatic functional groups and the gain of aromatic functional groups. As previously indicated by the H/C ratio, the aromatic functionality of the bark and coal increases upon hydrothermal treatment based on the relative peaks areas listed in Table II.2. The aromatic functionality of YB bark increased from 8% relative peak area to 32% and the WA coal aromatic functionality increased from 19% to 38%. The increase in
aromatic functionality is consistent with other artificial maturation studies of coals and biomass (Behar and Hatcher, 1995; Orem et al., 1996), where the characteristic lignin peaks no longer persist. The decrease in the relative peak area of the aliphatic region is due to the cracking of aliphatic C-C bonds which lead to the production of hydrocarbon-rich liquid products. The crystalline and amorphous peaks associated with suberan at 30 and 33 ppm can be observed in the spectra of the respective spent residues, but this indicates that a longer time heating is probably necessary to completely convert the aliphatic functionality to additional expelled oil.

3.1.3. Flash pyrolysis data

Flash pyrolysis data for the YB bark and WA coal are shown as both total ion chromatograms (TICs) and extracted ion chromatograms (EICs) in Figure II.3. The TICs of both the bark and coal display the complex mixture of products produced during pyrolysis whereas the EICs display the compounds containing the m/z 57, which are mainly n-alkanes and n-alkenes or branched alkanes/alkenes. In both samples a homologous n-alkane and n-alkene series is observed ranging from C9-C31 in the YB bark and from C9-C33 in the WA coal, indicating that both samples are highly aliphatic and made up of long-chain polymethylenic structures. A similar homologous series has been observed for suberan (Turner et al., 2013), and this suggests the presence of suberan in the bark and coal samples. Nip et al. (1986) observed a similar pattern in fossil cuticular coal material that is also thought to be derived from an aliphatic biopolymer, in this instance cutan. It is possible that the aliphatic biopolymers in the WA coal are cutan-related. The majority of the observed peaks in the TICs of the bark and coal samples (Fig.
Figure II.3. py-GC-MS chromatograms of the untreated YB bark and WA coal; A) TIC of YB bark, B) EIC ($m/z$ 57) of YB bark; C) TIC of WA coal, D) EIC ($m/z$ 57) of WA coal.

II.3A and C) are associated with $n$-alkanes and $n$-alkenes which are displayed in Figure II.3B and D using the $m/z$ 57. The two prominent peaks at 11 and 14 min in Figure II.3C have been identified as prist-1-ene and a benzofuran-like compound most likely produced from the condensation of catechols, respectively. Prist-1-ene is likely a product of chloroplast material (Nip et al., 1986), whereas the benzofuran-like compound is a structure that is consistent with the kinds of reactions taking place in wood-derived macerals (Hatcher and Clifford, 1997). The abundance of $n$-alkane and $n$-alkene products suggests that upon heating the YB bark and WA coal have the potential to yield petroleum-like products.
Figure II.4. py-GC-MS chromatograms of the YB bark and WA coal thermally altered spent residues; A) TIC of spent YB bark, B) EIC \((m/z\) 57) of spent YB bark; C) TIC of spent WA coal, D) EIC \((m/z\) 57) of spent WA coal.

The thermally altered spent residues of the YB bark and WA coal that remain after HTL were also subjected to py-GC-MS analysis and the chromatograms are displayed in Figure II.4. It is clear in both the TICs and the EICs that, even after thermal treatment the bark (Fig. II.4A and B) and coal spent residues (Fig. II.4C and D) maintain a homologous \(n\)-alkane and \(n\)-alkene pattern. This implies that suberan is highly resistant to thermal degradation and is a main contributor of \(n\)-alkanes in systems that potentially form Type III kerogen. The WA coal chromatograms, both before and after thermal alteration (Fig. II.3C and D, Fig. II.4C and D), display an odd-over-even predominance in chain lengths...
Figure II.5. GC-MS chromatograms of expelled oil after subjecting the YB bark to HTL; A) TIC, B) EIC (m/z 57).
longer than C19. A predominance of odd number carbon has been suggested to be associated with immature source rocks of terrestrial origin (Chaffee et al., 1983; Tissot and Welte, 1978).

3.2. Expelled oil characterization

3.2.1. GC-MS

The main observed product, other than the spent residue, after subjecting the YB bark and WA coal to HTL at 360 °C for 72 h, was the expelled oil. The TICs and EICs (m/z 57) of the benzene oil extracts are displayed in Figures II.5 and II.6. GC-MS analyses reveal the presence of homologous series of n-alkanes extending from C8-C31 for the YB bark extract and from C8-C33 for the WA coal extract. The distribution of n-alkanes recovered is rather similar to the distribution of waxy crude oils of Type III source rocks (Tissot and Welte, 1978).

In addition to the n-alkanes, a series of branched alkanes are also observed. These are seen as peaks that elute at intermediate retention times between the peaks for n-alkanes. Examination of the TIC for both the coal and YB bark oils indicates a complex series of alkyl benzenes, alkyl naphthalenes, alkyl phenanthrenes, and various hydroaromatic structures. These are probably derived from cyclization reactions occurring during HTL. Their occurrence in the expelled oil is quite desirable as these components are important to refining the oils for production of high octane fuels.

Estimates of liquid and gas hydrocarbon carbon yields from the artificial maturation of the bark and coal samples were made based on the observed loss of signal from the CPMAS-13C NMR data with the approximate assumption that the aromatic carbon behaves conservatively during HTL. The percent carbon conversions were calculated
Figure II.6. GC-MS chromatograms of expelled oil after subjecting the WA coal to HTL;

A) TIC, B) EIC (m/z 57).
using the percent distribution of carbon atoms listed in Table II.2 of the bark and coal before and after HTL. The estimated percent carbon conversion to liquid and gas products from YB bark is 53% and from the WA coal is 22%. It is expected that the coal would have a lower conversion percent since the material has already undergone some degradation and has less available aliphatic carbon than the bark as indicated by the percent carbon distributions listed in Table II.2. Additional details regarding carbon conversion calculation are discussed in Chapter V.

4. Conclusions

Results from this study of YB bark and WA coal indicate there are significant similarities between the untreated YB bark and WA coal samples and their products generated after subjecting them to HTL at 360 °C for 72 h. The results suggest that during the artificial maturation of YB bark the aliphatic biopolymers within in the bark undergo thermal degradation and are likely the main contributors of \( n \)-alkanes in systems that potentially form Type III kerogen or coal. This hypothesis is supported with the results obtained from the artificial maturation of a coal rich in crypto-eugelinite submacerals, which are believed to originate from root material.

Both the YB bark and WA coal display crystalline and amorphous peaks in solid-state CPMAS-\(^{13}\)C NMR, which is indicative of the presence of suberan. The presence of suberan in these samples is supported by a homologous series of \( n \)-alkanes upon subjecting the samples to py-GC-MS. Products generated after artificial maturation of the YB bark and WA coal include a thermally altered residue, expelled oil, and gases. Analyses of the thermally altered residue from both the bark and coal reveal that the majority of the aliphatic character has been removed, and likely contributed to the formation of the
petroleum products. GC-MS chromatograms of the benzene extracts of residual oil reveal a homologous series of \( n \)-alkanes ranging from \( \text{C}_8 \)-\( \text{C}_{31} \) for the YB bark extract and from \( \text{C}_8 \)-\( \text{C}_{33} \) for the WA coal extract. Crude model estimates of percent carbon conversions to liquid and gas hydrocarbons reveal that the YB has a 53% carbon conversion and the WA coal has a 22% carbon conversion.

These results indicate that upon thermal maturation the aliphatic components of bark and coal are being thermally cracked to produce saturated hydrocarbon products. From these studies, it appears that suberan, and likely also cutan, can readily explain the existence of waxy crude oils typically associated with Type III source rocks.
CHAPTER III
HYDROTHERMAL LIQUEFACTION OF ISOLATED CUTICLE OF AGAVE AMERICANA AND CAPSICUM ANNUUM: CHEMICAL CHARACTERIZATION OF PETROLEUM-LIKE PRODUCTS

Preface

The content of this Chapter was published in 2015 in Fuel, and below is the full citation. The formatting has been altered to incorporate the supporting information into the body of the manuscript. See Appendix A for the copyright permission.


1. Introduction

Currently, the world depends on carbon-rich fossil fuels, primarily oil, coal, and natural gas, to supply 80% of its energy needs (Hook and Tang 2013). As demands for fossil fuels grow, it becomes imperative to develop and utilize alternative fuels to address the impending energy shortage. Currently there are many established technologies to produce alternative energy, of which, many focus on renewable liquid transportation fuels and chemicals (Balat, 2011; Khodakov et al., 2007; Semelsberger et al., 2006). Biomass materials such as aquatic plants, agricultural crops and waste, municipal and animal wastes, and other unconventional materials have all demonstrated their value as feedstocks for the production of bio-oils (Biller and Ross, 2011; Mullen et al., 2010; Rushdi et al., 2013a;
Rushdi et al., 2013b; Yin et al., 2010); however for a biomass material to be ideal for the production of liquid hydrocarbons it needs to have 1) the potential for high bio-oil yield, 2) low production costs and 3) production of high quality product with minimal heteroatom content to avoid further costs associated with upgrading to usable fuels. Therefore, in order to produce a high quality bio-oil it is necessary to select a biomass source with desirable chemical characteristics. Certain plants contain aliphatic biopolymers in their cuticular material, e.g. the cuticle found on the epidermis of certain vegetables and leaves of crops, and these materials are a promising source of petroleum-like products using a conversion process such as hydrothermal liquefaction (HTL). Considering that the cuticular material is often discarded as waste or used as a bulking agent in animal feeds, repurposing this agricultural waste or feed for the generation of bio-oils could have abundant economic and market potential.

HTL is a promising technology that is able to convert waste materials into fuels with a high energy content (Rushdi et al., 2013a; Rushdi et al., 2013b; Zhu et al., 2014). The technique involves subcritical temperatures (200-370 °C), high pressures (4-20 MPa) (Behrendt et al., 2008; Tekin et al., 2014), and an oxygen free environment to artificially mature organic materials, such as biomass residues, in the presence of water (Lewan, 1979). The products generated from HTL are typically liquid and gaseous hydrocarbons. It is generally recognized that the unique properties of water exhibited at high temperatures and pressures is essential for the generation of bio-oils (Lewan, 1997; Peterson et al., 2008). It is generally recognized that the properties of water exhibited at high temperatures and pressures is essential for the generation of bio-oils (Peterson et al., 2008).

It is possible to use petroleum like products produced with HTL as a replacement liquid
fuel for gasoline or diesel. HTL has demonstrated its adaptability to a variety of materials, but may be a particularly promising technology for the conversion of plant cuticular material to bio-oil. Previous studies involving undifferentiated biomass materials have indicated that the chemical composition of bio-oils often closely resemble that of the original biomass (Czernik and Bridgwater, 2004), and often contain unwanted oxygen-rich compounds arising from carbohydrates, lipids, and proteins in the original biomass feedstock that lower the energy content of the bio-oil. Additional energy input is often needed to upgrade the produced bio-oils to render them usable as fuels (Bridgwater, 2012). As a result it is necessary to be discerning in selecting an appropriate biomass feedstock that will facilitate the generation of a valuable petroleum product.

Cuticular material has the potential to be a valuable biomass material in the production of bio-oils. It can often be easily isolated from the crop material with minimal chemical treatment and generally lacks oxygen-rich energy poor components that have proven to be problematic in the production of bio-oils from other biomass sources. Previous studies characterizing cuticular material from the skins of tomatoes and Agave americana have indicated that theses cuticular materials are highly aliphatic due to the presence of the biopolymers cutin and cutan (Deshmukh et al., 2005; Deshmukh et al., 2003; Tegelaar et al., 1989). These polymethylenic plant biopolymers are found in the epidermal surfaces of higher order plants, such as leaves and skins, which act as layers of protection against microbial infection and prevent desiccation (Boom et al., 2005; Kolattukudy, 1980). Cutin is primarily composed of C_{16} and C_{18} hydroxyl fatty acids and is depolymerized and solubilized upon saponification (Deshmukh et al., 2005; Kolattukudy, 1980). Conversely, cutan is non-saponifiable and non-extractable upon saponification implying that its
structure is highly cross-linked with a network of saturated and unsaturated long polymethylenic chains (Boom et al., 2005; Deshmukh et al., 2005; McKinney et al., 1996). The presence of cutin and cutan can be identified in cuticular material using cross polarization magic angle spinning (CPMAS)-$^{13}$C NMR as the characteristic peaks at 30 (amorphous aliphatic) and 33 (crystalline aliphatic) ppm (Deshmukh et al., 2005). As a result of the inherent molecular characteristics observed for the cuticular biopolymers cutin and cutan, it is likely that upon HTL treatment cuticular material containing these biopolymers will produce a high quality bio-oil product.

Little information is available regarding HTL of cuticular material and the possible influence aliphatic functionality has on the molecular distribution of expelled oil products. In this study two cuticular materials containing different distributions of amorphous and crystalline aliphatic carbon were employed to evaluate the propensity these cuticular materials have to generate petroleum-like products. Cuticles from Capsicum annuum (red chili pepper), containing primarily amorphous aliphatic carbon, and A. americana, which is dominated by crystalline aliphatic carbon, were selected for this study. A number of advanced analytical techniques were utilized for enhanced characterization of the molecular components of the starting cuticular material and the expelled oil products to assess the influence that aliphatic functionality has on the bio-oil products. These techniques include CPMAS-$^{13}$C nuclear magnetic resonance (NMR) (Turner et al., 2013), electrospray ionization-Fourier transform ion cyclotron resonance-mass spectrometry (ESI-FTICR-MS) (Jarvis et al., 2014; Rodgers et al., 2005) and two dimensional gas chromatography-mass spectrometry (GC X GC-MS) (Djokic et al., 2012; Tessarolo et al., 2013). The correlation of several data sets allows for a comprehensive characterization of
the expelled bio-oil product and a thorough evaluation of the potential these biomass residues offer for the production of alternative fuels. The main aim of this work was to obtain comprehensive view on the compounds present in bio-oils produced from cuticular materials by coupling several analytical techniques.

It is important to also mention that the two cuticular materials selected represent cuticles found in a large segment of plants and fruits used in commercial operations. The A. americana cuticle is representative of many different species of water-storing desert plants. A close relative is A. tequilana Weber azul used in large amounts for the production of tequila liquor. Recently, some researchers have found uses for the A. tequilana leaves, which are waste materials, as fiberboards and animal feed additives (Iñiguez-Covarrubias et al., 2001). In the case of C. annuum, representative of cuticles from many commercially packaged foods such as tomatoes, peppers, grapes, apples, etc., the cuticles are removed and either discarded in landfills or used to constitute bulking material in animal feeds (Laufenberg et al., 2003).

2. Materials and methods

2.1. Materials

2.1.1. Isolation of A. americana cuticle

Leaves of A. americana were collected from a local botanical garden and were extensively cleaned using deionized water prior to removing the cuticle. The cuticle was removed from the leaves by carefully cutting sections of the leaf followed by gently peeling the cuticle away from the leaf flesh with an x-acto blade knife. The isolated cuticle was washed, freeze-dried, and milled (20 mesh) prior to HTL treatment.

2.1.2. Isolation of C. annuum cuticle
Samples of *C. annuum* purchased from a local grocery store were selected for cuticular isolation. The fruits were washed with deionized water, cut into halves, and had the interiors removed. The materials free of pulp and seeds were boiled in water for approximately 2 h after which the cuticles were loose and could be easily separated. The isolated cuticle was carefully scrapped free of any residual flesh material and resuspended in boiling water with a stir rod for about 30 min to remove any associated matter. The isolated cuticular material was washed, freeze-dried, and milled (20 mesh) prior to HTL treatment.

2.2. *Hydrothermal Liquefaction apparatus and procedure*

2.2.1. *HTL one-step*

HTL experiments were performed using 22 mL stainless steel autoclaves at 360 °C for 72 h. Experimental conditions were selected based on previous hydrothermal liquefaction studies designed to simulate long-term cracking of the polymers into liquid products (Akhtar and Amin, 2011; Hartman and Hatcher, 2014; Lewan et al., 1985). HTL studies on biomass materials indicate an optimum bio-oil yield and heat value between 300-360 °C (Akhtar and Amin, 2011; Toor et al., 2013). The autoclaves were loaded with approximately 1.0 g of freeze-dried, milled (20 mesh) cuticular material, about 7.0 grams of milli-Q water, and flushed with Ar gas for approximately 3 min to ensure that all oxygen was removed. To ensure the cuticular material was restricted to the lower portion of the autoclave and remained submerged in water during HTL, a small Ni-Cr screen (16 mesh) was placed on top of the cuticular material.

After the reactions were complete, the autoclaves were cooled rapidly by immediately placing in an ice bath to terminate the reactions. In this study only the expelled oil products
from the HTL experiment were collected and analyzed. The expelled oils were collected after HTL by rinsing the inside of the autoclave with 5 mL of benzene, shaking extensively, and pouring the contents of the autoclave into a centrifuge tube. The contents were centrifuged to facilitate phase separation, and the organic and aqueous phases were transferred to separate vials and their volumes were recorded. The benzene extract was evaporated to dryness using a Büchi Rotovapor R-114 to determine the yields of expelled oils produced from HTL treatment of the cuticular materials by weighing. The experiments were conducted in duplicates, of which one autoclave was used to determine the mass recovery and the other was used for gas chromatography/mass spectrometry analysis of expelled oil without volume reduction.

2.2.2. HTL two-step

In some cases, two-step HTL experiments were performed using the same apparatus and setup procedures as the one-step experiments with the exception of the temperature and duration. The two-step HTL experiments were conducted first at 250 °C for 30 mins followed immediately by placing in an ice bath to cool. The aqueous phase was carefully decanted from the autoclaves and the masses were recorded. A replicate amount of milli-Q water was added to the autoclaves, which were then purged with Ar gas. The autoclaves were then heated at 360 °C for 72 h. The product collection procedure followed the details outlined in the one-step HTL treatment.
2.3. Analysis of cuticular biomass and expelled oil products

2.3.1. Elemental analysis

The proportions of carbon, hydrogen, nitrogen and sulfur in the untreated cuticular materials and the expelled oils were determined using a Flash 1112 series Elemental Analyzer in triplicate. Proportions of C, H, and N were obtained using a CHN column and proportions of S were obtained using a CHNS column. Sample response areas of carbon and hydrogen, nitrogen, and sulfur were calibrated to a standard curves using nicotinamide, L-aspartic acid, and sulfanilamide, respectively. Ash corrected proportions of C, H, N, and S in the untreated cuticular materials were measured. Percent ash was determined from the dry sample weights before and after oxidation in a muffle furnace at 575 °C for 4 h and cooled in a desiccator (Sluiter et al., 2008). Oxygen content was determined by difference.

2.3.2. Higher Heating Value

Dulong’s formula (Eq. III.1) was used to calculate the higher heating values (HHV) of the feedstock materials and the produced bio-oils (Tekin et al. 2012). The HHVs were calculated based on the percent of carbon (C), hydrogen (H), oxygen (O), and sulfur (S) (Table III.1 lists the CHNOS values and the calculated HHVs).

\[
\text{HHV (MJ kg}^{-1}\text{)} = 0.338C + 1.428 \left( H - \left( \frac{O}{8} \right) \right) + 0.095S
\]  

(III.1)
Table III.1. Percent distributions of C, H, N, O (based on ash-free dry weights) and HHVs of the cuticular materials and their expelled oils. The percent distribution of S was below the level of detection for all samples. Samples denoted with an asterisk have not been ash corrected. Ash content was not determined (ND) for the bio-oil samples.

<table>
<thead>
<tr>
<th></th>
<th>C. annuum cuticle</th>
<th>C. annuum oil*</th>
<th>A. americana cuticle</th>
<th>A. americana oil*</th>
<th>A. americana oil two-step*</th>
</tr>
</thead>
<tbody>
<tr>
<td>% C</td>
<td>62.4 ± 1.00</td>
<td>78.0 ± 0.56</td>
<td>63.5 ± 0.21</td>
<td>76.6 ± 1.76</td>
<td>80.0 ± 0.17</td>
</tr>
<tr>
<td>% H</td>
<td>9.4 ± 0.18</td>
<td>11.2 ± 0.14</td>
<td>9.7 ± 0.07</td>
<td>11.6 ± 0.10</td>
<td>12.8 ± 0.47</td>
</tr>
<tr>
<td>% N</td>
<td>1.5 ± 0.05</td>
<td>0.9 ± 0.06</td>
<td>0.4 ± 0.03</td>
<td>0.2 ± 0.03</td>
<td>0.2 ± 0.02</td>
</tr>
<tr>
<td>% O</td>
<td>26.7 ± 1.02</td>
<td>9.9 ± 0.58</td>
<td>26.4 ± 0.22</td>
<td>11.6 ± 1.76</td>
<td>7.0 ± 0.50</td>
</tr>
<tr>
<td>ash %</td>
<td>0.5 ± 0.02</td>
<td>ND</td>
<td>3.2 ± 0.01</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>molar H/C</td>
<td>1.8 ± 0.05</td>
<td>1.7 ± 0.03</td>
<td>1.8 ± 0.02</td>
<td>1.8 ± 0.02</td>
<td>1.8 ± 0.02</td>
</tr>
<tr>
<td>HHV (MJ kg⁻¹)</td>
<td>29.9</td>
<td>40.5</td>
<td>31.1</td>
<td>40.4</td>
<td>44.1</td>
</tr>
</tbody>
</table>

2.3.3. GC-FID

GC analyses were performed according to previously reported experimental conditions (Hartman and Hatcher, 2014), using an HP6890N GC-Flame Ionization Detector (FID) equipped with a Rtx-5 column (30 m x 0.25 mm x 0.25 µm of 5% phenyl-95% dimethyl polysiloxane) supplied by Restek (USA).

2.3.4. GC X GC-MS

Two dimensional GC analyses of the expelled oils were conducted using an Agilent 6890 2D GC coupled to Leco Pegasus IV Time of Flight Mass Spectrometer (TOFMS) fitted with a dual stage quad jet thermal modulator. GC x GC-MS analyses were performed following the conditions outlined in Hartman and Hatcher (2014). The first dimension was
a nonpolar Restek Rtx-5 (30 m x 0.25 mm x 0.25 µm 5% phenyl-95% dimethyl polysiloxane) column and the second dimension was a polar Restex Rxi-17 (1.1 m x 0.1 mm x 0.1 µm 50% diphenyl-50% dimethyl polysiloxane) column.

2.3.5. **Solid-state CPMAS-\textsuperscript{13}C NMR spectroscopy**

Solid-state \textsuperscript{13}C NMR analyses of the untreated cuticular materials were performed using a 400 MHz Bruker AVANCE II spectrometer equipped with a solid-state MAS probe. Samples were packed into a 4 mm Zirconia rotor and sealed with a Kel-F cap. Samples were spun at 12 kHz at the magic angle (54.7°). All spectra consist of 2048 scans, a contact time of 2.5 ms, and a 1 s recycle delay. The contact time was chosen based on the results of variable contact time experiments and the recycle delay time was selected based on previous NMR studies of cuticular materials (Deshmukh et al., 2005; Turner et al., 2013). Cross polarization \textsuperscript{13}C NMR spectra were obtained with the basic ramp cross polarization pulse program (cp.av) with a two pulse phase modulated decoupling. Chemical shift calibration was performed with a glycine secondary standard and referenced to the carboxyl signal at 176 ppm.

2.3.6. **ESI-FTICR-MS**

The expelled oils were prepared immediately prior to analysis by ESI-FTICR-MS. The samples were diluted with 1:1 (v/v) Tetrahydrofuran (THF):Methanol (MeOH) to achieve a final carbon concentration of approximately 30 ppm and were analyzed in the negative ion mode using an Apollo II ESI source of a Bruker Daltonics 12 T Apex Qe FTICR-MS (College of Sciences Major Instrument Cluster (COSMIC) facility at Old Dominion University, Virginia). ESI-FTICR-MS analyses were conducted as previously described (Hartman and Hatcher, 2014).
Mass spectra were externally calibrated using a polyethylene glycol standard and were internally calibrated using naturally present fatty acids and other homologous series detected within the sample (Sleighter et al., 2008). Only peaks with a S/N > 3 were assigned a molecular formula. An in-house MatLab (The MathWorks Inc., Natick, MA) code produced empirical formula containing the elements C, H, O, N, and S with an accuracy of < 1 ppm. Additional details of data treatment are described elsewhere (Stubbins et al., 2010; Hartman and Hatcher, 2014).

3. Results and discussion

3.1. Feedstock composition

Solid-state NMR spectra of the two cuticles are displayed in the Figure III.1 along with the percent carbon distributions (Table III.2). Both the C. annuum and A. americana cuticular materials are dominated by intense signals in the aliphatic region (0-45 ppm), accounting for 42.2% and 53.1% of the relative peak area, respectively. These strong aliphatic signals are due to the presence of the polymethylenic carbons associated with

Table III.2. Percent distributions of carbon in the CPMAS-\(^{13}\)C NMR spectra of C. annuum cuticle and A. americana cuticle untreated and heated at 250 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(^{13})C Chemical Shift (ppm)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aliphatic (0-45)</td>
<td>Alkyl-O (45-110)</td>
</tr>
<tr>
<td>C. annuum cuticle</td>
<td>42.2</td>
<td>46.0</td>
</tr>
<tr>
<td>A. americana cuticle</td>
<td>53.1</td>
<td>38.5</td>
</tr>
<tr>
<td>spent A. americana cuticle (250 °C)</td>
<td>75.5</td>
<td>25.5</td>
</tr>
</tbody>
</table>
Figure III.1. CPMAS-$^{13}$C NMR of A) untreated *A. americana* cuticle B) *A. americana* cuticle that has been heated at 250°C for 30 min and C) untreated *C. annuum* cuticle.

biopolymers, cutin and cutan. Previous studies on such biopolymers have indicated that cutin is characterized by a large resonance signal at 30 ppm indicative of amorphous polymethylene groups, whereas cutan is predominantly composed of crystalline polymethylene groups, denoted by the peak at 33 ppm (Deshmukh et al., 2005; Deshmukh et al., 2003). The distribution of amorphous and crystalline polymethyleneic carbons is noticeably different between the two cuticular samples based on the NMR
spectra. The *A. americana* cuticle is largely made up of crystalline polymethylenes (cutan) and the *C. annuum* cuticle is dominated by amorphous polymethylenes (cutin). Because these two samples contain different distributions of polymethylenic carbons, it can be concluded that these samples are appropriate feedstock materials to investigate the influence aliphatic functionality has on the molecular distribution of expelled oil products.

In addition to the amorphous and crystalline peaks, the *C. annuum* cuticle also displays a doublet at 25.8 and 26.5 ppm. While additional experiments are needed to confirm the identity of these peaks, they may be attributed to cycloalkanes. A previous study by Moeller et al. (1984) has shown that high molecular weight cycloalkanes have resonance signals similar to the ones observed in *C. annuum* cuticle. The presence of cycloalkanes in the *C. annuum* cuticle would explain the origin of cycloalkanes observed in the bio-oil (discussed in section 3.2.2.).

The spectrum obtained for *C. annuum* and *A. americana* are consistent with previously reported solid-state $^{13}$C NMR spectra of the samples (Deshmukh et al., 2005; Johnson et al., 2007). Further examination of *C. annuum* and *A. americana* spectra indicates a significant amount of signal attributable to alkyl-O carbons (*C. annuum* 46.0% and *A. americana* 38.5%), from carbohydrates, ethers, or esters. The large amount of signal in this region suggests that my cuticular isolation procedure does not completely remove carbohydrates and would require chemical treatment to remove these compounds. Additionally, a carboxyl peak at 172 ppm is observed in both samples. There are no signals attributed to aromatic or aryl-O carbons in either cuticle sample.

In attempt to lower the oxygen content of the expelled oils, a two-step HTL experiment was conducted on the *A. americana* cuticle. The recovered cuticle after the first step (250
°C for 30 min) is displayed in Figure III.1B (integration regions are listed in Table III.2). Based on the NMR results, it appears that the 250 °C heating greatly reduced the amount of alkyl-O carbons, which are associated with carbohydrates. Previous studies of cellulose and hemicellulose have indicated that they become soluble in water at temperatures > 180 °C (Toor et al., 2011 and references within). The loss of alkyl-O compounds is quite desirable as a cuticular material that contains less oxygen functionality has the potential to yield a bio-oil with low heteroatom content.

In addition to the NMR analyses, elemental analysis was also conducted on the cuticular materials. The raw materials were analyzed for C, H, N, O, and S; however S was below the limit of quantification (< 0.033 mg) and/or was not detected in all the analyzed samples. It is valuable to conduct elemental analysis on the feedstock materials as the produced bio-oil will have similar chemical composition as the starting material (Czernik and Bridgwater, 2004). Both the C. annuum and A. americana cuticles have relatively low contributions of heteroatoms (N and S). The abundance of oxygen is likely due to residual carbohydrates that were not removed from the cuticular materials during the isolation procedures. Additionally, the H/C molar ratios of C. annuum and A. americana cuticles are approximately 1.80 which is indicative of a highly aliphatic substance and is consistent with the results obtained through solid-state NMR. The NMR and elemental analyses of the cuticular materials suggest that when subjected to HTL these cuticular materials will yield a hydrocarbon rich bio-oil.
3.2. Characterization of bio-oil

3.2.1. Bulk analyses

Upon completion of the HTL treatment of the cuticular materials, bio-oils were produced and existed as thin layers of brownish-red liquid atop the aqueous phase. A relatively high conversion of both agricultural waste feedstock materials to bio-oils was observed. Based on mass recoveries, the *C. annuum* and the *A. americana* cuticle bio-oil yields were approximately 41% and 38%, respectively. Elemental analysis results (Table III.1) show that the HTL bio-oils produced in this study have a significantly higher percentage of carbon (77.98 and 76.58%, respectively) and hydrogen (11.15 and 11.64%, respectively) and a lower percentage of heteroatoms (N and O) than the original feedstock materials (Table III.1). Similar to the starting raw materials, the bio-oils sulfur content was below the limit of quantification and/or was not detected in the samples. Low heteroatom contents are quite desirable in petroleum-like products as N and S can form environmentally hazardous oxides upon combustion and require removal during refining processes to meet EPA standards.

While the oxygen content of the bio-oils is lower than the original feedstocks, it would be advantageous to obtain lower values because oxygen has to be removed during refining process for use in transportation fuels. In an attempt to lower the oxygen content, a two-step HTL treatment was utilized. Based on the resulting EA data (Table III.1), employing the two-step HTL treatment effectively lowers the oxygen content of the *A. americana* bio-oil. At the low temperature, primary thermal decomposition reactions occur making oxygen containing compounds, such as carbohydrates, soluble in water. This hypothesis is consistent with previous studies that have shown cellulose is decomposed and becomes
water soluble at 250 °C (Sakaki et al., 1996). These oxygen containing compounds are removed from the HTL system by decanting off the water of the first, low temperature short duration HTL. Overall, the decreased heteroatom content results in the HHVs of all the bio-oils (approximately 40.5 MJ kg\(^{-1}\)) being significantly greater than their initial raw materials (approximately 30.0 MJ kg\(^{-1}\)). This is a considerable upgrade and the produced bio-oils are comparable to HHVs of a typical petroleum crude (42.7 MJ kg\(^{-1}\), Anastasakis and Ross, 2011).

Using the HHV results the Fossil Energy Ratio (FER, Xu et al., 2011) was able to be calculated using equation III.2.

\[
\text{FER} = \frac{\text{HHV}\text{biofuel}}{E_{\text{input}}} \left[ \frac{\text{GJ products}}{\text{GJ fossil energy input}} \right]
\]  
(III.2)

This calculation allows us to assess the energy efficiency of the process. Because the experiments were conducted on a lab-scale, several assumptions were made in the FER calculation to be consistent with industrial operations including upscaling the HTL operation. These assumptions included increasing the water to cuticle ratio to 3:1, a 50% energy recovery, and that the autoclave was well insulated. From the calculations it was determined that the FER is greater than 4 indicating there would be a favorable gain in energy from the process. In principle, it is envisioned that a commercial facility would be able to conduct one or two-step HTL efficiently and the bio-oils would separate from the aqueous phase such that decantation would be possible.

Both bio-oil samples exhibit high H/C molar ratios, averaging at 1.76. Oils containing high H/C molar ratios are indicative of samples rich in alkanes. Surprisingly, the elemental analysis results are more comparable to bio-oils produced through HTL of algal materials (Anastasakis and Ross, 2011; Toor et al., 2013) rather than other agricultural materials.
(Akalm et al., 2012; Zhu et al., 2014). This is likely due to the minimal amount of carbohydrates and proteins in the original cuticular materials as discussed in section 3.1.

3.2.2. *GC analyses*

The bio-oils were analyzed by two GC techniques to investigate the volatile nonpolar fraction of the oils. GC-FID was first employed to gain an understanding regarding the complexity of the bio-oil samples. The resulting chromatograms are displayed in the Figure III.2 and the complexity of the samples is clearly visible. Although the bio-oils contain similar elemental compositions, their molecular compositions are visibly different as is demonstrated by their different GC-FID chromatograms. The chromatogram of the *A. americana* bio-oil (Figure III.2B) is dominated by a homologous series of *n*-alkanes ranging from C₈-C₃₂. Conversely, the chromatogram of the bio-oil from *C. annuum* (Figure III.2A) does not display the same dominant *n*-alkane homologous series. In the *C. annuum* bio-oil the *n*-alkanes are present, but they are buried amongst other compound series. The unresolved hump observed at 21 min in Figure III.2A is characteristic of polar compounds such as fatty acids and makes it challenging to observe other compounds that have a similar retention time.

Due to the complexity of the bio-oil samples, it is often challenging to accurately identify compounds utilizing conventional GC techniques given the large number of compounds having similar affinities for the column. This results in coeluting peaks and an inaccurate evaluation of the sample. The challenge of overlapping peaks has been greatly improved with the introduction of two dimensional GC, which utilizes two chromatographic columns, typically of varying polarities. Employed in this study were a nonpolar first dimension column and a polar second dimension column. The use of two
columns with different retention affinities provides effective separation of coeluting analytes enabling complete sample characterization. 2D GC has demonstrated its ability to separate complex mixtures, such as bio-oils (Djokic et al., 2012; Tessarolo et al., 2013), and is well suited for characterizing the samples examined in this study. Two dimensional GC-MS was applied to both bio-oils and their total ion chromatograms are displayed in Figure III.3. Similar to the GC-FID chromatograms, the two bio-oil samples have different distributions of compounds.

Figure III.2. GC-FID chromatograms of A) C. annuum bio-oil and B) A. americana bio-oil.
Figure III.3. GC X GC-MS total ion chromatograms of expelled oils after subjecting the A) *C. annuum* and B) *A. americana* cuticles to HTL. Compound classes have been circled and classified. The classification codes are listed in Table III.3. Peaks have been identified with relative bubble markers which are proportional to the peaks’ intensity.
Several compound classes have been highlighted in Figure III.3 and their corresponding percent contributions of total peak area and total peak count for each bio-oil sample are listed in Table III.3. The *A. americana* bio-oil is predominantly composed of *n*-alkanes, consistent with the GC-FID data, ranging from C<sub>9</sub> – C<sub>31</sub>. This compound class accounts for 50.6% of the total peak area and 24.2% of the total number of peaks. Conversely, this compound class only accounts for 8.2% of the total peak area and 8.0% of the total number of peaks in the *C. annuum* bio-oil. An interesting similarity between the *n*-alkane series in the two bio-oils is that while both bio-oils display evidence of *n*-alkanes from C<sub>9</sub>-C<sub>31</sub>, the most intense *n*-alkanes are between C<sub>10</sub>-C<sub>15</sub>, commonly referred to as the petroleum cut kerosene. It is possible that the accumulation of this carbon range is the result of random cracking of C-C bonds.

**Table III.3.** GC X GC-MS compound classes’ classification codes, total area percentage and peak count percentages corresponding to Figure III.3.

<table>
<thead>
<tr>
<th>Classification Code</th>
<th>Compound Class</th>
<th><em>C. annuum</em> oil</th>
<th></th>
<th></th>
<th></th>
<th><em>A. americana</em> oil</th>
<th></th>
<th></th>
<th></th>
<th><em>A. americana</em> two-step oil</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Alkanes</td>
<td>8.2</td>
<td>8.0</td>
<td></td>
<td></td>
<td>50.6</td>
<td>24.2</td>
<td></td>
<td></td>
<td>43.4</td>
<td>23.2</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>Cycloalkanes and Alkenes</td>
<td>41.9</td>
<td>30.8</td>
<td></td>
<td></td>
<td>21.7</td>
<td>28.3</td>
<td></td>
<td></td>
<td>9.6</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>Bicyclic alkanes and Cycloalkenes</td>
<td>10.5</td>
<td>9.8</td>
<td></td>
<td></td>
<td>4.2</td>
<td>6.7</td>
<td></td>
<td></td>
<td>4.1</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>Alkyl benzenes and Ketones</td>
<td>18.3</td>
<td>25.3</td>
<td></td>
<td></td>
<td>11.8</td>
<td>18.1</td>
<td></td>
<td></td>
<td>20.3</td>
<td>26.5</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Indanes</td>
<td>6.3</td>
<td>4.7</td>
<td></td>
<td></td>
<td>6.2</td>
<td>7.1</td>
<td></td>
<td></td>
<td>6.9</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>Phenols</td>
<td>5.0</td>
<td>4.2</td>
<td></td>
<td></td>
<td>2.4</td>
<td>5.3</td>
<td></td>
<td></td>
<td>5.1</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>VII</td>
<td>Naphthalenes</td>
<td>4.7</td>
<td>15.8</td>
<td></td>
<td></td>
<td>3.0</td>
<td>10.0</td>
<td></td>
<td></td>
<td>10.3</td>
<td>29.3</td>
<td></td>
</tr>
<tr>
<td>VIII</td>
<td>Fatty acids</td>
<td>5.0</td>
<td>1.3</td>
<td></td>
<td></td>
<td>0.0</td>
<td>0.0</td>
<td></td>
<td></td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>IX</td>
<td>Cyclopentanones</td>
<td>0.1</td>
<td>0.2</td>
<td></td>
<td></td>
<td>0.1</td>
<td>0.2</td>
<td></td>
<td></td>
<td>0.3</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>100.0</td>
<td>100.0</td>
<td></td>
<td></td>
<td>100.0</td>
<td>100.0</td>
<td></td>
<td></td>
<td>100.0</td>
<td>100.0</td>
<td></td>
</tr>
</tbody>
</table>
Aside from the distribution of \( n \)-alkanes, another striking difference between the bio-oil samples is the varying amounts of cycloalkane and alkene compounds. These two compound classes have been grouped together and are labeled as region II in Figure III.3. This region accounts for 21.7% and 41.9% of the \( \textit{A. americana} \) and \( \textit{C. annuum} \) bio-oil total peak areas, respectively. Additionally, the two most intense peaks of the \( \textit{C. annuum} \) bio-oil are located within this region, octylcyclohexane with a retention time of 2260 s/0.870 s and nonylcyclohexane with a retention time of 2504 s/0.870 s. Cycloalkanes are quite desirable in crude oils as they have a greater calorific value per unit volume than their counterpart straight chain alkanes (Schobert, 1990). This is particularly important when the amount of fuel is restricted by the volume of fuel tanks as is the case in most vehicles. The majority of the peaks within region II for both bio-oil samples are 6-membered cycloalkane rings with alkyl substituents (lengths range between C\(_2\)-C\(_{12}\)); there is also a small amount of 5 membered rings observed in the samples.

Further examination of Figure III.3 indicates that the bio-oil samples are a complex assortment of compound classes. In addition to the alkanes, alkenes, and cycloalkanes the samples contain bicyclic alkanes/cycloalkenes, alkyl benzenes/ketones, indanes, phenols, naphthalenes, fatty acids, and cyclopentanones. The occurrence of aromatics, cyclic, and hydroaromatic compounds in the expelled oil is quite desirable as these components are important to refining the oils for the production of high octane fuels. It is likely that the presence of these compounds in the bio-oils is the result of structural components of the cuticular materials or is produced through aromatization reactions that occurred during HTL. Considering the fact that the solids NMR data in Figure III.1 show no aromatic carbons in the untreated cuticles, it is unlikely that aromatics are structurally present prior
to heating. Overall, aromatic compounds, those containing only aromatic rings and alkyl chains, account for 16.8% of the total peak area and 29.9% of total peak count in the A. americana bio-oil and 31.7% of the total peak area and 41.8% of total peak count in the C. annuum bio-oil. Alkyl benzenes are responsible for the majority of the aromatic compounds and are the third most prominent compound class in both the A. americana and C. annuum bio-oils, second to alkanes and cycloalkanes/alkenes. This region represents 7.6% and 15.7% of the total peak areas and 12.8% and 21.3% of the total peak count in the A. americana and C. annuum bio-oils, respectively.

Oxygenated aromatic compounds like the ketones and phenols, can be troublesome in refinery operations as they lower energy content of fuels and make bio-oils incompatible for direct use as transportation fuels. The oxygenated compounds account for a small percent, approximately 7.2%, of the total peak area in both bio-oil samples. Based on the elemental analysis data discussed in section 3.2.1, it is not surprising that the cuticular bio-oils contain oxygenated compounds. It is likely that the presence of ketones, phenols, and other oxygenated compounds in the bio-oils are the result of decomposition of residual carbohydrates that were present in the cuticular materials prior to HTL treatment (Shuping et al., 2010; Toor et al., 2011). This hypothesis is supported by the NMR data which provides evidence of carbohydrates in the cuticular materials.

3.2.3. ESI-FTICR-MS analyses

Ultrahigh-resolution mass spectrometry, specifically Fourier transform ion cyclotron resonance, has proven itself to be an invaluable analytical technique in its ability to provide molecular fingerprints of fossil fuels and bio-oils demonstrated by many petroleomic studies (Jarvis et al., 2014; Rodgers et al., 2005). Utilizing FTICR-MS, which is compatible
with the heavier, polar, non-volatile compounds of the bio-oils, along with 2D GC-MS a comprehensive molecular understanding of the bio-oils was obtained, which is necessary for understanding their potential application as replacement transportation fuels. Due to its ultrahigh-resolution and mass accuracy, FTICR-MS is able to detect and identify thousands of molecular formulas and is thus able to provide a vast amount of sample information regarding the complex bio-oil samples.

Table III.4. FTICR-MS heteroatom content and compound classes’ relative peak magnitudes and peak count percentages of the *A. americana* bio-oil and *C. annuum* bio-oil. Relative peak magnitudes were calculated by dividing the sum of the peak magnitudes of interest (e.g. CHO, CHON, CHONS, etc.) by the summed total peak magnitude of the sample.

<table>
<thead>
<tr>
<th>Compound Class</th>
<th>C. annuum oil</th>
<th>A. americana oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Relative Peak</td>
<td>Peak Count</td>
</tr>
<tr>
<td></td>
<td>Intensity %</td>
<td>%</td>
</tr>
<tr>
<td>CHO</td>
<td>87%</td>
<td>64%</td>
</tr>
<tr>
<td>CHON</td>
<td>8%</td>
<td>27%</td>
</tr>
<tr>
<td>CHOS</td>
<td>4%</td>
<td>6%</td>
</tr>
<tr>
<td>CHONS</td>
<td>1%</td>
<td>3%</td>
</tr>
<tr>
<td>total</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Lipid</td>
<td>91%</td>
<td>72%</td>
</tr>
<tr>
<td>Unsaturated Hydrocarbon</td>
<td>4%</td>
<td>14%</td>
</tr>
<tr>
<td>Condensed Aromatic</td>
<td>0.1%</td>
<td>0.4%</td>
</tr>
<tr>
<td>Lignin</td>
<td>3%</td>
<td>9%</td>
</tr>
<tr>
<td>Protein</td>
<td>0%</td>
<td>2%</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>0%</td>
<td>0.1%</td>
</tr>
<tr>
<td>total</td>
<td>99%</td>
<td>97%</td>
</tr>
</tbody>
</table>
The number of uniquely assigned molecular formulas was 1683 (94%) and 861 (80%) for the *C. annuum* and *A. americana* bio-oil samples, respectively. The majority of the molecular formulas assigned in both bio-oils samples were CHO compounds (the complete compound distribution is listed in Table III.4) accounting for 88% and 64%, of the total peaks in the *A. americana* bio-oil and the *C. annuum* bio-oil. Additionally, the CHO compounds were also present in the greatest relative abundance. Both samples also contained CHON, CHOS, and CHONS compounds. The distribution of the molecular formula assignments of the bio-oils are consistent with the elemental analysis data (Table III.1), which shows that the majority of the both bio-oils, based on weight, are C, H, and O. An interesting difference between the two bio-oil samples is the amount of nitrogen containing compounds. The *C. annuum* bio-oil molecular contains a greater number of nitrogen containing compounds than the *A. americana* bio-oil. The elemental analysis data revealed that the *C. annuum* bio-oil has a greater amount of nitrogen present based on weight, which can explain why there are more nitrogen molecular formulas in the FTICR-MS data.

Between the two bio-oil samples there were 648 common molecular formulas. The majority of the common formulas were CHO formulas, accounting for 95%, and the remaining formulas were CHON and CHOS. There were no CHONS common formulas. All the common molecular formulas have high H/C (>1.0) and low O/C (<0.4) values, the majority of them plotting in the lipid-like regions of the van Krevelen diagrams displayed in Figure III.4.
Figure III.4. van Krevlen diagrams using all assigned molecular formulas from the A) *C. annuum* bio-oil and B) *A. americana* bio-oil produced after HTL. CHO (continued)
**Figure III.4.** (continued) compounds are identified as blue dots, CHON compounds are red dots, CHOS compounds are green dots, and CHONS compounds are purple dots. The size of the bubble is proportional to the magnitude of the molecular formula peak. Boxes overlain on the plot indicate molecules having structural similarity to the molecular group listed and were adapted from (Hockaday et al., 2009). Peaks with an intensity great than E8 have been reduced by an order of magnitude to allow for the visualization of the lower intensity peaks.

In an attempt to simplify the complex data set obtained from FTICR-MS analysis, the molecular formulas of the bio-oils have been plotted using van Krevelen diagrams (Kim et al., 2003; Van Krevelen, 1950). This approach provides visual diagrams that can be used to elucidate structural information from the molecular formulas. Van Krevelen diagrams for the *A. americana* bio-oil and *C. annuum* bio-oil are displayed in Figure III.4. It is immediately apparent that both bio-oil samples are primarily lipid-like, representing 83% of the *A. americana* bio-oil molecular formulas and 72% of the *C. annuum* bio-oil molecular formulas. Additionally, this region is responsible for 90% and 91% of the relative peak magnitudes in the *A. americana* bio-oil and *C. annuum* bio-oil, respectively. Fatty acids, with varying degrees of unsaturation, are responsible for the majority of the relative peak magnitudes of the two bio-oil samples. It is likely that the observation of fatty acids can be attributed to the presence of the biopolymers cutan and cutin, which were present in the original feedstocks. Previous studies regarding the structure of cutin and cutan have indicated that both biopolymers are comprised of ester-linked fatty acids (Deshmukh et al., 2003; Kolattukudy, 1980; Stark et al., 2000), which upon heating during
the HTL treatment release the observed fatty acids. Considering the fact that the final pH of the HTL aqueous solutions was acidic (pH≈4), the fatty acids would be expected to be present within the bio-oils recovered by benzene extraction. The high H/C and low O/C molecular formulas observed in the bio-oils is consistent with the aforementioned elemental analysis data.

Of the molecular formulas assigned, the three main classes were CHO, CHON, and CHOS (Table III.4), representing 97% and 98% of the *C. annuum* and *A. americana* bio-oil total molecular formulas. To better display the relationship of compounds within a given class (i.e. CHO, CHON, and CHONS) the assigned molecular formulas were plotted in diagrams displaying the molar H/C ratios vs carbon number (Figure III.5). Formulas that are part of the same homologous series plot along the same trend line, some of which have been labeled in Figure III.5. Similar to the van Krevelen, this type of diagram can provide some structural information regarding the carbon skeleton of the molecular formulas. Compounds with low degrees of unsaturation, such as aliphatic (linear and branched) or alicyclic (mono- or poly-) will plot along trend lines between C_nH_{2n} through C_nH_{2n-6}. Conversely, aromatic compounds such as alkyl benzenes, naphthalenes, and phenanthrenes, will plot with an H/C value ≤ 1.7 (Salmon et al., 2011).

In both bio-oil samples, the CHO class contains the largest magnitude peaks, denoted as red dots, the majority of which plot along an aliphatic/ Alicyclic trend line. The distribution of CHO formulas for both bio-oils is quite similar, ranging from C_{10}-C_{51}. In the *C. annuum* bio-oil there is a greater number of high magnitude peaks with lower H/C values than in the *A. americana* bio-oil. These peaks are likely cyclic compounds, consistent with the 2D GC-MS data discussed in section 3.2.2.
Figure III.5. H/C ratio versus number of carbon atoms per molecule for A) *C. annuum* bio-oil molecular formulas and B) *A. americana* bio-oil molecular formulas. Compound families have been plotted according to the Roman numeral codes I) CHO and II) CHON. Molecules that are part of the same series fall along the same trend line; several series have been identified and labeled within the plots. Peaks have been identified with bubble markers, relative to peaks within the specified class, which are proportional to the peaks’ magnitude. Peaks with a magnitude greater than E8 had to be reduced by an order of magnitude to allow for the visualization of the lower magnitude peaks.
Another noteworthy difference between to the two bio-oil samples is the distribution of CHON compounds in Figures III.5AII and III.5BII. The *C. annuum* bio-oil has much larger amount of continuous homologous series compounds, 15 dominant series ranging from C_{13}-C_{43}, than the *A. americana* bio-oil, which only contains 3 dominant series ranging from C_{28}-C_{45}. The majority of the CHON series in *C. annuum* bio-oil begin with a high carbon number (≥ C_{20}), additionally more than half of the series have an H/C ≤ 1.7, indicating that these compounds are likely unsaturated and may have an aromatic or alicyclic carbon backbone. This is consistent with my hypothesis that the *C. annuum* cuticle is comprised of cyclic compounds which was discussed in section 3.1 with the NMR results.

4. Conclusions

In this study a petroleum-like product was effectively produced from agricultural waste materials using HTL. Bio-oil yields were greater than 30% for both cuticular feedstocks. The HHVs of the *C. annuum* and *A. americana* bio-oils were 40.50 MJ kg\(^{-1}\) and 40.44 MJ kg\(^{-1}\), respectively, with a 30-35% increase in energy of the cuticles. The results indicate that in order to obtain a complete characterization of bio-oils, it is necessary to couple data sets from several advance analytical techniques. A detailed chemical characterization of these bio-oils yields information regarding the future application of bio-oils, such as replacement transportation fuels.
CHAPTER IV

A NON-THERMOGENIC SOURCE OF BLACK CARBON IN PEAT AND COAL

Preface

The content of this Chapter was published in 2015 in the International Journal of Coal Geology, and below is the full citation. The formatting has been altered to incorporate the supporting information into the body of the manuscript. See Appendix A for the copyright permission.


1. Introduction

Several recent reports suggest that black carbon (BC), which broadly encompasses charcoal, soot, and other forms of pyrogenic carbon, may constitute more than half of the refractory carbon in soil and sediments (Masiello and Druffel, 1998). BC itself represents a sink for biospheric and atmospheric carbon dioxide, and is intimately tied to the biogeochemical cycling of both carbon and oxygen through its role in organic matter cycling. While the origin of BC is considered to be from thermal oxidation of organic matter at elevated temperatures, a recent report suggests that photochemical oxidation of dissolved organic matter (DOM) in peat swamps generates a similar material (Chen et al., 2014). Drawing from this observation, provided is molecular evidence for BC in several peats and suggest that some, if not most, of the BC observed can derive from photochemical alteration of DOM.
The apparent ubiquity of BC in peats and coal is well recognized, especially in coals where it is often categorized petrographically as fusinite, macrinite, micrinite, and related inertinite coal macerals (Stach et al., 1982; Mukhopadhyay and Hatcher, 1993; Hower et al., 2009). BC is a generic term used to describe several forms of pyrogenic carbon that encompasses soot, charcoal, graphite, and products of incomplete combustion (Goldberg, 1985) and in some instances, can arguably be operationally defined depending on the method used to estimate or quantify the amount of BC (Gustafsson et al., 1996; Gustafsson et al., 2001; Schmidt et al., 2001). The global production of BC from all sources, including biomass burning and fossil fuel burning, has been estimated to be between 50-270 x 10^{12} g of C yr^{-1} (Chen et al., 2014) with 80-90% remaining as residues in terrestrial environments (Kuhlbusch and Crutzen, 1995; Suman et al., 1997). Several investigations claim that a significant portion of the total amount of terrestrial organic carbon is in the form of BC. For instance, BC has been reported to represent as much as 30-45% of the total soil organic carbon (Skjemstad et al., 1996; Schmidt et al., 1999; Glaser et al., 2000), and 21-69% of peat carbon (Leifeld et al., 2007). On a global scale, the organic C to a depth of 1 m in peatlands contributes about 225 x 10^{15} g C compared to 2000 x 10^{15} g C for all soils (Bolin et al., 2000). If 25% of this is BC, then 56 x 10^{15} g C is the current standing stock of BC in peats.

As the peat undergoes burial and maturation in the subsurface to brown coal and then on to higher rank coals, this BC, especially charcoal, becomes recognized as fusinite macerals if it remains preserved petrographically. If the BC becomes disaggregated or finely comminuted, then it probably contributes to detrine, micrinite, or macrinite coal macerals. As a whole, inertinite macerals often constitute lower proportions compared with
the vitrinite macerals but in some cases can dominate the coal’s composition, as in the case of Gondwana coals (Stach et al., 1982; Teichmüller, 1989).

Recent observations and experimentation (Chen et al., 2014) show that a non-pyrogenic source of BC-like molecules can be obtained photochemically from DOM that is predominantly derived from dissolution of a woody peat in the Dismal Swamp, Virginia, an ombrotrophic black-water swamp. The molecular characterization by electrospray ionization-Fourier transform ion cyclotron resonance-mass spectrometry (ESI-FTICR-MS) shows the material which readily flocculates when subjected to photoirradiation by simulated sunlight to contain a significant proportion of BC-like molecules. Simultaneously, molecules that are mainly aliphatic in nature are produced by the photochemical transformation of the DOM. These molecules appear to have a polycyclic aliphatic nature and are substituted by carboxyl groups. Accordingly they have been likened to molecules found ubiquitously in aquatic and marine DOM, e.g., CRAM (carboxyl-rich alicyclic molecules). The BC-like, called photoBC, and CRAM-like molecules flocculate in the water but readily redissolve in alkaline aqueous solutions much like humic acid-like substances in soils and peats. The produced molecules were not initially present in the DOM prior to photoirradiation suggesting that the photoBC molecules were generated by photodegradation.

Accordingly, it is hypothesized that in peat swamps like the Dismal Swamp, this source could be quantitatively significant compared with pyrogenic sources for BC and that this process may be central to the humification of organic matter in peat. Moreover, it is likely that this flocculating organic matter contributes in the peat as a precursor to petrographically distinct submacerals of the inertinite maceral groups in coal. In the current
study, the studies described by Chen et al. (2014) for the Dismal Swamp, Virginia, are extended to examine peats from other well-known coal-forming localities in the USA. Also, the peat samples are compared with a low-rank coal of the Gippsland Basin, Australia, which represents a more mature form of peat along the natural maturation pathway. Because peat organic matter is known to undergo significant chemical modifications at increased coal ranks and becomes less easily extracted from the coal, a requirement for ESI-FTICR-MS, the study was limited to a low-rank brown coal so as to more readily make comparisons with the organic materials in peat.

Peat samples from the Dismal Swamp, Virginia; the Okefenokee Swamp, Georgia; and the Everglades, Florida (Pahokee peat), as well as the Yallourn Open Cut coal were subjected to solid-state $^{13}$C NMR and ultrahigh-resolution mass spectrometry for characterization of their molecular composition achieved by alkali extraction to recover a fraction of the peat and coal that can be analyzed by ESI-FTICR-MS. The extract prepared is essentially defined operationally as humic acids (HA) and usually contributes 25% of the total peat (Hatcher et al., 1983).

2. Materials and methods

2.1. Sample descriptions

A variety of samples were evaluated in this study to examine the occurrence of photochemically produced molecules in various coal-forming peats, a low-rank coal, and a naturally degraded wood sample. The three peat samples utilized for this study were collected from the Dismal Swamp, Virginia; the Okefenokee Swamp, Georgia; and the Everglades, Florida. These selected peats are representative of coal-forming environments from across the United States. The low-rank coal was collected from the upper bench of
the Yallourn Open Cut (YOC) in Victoria, Australia (Bates and Hatcher, 1989). The coal sample was chosen to represent an intermediate stage of coalification. A naturally degraded Douglas fir sample was obtained from Mount Rainier, WA (Hatcher, 1987). The sample has been exposed to brown-rot fungi and as a result the cellulosic materials have been degraded and the wood is primarily lignin in character.

All samples were dried and subjected to an alkali extraction to render the materials suitable for analysis by ESI-FTICR-MS.

2.2. *Humic acid isolation*

The humic acids were extracted from the Dismal Swamp peat, the Okefenokee Swamp peat, the Mt. Rainier wood and the coal sample in house. These samples were prepared following a conventional humic acids procedure (Sparks, et al. 1996) involving extraction with 0.5 M NaOH, removal of sodium with cation exchange resin, and precipitation by adjusting the solution to pH 2. The residue was isolated by centrifugation, rinsed with several times with dilute HCl, and freeze-dried. The Everglades peat humic acid (Pahokee peat) sample was purchased from the International Humic Substance Society.

2.3. (-) *ESI-FTICR-MS analysis*

Humic acid samples were prepared immediately prior to analysis. All humic acid samples had to be in solution, which was achieved by suspending between 0.5-1.0 mg of solid material in 1-3 mL of ultra-quality water. For complete solubility small additions of NH₄OH adjusted the pH from pH 9 to 12. The solution was then diluted 50% with methanol for ESI-FTICR-MS analysis. Prior to analysis, the instrument was externally calibration with a polyethylene glycol standard. Each sample was introduced to a Bruker Daltonics 12 T Apex Qe FTICR-MS at a flow rate of 120 µL h⁻¹ using an Apollo II ESI ion source in
the negative ionization mode housed at the College of Sciences Major Instrumentation Cluster (COSMIC), Old Dominion University, VA. The spray current of the ESI was optimized for each sample. Ion accumulation time in the hexapole varied for each sample, ranging between 2.0-3.0 s, before being transferred into the ICR cell, where 300-500 scans were co-added in broadband mode using a \( m/z \) range of 200-1200.

2.4. **(-) ESI-FTICR-MS data processing**

All mass spectra were internally calibrated using naturally present fatty acids and other homologous series present within the samples (Sleighter et al., 2008). Prior to molecular formula assignment salt, and \(^{13}\text{C}\) peaks were removed from the mass list and only peaks with a S/N > 3 were considered for formula assignment. Empirical molecular formulas were assigned using an in-house MatLab (The MathWorks, Inc., Natick, MA) code according to the following criteria: \(^{12}\text{C}\)\(_{2-50}\), \(^{1}\text{H}\)\(_{5-120}\), \(^{14}\text{N}\)\(_{0-6}\), \(^{16}\text{O}\)\(_{0-30}\), \(^{32}\text{S}\)\(_{0-2}\), and \(^{31}\text{P}\)\(_{0-2}\) within an error of 1 ppm. Treatment of the data is consistent with other published procedures (Stubbins et al., 2010; Chen et al., 2014).

2.5. **Solid-state multiple cross polarization magic angle spinning-\(^{13}\text{C}\) NMR spectroscopy**

The peat and coal humic acids were examined by solid-state \(^{13}\text{C}\) NMR. Solid-state multiple cross polarization magic angle spinning (multiCPMAS) \(^{13}\text{C}\) spectra were acquired on a 400 MHz Bruker AVANCE II NMR spectrometer, equipped with a 4 mm H-X MAS probe. MultiCPMAS provides quantitative spectra that are comparable to direct polarization NMR techniques with enhanced S/N without the long experiment times (Johnson and Schmidt-Rohr, 2014). MultiCP was performed using the ramp-CP pulse program outlined in Johnson and Schmidt-Rohr (2014) consisting of 11 steps of 100 \(\mu\)s duration and a 1% amplitude increment from 90 to 100%. The sample (ca. 40 mg) was
packed into a 4 mm zirconium rotor and sealed with a Kel-F cap for multiCPMAS analysis. The multiCPMAS acquisition parameters were as follows: spectral frequency of 100 MHz for $^{13}$C and 400 MHz for $^1$H, spinning rate of 14 kHz, 8192 scans, and line broadening of 100 Hz. The recycle delays were 0.25 s for all samples and variable repolarization period ($t_z$) experiments were conducted to determine the optimal time of 0.25 s.

The spectra were integrated into the following chemical shift regions: aliphatic carbon (-10-45 ppm); alkyl-O carbon (45-60, 60-95, and 95-110 ppm); aromatic carbon (110-145 ppm); aryl-O carbon (145-165 ppm); and carboxyl and carbonyl carbon (165-210 ppm). Integration regions were chosen according to Nelson and Baldock (2005). All solid spectra were externally calibrated to the glycine standard (176.03 ppm).

2.6. Assignment of multiCPMAS signals to biochemical classes

Nelson and Baldock (2005) described the Molecular Mixing Model (MMM) for deconvoluting solid-state NMR spectra to estimate the content of major biochemical classes present in organic material. To estimate the amount of carbohydrates, proteins, lignin, aliphatic, carbonyl, and char material present in the five samples were subjected to the MMM technique utilizing the N/C ratios listed in Table IV.1 and the percent C distributions from multiCPMAS-$^{13}$C NMR listed in Table IV.2.
Table IV.1. Proportions of C, H, and N present in the Okefenokee Swamp Peat HA, Pahokee Peat HA, Dismal Swamp Peat HA, Mt. Rainier wood HA, and YOC coal HA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>molar H/C</th>
<th>molar N/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Okefenokee Swamp Peat HA</td>
<td>52.18 ± 0.15</td>
<td>5.07 ± 0.01</td>
<td>3.24 ± 0.02</td>
<td>1.16</td>
<td>0.053</td>
</tr>
<tr>
<td>Pahokee Peat HA</td>
<td>51.31</td>
<td>3.53</td>
<td>2.34</td>
<td>0.82</td>
<td>0.039</td>
</tr>
<tr>
<td>Dismal Swamp Peat HA</td>
<td>55.05 ± 0.30</td>
<td>5.65 ± 0.02</td>
<td>1.45 ± 0.03</td>
<td>1.22</td>
<td>0.023</td>
</tr>
<tr>
<td>Mt. Rainier HA</td>
<td>56.82 ± 0.42</td>
<td>5.00 ± 0.07</td>
<td>0.33 ± 0.01</td>
<td>1.05</td>
<td>0.005</td>
</tr>
<tr>
<td>YOC Coal HA</td>
<td>57.39 ± 1.37</td>
<td>4.11 ± 0.08</td>
<td>1.61 ± 0.04</td>
<td>0.85</td>
<td>0.024</td>
</tr>
</tbody>
</table>

Table IV.2. Distribution (%) of carbon atoms in Okefenokee Swamp Peat HA, Pahokee Peat HA, Dismal Swamp Peat HA, Mt. Rainier wood HA, and YOC coal HA.

Distribution of samples determined from solid-state mulitCPMAS-$^{13}$C NMR spectroscopy spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{13}$C Chemical Shift (ppm)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aliphatic</td>
<td>Alkyl-O</td>
</tr>
<tr>
<td></td>
<td>(-10-45)</td>
<td>(45-60)</td>
</tr>
<tr>
<td>Okefenokee Swamp Peat HA</td>
<td>26.4</td>
<td>9.7</td>
</tr>
<tr>
<td>Pahokee Peat HA</td>
<td>24.7</td>
<td>7.6</td>
</tr>
<tr>
<td>Dismal Swamp Peat HA</td>
<td>34.2</td>
<td>6.1</td>
</tr>
<tr>
<td>Mt. Rainier HA</td>
<td>9.8</td>
<td>13.2</td>
</tr>
<tr>
<td>YOC Coal HA</td>
<td>25.1</td>
<td>7.1</td>
</tr>
</tbody>
</table>
2.7. Elemental analysis

The elemental composition (CHN) of all the humic acid samples was evaluated using a FlashEA 1112 elemental analyzer containing a CHN column. Samples were prepared in triplicate and calibrated to standard curves of Acetanilide or L-Aspartic Acid.

3. Results and discussion

3.1. Ultrahigh-resolution mass spectral data

Humic acids from the three peats display ESI-FTICR-MS spectra showing the same enormous complexity as natural organic matter from numerous natural organic matter sources (Kujawinski et al., 2002; Kim et al., 2003; Kramer et al., 2004; Hertkorn et al., 2006; D’Andrilli et al., 2010). Obtaining unique molecular formulas from the highly resolved and accurate spectral peaks allows for plotting the formulas on a van Krevelen diagram which provides glimpses into the compositional motifs for the formulas (van Krevelen, 1950; Kim et al., 2003). It is from this type of analysis that one can discern the kinds of molecules comprising the humic acid samples. The current study focuses only on molecular formulas that have C, H, and O atoms as these comprise the dominant components of humic acids and molecular formulas containing N and S atoms along with C, H, and O atoms typically contribute less than 20% of all formulas. Also, some recent studies (Sleighter et al., 2014) show that natural organic matter made up of C, H, O, N, and S formulas show a similar van Krevelen pattern as the C, H, and O formulas.
Figure IV.1. van Krevelen plots of CHO molecular formulas for humic acids isolated from the A) Okefenokee Swamp peat, B) Pahokee peat, C) Dismal Swamp peat, and D) brown-rotted wood sample (Hatcher, 1987). CCAM-like molecules are located in the blue rectangular region, lignin-derived molecules are located in the yellow rectangular region, aromatic compounds ($\text{AI}_{\text{mod}} \geq 0.5$) and condensed aromatic ($\text{AI}_{\text{mod}} \geq 0.67$, Koch et al., 2006) are located below the designated lines, and BC-like molecules are located in the gray ellipse. Molecular formulas of the peat and wood humic acids that match exactly with formulas from photochemically produced particulate material (photoPOM) in the studies of Chen et al. (2014) are presented as red dots.
Figure IV.1 shows the van Krevelen plots for the peat humic acids and a wood sample that has been exposed to brown-rot fungi. The spectra of the peat humic acids (Fig. IV.1A-C) display numerous formulas plotting in the lignin region as noted with a yellow square in Figure IV.1. These molecules are most likely lignin-derived and can be expected to originate from woody material decomposed within the swamp environment. The van Krevelen plot of an extract of brown-rotted wood collected from Mt. Rainier, WA (Hatcher, 1987) is shown in Figure IV.1D to depict the formulas expected for lignin-derived organic matter. Previous studies (Hatcher, 1987; 1988) have shown that the brown-rot fungi selectively attack cellulose and minimally alter the lignin in this sample.

Clusters of molecules in other regions of the van Krevelen diagram are observed and noted in Figure IV.1. One of these clusters is assigned to aromatic ($A_{mod} \geq 0.5$) and condensed aromatic molecules ($A_{mod} \geq 0.67$, Koch et al., 2006), which plot in H/C region between 0.30 and 0.80 and the 0.20 to 0.60 O/C region. The formulas in this region are very similar to BC-like molecules from extracts of aged charcoal or from photoBC (Hockaday et al., 2006; Chen et al., 2014).

Another region of interest is a cluster of molecular formulas that range in H/C from 0.85 to 2.00 and O/C from 0 to 0.40. These molecules are mainly aliphatic in nature and comprised mainly of molecules having H/C ratios centered at 1.4, suggesting that they are alicyclic and/or olefinic in nature (Bolin et al., 2000) rather than saturated/linear or branched aliphatic molecules (Chen et al., 2014). There is evidence that some of the formulas in this region are aliphatic, defined by Perdue (1984), specifically the saturated mono- and di-acids. Additionally, through the use of Kendrick Mass Defect plots it is observed that the majority of these formulas have carboxylic functionality. Accordingly,
these formulas are referred to as carboxyl-containing aliphatic molecules, or CCAM. These molecules differ from the previously reported CRAM (Hertkorn et al., 2006) in that they encompass both aliphatic and alicyclic molecules and only require the presence of one carboxylic acid (determined using minimum number of two oxygens and at least one double bond equivalent). Furthermore, the formulas referred to in this paper are observed in peats and coals whereas CRAM is affiliated with DOM, thus I feel it necessary to use new terminology in reference to these formulas. It is possible that CRAM-like formulas are included within the CCAM region (H/C 0.85-2.0, O/C 0-0.4).

To confirm that the “photo” formulas (photoPOM) are newly produced organic compounds and are not affiliated with lignin, a major source for the Dismal Swamp DOM, the photochemically produced formulas are overlaid with the formulas obtained from the humic acids extracted from a Mt. Rainier wood sample in a van Krevelen diagram (Figure IV.2). The formulas associated with lignin in Figure IV.2 do not significantly overlap with photoBC or aliphatic photoCCAM formulas obtained from photochemical degradation of DOM collected from the Dismal Swamp.
Figure IV.2. A van Krevelen plot of CHO molecular formulas of photochemically produced particulate material from Dismal Swamp DOM (Chen et al., 2014) and a humic acid extract of a brown-rotted wood sample collected from Mt. Rainier, WA (Hatcher, 1987). The photoPOM (red dots) yielded both CCAM-like molecules (photoCCAM, blue rectangular region) and aromatic molecules (photoBC, gray ellipse region). The wood humic acids (black dots) are predominantly lignin-derived compounds (yellow rectangular region).
Figure IV.3. Percent distributions of CHO molecular formula of CCAM- (black), lignin- (dark gray), CCAM & lignin- (light gray), aromatic- (gray diagonal), and condensed aromatic like (black checkered) observed in Okefenokee Swamp peat humic acid, Pahokee peat humic acid, Dismal Swamp peat humic acid, and YOC coal humic acid. The percent distributions correspond with the distribution of molecular formulas outlined in Figure IV.1A-C and Figure IV.5.

The Okefenokee Swamp, Pahokee peat, and Dismal Swamp peat humic acids all contain lignin-like formulas but also photoCCAM and photoBC molecular formulas (Fig. IV.1A-C and Fig. IV.3) suggesting that photochemical degradation of DOM is not a unique occurrence to the Dismal Swamp. Considering the fact that photochemical degradation of DOM occurs continually in surface waters of the Dismal Swamp, as well as other swamps, it is anticipated that photoflocculation is providing sufficient newly formed organic matter
to the accumulating peat. It is also likely that a similar photoflocculation phenomenon occurs in the other black-water swamps based on the observed similarities between the van Krevelen diagrams in Figure IV.1.

**Figure IV.4.** Percent distributions of photoPOM CHO molecular formulas obtained from Chen et al., (2014) observed in Okefenokee Swamp peat humic acid, Pahokee peat humic acid, Dismal Swamp peat humic acid, and YOC coal humic acid. Distributions of CHO formulas are total photoPOM (black), CCAM- (dark gray), lignin- (light gray), aromatic- (black checkered), and condensed aromatic like (light gray with black dots). The percent distributions correspond with the distribution of molecular formulas outlined in Figure IV.1A-C and Figure IV.5.
Figure IV.5. A van Krevelen plot of CHO molecular formulas of humic acids isolated from a low-rank coal. CCAM-like molecules are located in the blue rectangular region, lignin-derived molecules are located in the yellow rectangular region, aromatic compounds ($\text{AI}_{\text{mod}} \geq 0.5$) and condensed aromatic ($\text{AI}_{\text{mod}} \geq 0.67$, Koch et al., 2006) are located below the designated lines, and BC-like molecules are located in the gray ellipse. Molecular formulas of the coal humic acids that match exactly with formulas from photochemically produced particulate material (photoPOM) in the studies of Chen et al. (2014) are presented as red dots.

Because pyrogenically-produced BC can also contribute to the peat, especially in regions of the swamp subjected to burning events, it is likely that the photoBC-like material is co-mingling with thermogenic-derived BC. The fire-impacted areas of the Dismal Swamp are recent, sporadic, and laterally limited in extent (Laing et al., 2011). I believe that fire events cannot solely account for the large amounts of BC observed in the peat. The humic acid extract of the Dismal Swamp peat (Fig. IV.1C) was collected from an area not
directly impacted by fire in recent history and thus can be viewed as a minimal source of the observed BC formulas. The mass spectrum obtained for this sample displays a significant portion of the BC-like molecules that were observed in the photoflocculated organic matter of Chen et al. (2014) (11% of total CHO formulas). A clear BC signature is observed from the van Krevelen diagrams of the humic acids of the Okefenokee Swamp peat, Pahokee peat, and Dismal Swamp peat (Fig. IV.IA-C) and is a significant percentage of the formulas plotting in the region of condensed aromatic molecules (Figure IV.3) like those of BC (Hockaday et al., 2006) and photoBC (Chen et al., 2014).

Figure IV.3 displays the percent distributions of the molecular formulas of the three peat humic acid samples. In the figure, it is clearly observed that all three peat samples contain primarily CCAM-, lignin-, and aromatic-like formulas. It is important to note that the CCAM and lignin-like regions have some overlap. The overlap region is defined as “CCAM & lignin-like” to reflect the fact that one cannot determine whether the molecules belong to CCAM-like or lignin-like structures by the elemental analysis alone. The Okefenokee peat, Dismal Swamp peat, and Pahokee peat humic acids all contain approximately 25% CHO lignin-like formulas. These results are consistent with the solid-state NMR data discussed below in section 3.2. There are no “photo” formulas observed in the CCAM & lignin-like region for any of the peat samples. Additionally, using the data displayed in Figures IV.3 and IV.4, it is possible to calculate that photoCCAM formulas account for an average of 24% of the CCAM-like CHO formulas and photoBC formulas account for an average of 9% of condensed aromatic CHO formulas in the three peat samples.

The presence of photoPOM formulas in the three peat samples could explain the
existence of some of the CCAM- and BC-like compounds found in coals originating from peat environments. To evaluate the persistence of photoflocculated materials and their ability to become incorporated into coals, the humic substances obtained from a low rank coal were compared with the photoPOM molecules obtained by Chen et al. (2014). The van Krevelen diagram (Fig. IV.5) of the humic substances obtained from the coal is visually similar to the van Krevelen diagrams of the peat humic acid samples shown in Figure IV.1, where the coal sample displays a complex mixture primarily composed of CCAM-, lignin-, and BC-like compounds. However, a striking difference between the coal and peat van Krevelen diagrams is the shift towards lower O/C values in the coal sample. This shift is the result of alterations to lignin during peatification and coalification involving loss of methoxy functionality to form catechol-like structures (Hatcher et al., 1989; Hatcher and Clifford, 1997). Due to the loss of oxygen, the resulting structures in the coal have lower O/C ratios than the precursor lignin material in the peats. These results are consistent with the NMR studies discussed in section 3.2.

Closer examination of the molecular formulas obtained for the humic acids from the coal reveals approximately 63% of the CHO molecular formulas are aromatic, of which 19% match with photoBC formulas. Similarly, the CCAM-like formulas account for large portion of the total CHO formulas, 37%; and 22% of the CCAM-like CHO formulas are photoCCAM formulas. In total, the photoPOM formulas represent 22% percent of all formulas observed in the HA extract of the coal. These results indicate that the photoPOM formulas observed by Chen et al. (2014) are, in fact, persistent within peat environments and ultimately contribute to the chemical nature of coal which derives from these types of aquatic systems.
3.2. NMR data

Solid-state NMR analysis is able to provide valuable bulk information regarding the sample of interest and was conducted on the three peat humic acids, the Mt. Rainier wood HA, and the coal HA. The five resulting spectra are displayed in Figure IV.6. All of the peat humic acid samples are primarily composed of aliphatic (ca. 29%), alkyl-O (ca. 26%), and aromatic carbons (ca. 22%), which are consistent with the distribution of molecular formulas displayed in Figure IV.3. Similarly, the multiCPMAS spectrum of humic acids obtained from the low-rank coal is dominated by aliphatic and aromatic carbon signals, representing 25.1% and 31.7% of the peak area, respectively. Because the coal has undergone peatification and the early stages of coalification, it is expected that minimal signal attributable to carbohydrates and proteins would be observed (Hatcher and Clifford, 1997; Scott, 2002). The Mt. Rainier wood sample has already been previously discussed in detail (Hatcher, 1987) and has been characterized as primarily lignin.
Figure IV.6. MultiCPMAS-$^{13}$C NMR spectra of humic acids from A) Okefenokee Swamp peat, B) Pahokee peat, C) Dismal Swamp peat, D) Mt. Rainier wood, and E) the YOC coal. Spinning sidebands are denoted with a black dot.
**Table IV.3.** Distribution (%) of biochemical classes in humic acids of the Okefenokee Swamp Peat, Pahokee Peat, Dismal Swamp, Mt. Rainier wood, and YOC coal. Distributions were determined using the Molecular Mixing Model (Nelson and Baldock, 2005).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Biochemical class</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbohydrate</td>
<td>Protein</td>
</tr>
<tr>
<td>Okefenokee Swamp Peat HA</td>
<td>9.9</td>
<td>16.6</td>
</tr>
<tr>
<td>Pahokee Peat HA</td>
<td>4.0</td>
<td>12.2</td>
</tr>
<tr>
<td>Dismal Swamp Peat HA</td>
<td>17.8</td>
<td>7.2</td>
</tr>
<tr>
<td>Mt. Rainier HA</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>YOC Coal HA</td>
<td>1.3</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Utilizing the MMM (Nelson and Baldock, 2005), it was possible to quantify the content of biomolecular components (carbohydrate, protein, lignin, aliphatic, carbonyl, and char) present in the peat, wood, and coal humic acids. The mathematical technique was applied to all five samples and the resulting distributions of biomolecular components are listed in Table IV.3. It is clear that all five samples displayed in Figure IV.6 have very little signal attributed to carbohydrates (peak at 72 ppm), which is confirmed by the results of the MMM (Table IV.3). This is consistent with the results displayed in the van Krevelen diagrams in Figures IV.1 and IV.5 where few formulas plot in the carbohydrate region (H/C >1.5 and O/C > 0.3 (Hockaday et al., 2009)). Additionally, it was possible to accurately estimate the amount of lignin present in the samples. It is apparent that the amount of lignin present in the peat humic acid samples, based on the methoxy peak at 55
ppm and the results of the MMM, increases in the following order: Dismal Swamp < Pahokee peat < Okefenokee Swamp peat. Lignin accounts for an average of 25% of the biochemical distribution in the peat humic acids. These results are expected as lignin is a primary source of organic material to swamps. The results obtained from NMR and the MMM are consistent with percent distributions of molecular formulas assigned to lignin-like molecules listed in Figure IV.3.

Additional regions of the NMR spectra that are of particular interest, due their relation to the photoCCAM and photoBC formulas obtained using FTICR-MS, are the aliphatic (-10-45 ppm) and aromatic (110-145 ppm) regions. The Okefenokee, Pahokee, and Dismal Swamp peat humic acids (Figure IV.6A-C) all display strong signals in the aliphatic region, with a sharp peaks at 30 and 33 ppm. These peaks have been previously associated with aliphatic biopolymers, cutan, cutin, suberan, and suberin (Deshmukh et al., 2005; Turner et al., 2013); however, I believe that photoCCAM materials are also contributing to the signal in the aliphatic region.

MultiCPMAS yields quantitative spectra, which can be a challenge to achieve using traditional CP techniques due to the varying relaxation times of aliphatic and aromatic carbons. The value of multiCPMAS is clearly demonstrated in the aromatic region of the spectra, where signal intensities comparable to direct polarization techniques are observed (Johnson and Schmidt-Rohr, 2014). The spectra of the Okefenokee Swamp and Pahokee peat are both dominated by aromatic signals representing 21.2% and 27.5%, respectively, of the total area. Contrary to the Okefenokee Peat and Pahokee Peat samples, the Dismal Swamp peat humic acids do not display a strong aromatic signal. This is likely due to interference of Fe that is bound to the aromatic compounds (Chen et al., 2014). It is well
known that the Dismal Swamp contains Fe in both the water (Minor et al., 2006) and the peat (Chen et al., 2014) and it is likely that the presence of Fe in the peat humic acids is selectively quenching the NMR signals of aromatic molecules that contains more carboxyl functionalities to complex with Fe than the aliphatic molecules (Chen et al., 2014).

It is hypothesized that a significant portion of the aliphatic and aromatic signals in the three peat humic acid samples (Figs. IV.6A-C) are due to the photoCCAM and photoBC molecules that were identified in the FTICR-MS analyses. Previous studies of peats (Hertkorn et al., 2002; Guignard et al., 2005; Zaccone et al., 2007) have affiliated the aliphatic region to refractory algal or terrestrial remains, which are likely present in the peat but with the discovery of photoCCAM molecules it is more likely photoCCAM molecules are the primary source of aliphatic signal in the peat. Likewise, the aromatic region, which has been thought to derive from lignin (Hatcher et al., 1983; Guignard et al., 2005) and thermogenic BC, may actually be heavily influenced by photoBC.

The accumulation of these molecules is also observed in the solid-state NMR spectrum of the low-rank coal displayed in Figure IV.6E. Similar to the aliphatic and aromatic regions in the peat humic acid samples, the multiCPMAS spectrum of the coal HA is primarily aliphatic, 25.1%, and aromatic, 31.7%. Furthermore, the MMM indicates a significant portion of the coal is aliphatic- and char-like. These results confirm what was observed in the FTICR-MS data (section 3.1.). It is likely that a significant portion of the observed signal in these regions is due to the preservation of photoCCAM and photoBC molecules in the coal.
4. Conclusions

The presence of photoPOM molecules in humic acids isolated from peats located around the United States indicates that the photoflocculation phenomenon, initially observed by Chen et al., (2014), is not a unique occurrence to Dismal Swamp DOM, but is possibly occurring in numerous swamp environments around the country and, likely, around the world. PhotoCCAM and photoBC molecules may account for a significant portion of the aliphatic and condensed aromatic molecules in the peats.

Furthermore, these compounds show evidence of geologic preservation as the photoCCAM and photoBC molecules were also observed in humic acids obtained from a low-rank coal. The observation of “photo” formulas in coals is particularly important to understanding the origin of unstructured coal macerals that are not assigned with certainty to a precursor source, as in the case of wood (vitrinite), charcoal (fusinite), algae (alginite), or spores (sporinite).

Many of the macerals and sub-macerals in coal have been assigned to specific names based on their microscopic architecture (Stach et al., 1982; Taylor et al., 1998). In many instances microscopic architecture is all that is utilized to ascribe a potential plant precursor origin to the maceral. While this approach is generally valid, in some cases, there could be many interpretations, especially in cases where microscopic small-scale architecture or macerated appearances precludes connection to well-ordered architectures of plant tissues or parts. Maceration often infers a biological comminution whereby the material in the peat travels through the gut of organisms and takes on a physical architecture that is now recognized in microscopy of the coal. However, it is likely that the original ingested material could have a multitude of sources and based on the results of this study,
photoflocculating materials in peat swamps should be considered as a source material.

In light of the findings of this study, it is possible that photoCCAM organic material might be responsible for some formation of the maceral liptodetrinite. Similarly, the photoBC organic material is possibly one precursor material for some forms of inertinite, more specifically the macerals macrinite, and micrinite. I do not mean to imply that fungally-degraded plant material is not important as a source, because it has been clearly argued (Hower et al., 2011) that physical remnants of arthropod fecal pellets can be recognized and the arthropods tend to seek out digestible organic matter but also eat whatever is in their path. In the process, they can ingest the photoCCAM material that becomes finely disseminated within the peat matrix and excrete it if there is no metabolic value. It is perhaps intriguing to consider that fecal pellets and other finely disseminated organic matter could be largely composed of the ingested and excreted photoCCAM because the more digestible cellulosic materials would presumably be consumed and transformed to organism biomass, CO₂, and other metabolic substances.

Based on the findings reported in this study, it is likely that the photochemical degradation of DOM observed by Chen et al. (2014) is occurring in a variety of aquatic systems and accounts for a large portion of CCAM- and BC-like compounds observed in sediments, coals and kerogens and can explain the occurrence of certain aliphatic and BC compounds in these peat environments.
CHAPTER V

VALUABLE CRUDE OIL FROM HYDROTHERMAL LIQUEFACTION OF AN ALIPHATIC COAL

Preface

The content of this Chapter was published in 2014 in Energy & Fuels, and below is the full citation. The formatting has been altered to incorporate the supporting information into the body of the manuscript. See Appendix A for the copyright permission.


1. Introduction

With the world’s energy consumption continuously growing, the demand for alternative fuels is urgent. Concerns regarding energy security has driven an interest in the artificial generation of liquid hydrocarbons for use in alternative fuels production. Coal, due to its relatively low price and abundance in both the U.S. and in other parts of the world, has been considered a suitable substrate for the production of liquid fuels ever since the early 1900’s. Production of liquid fuels from coal is possible through a variety of conversion processes (e.g., Fischer-Tropsch synthesis, pyrolysis, or direct coal catalytic liquefaction) but one in particular, hydrothermal liquefaction (HTL), often referred to as hydrous pyrolysis, is attractive due to its relatively low cost and ease of implementation (Höök and Aleklett, 2010; Lewan, 1997; Morgan and Kandiyoti, 2013). While the Fischer-Tropsch approach has been preferred for commercial production of synthetic fuels, there
are disadvantages due to costs and the high production of CO$_2$ (Dry, 2002; Kreutz et al., 2008). A challenge of direct coal liquefaction is it requires costly catalysts (Vasireddy et al., 2011).

HTL is particularly valuable because of its ease, lack of a need for catalysts or solvents, and does not require feedstock drying. Another benefit of HTL is its ability to closely simulate the naturally-occurring thermal maturation of organic material that results in the formation of petroleum (Lewan, 1993; Lewan, 1979). This offers valuable insight regarding the formation of petroleum from biomass, coals, and kerogens which chemical processes cannot provide. Along with the advantages of HTL there are challenges that arise with utilizing this technique, specifically its ability to adapt to industrial demands. A main hurdle of upscaling HTL from laboratory-scale to industrial-scale is the significant upfront cost required (Toor et al., 2011).

In recent years, HTL and fast pyrolysis are two methods that have gained an increased interest for their use in the generation of biofuels. Fast pyrolysis is commonly used to convert dry biomass materials into bio-oil, which can be used as a replacement liquid fuel for gasoline or diesel after upgrading (Czernik and Bridgwater, 2004; Mohan et al., 2006; Oasmaa and Czernik, 1999). The chemical composition of bio-oils often resembles that of the original biomass rather than a crude oil. Because biomass materials are inherently high in oxygen content, mainly from carbohydrates, lipids, and proteins the resulting bio-oils typically exhibit a high oxygen content (30-40 wt%) (Oasmaa and Czernik, 1999; Scholze and Meier, 2001). A high oxygen content in bio-oils results in a lower energy content and makes bio-oils not compatible for use directly as a transportation fuel (Czernik and Bridgwater, 2004; Huber et al., 2006; Zhou et al., 2010). There are solutions to addressing
the high oxygen content of bio-oils such as pretreatment of the biomass or hydروprocessing, but these techniques are time consuming and expensive (Bridgwater et al., 1999; Elliott, 2007).

HTL is a process that involves use of subcritical liquid water in the absence of oxygen to artificially mature coal, kerogen, and biomass samples. HTL does not require sample drying since the reaction medium is water, saving valuable time and money. The process generates low molecular weight hydrocarbons, mainly alkanes. The role of water in the conversion of organic material to petroleum-like products, referred to as bio-oil, has been shown to be essential for generating the maximum amount of expelled oils (Lewan, 1997). The use of subcritical water as a reaction medium has become attractive since water is abundantly available and inexpensive.

Numerous studies have employed HTL to generate bio-oils using unconventional materials including biomass, sewage, and tires (Barth, 1999; Rushdi et al., 2013a; Rushdi et al., 2013b; Valdez et al., 2011; Vardon et al., 2011). In addition to requiring upscaling, there can be excessive costs involved in growing and harvesting the biomass required for bio-oil production (Chisti, 2007; Elliott, 2007). A valuable alternative starting material for bio-oil production is coal. Coals originate from the same materials that are used in most of these previously mentioned HTL studies of biomass; however, most of the problematic energy poor and oxygen-rich compounds such as carbohydrates, lipids, and proteins, have been removed during peatification and coalification (Hatcher and Clifford, 1997; Scott, 2002). Utilizing coal would provide an oil from HTL that would potentially contain higher amounts of energy-rich components. Therefore, the goal of this study is to chemically characterize expelled oil from an appropriate low rank lignite after HTL treatment.
Oils produced from HTL are generally very complex and thus it is necessary to couple several complementary analytical techniques to obtain a complete characterization of produced oils. Utilizing several analytical techniques allows one to evaluate the feasibility of using the expelled oil as a transportation fuel and if downstream processing is necessary. Accordingly, this study employs a much more comprehensive analytical examination of the liquid products than has been previously reported in the literature. A coal having a high potential to yield liquid products upon pyrolysis was specifically sought out for this study. Stanton et al. (2005) identified coal from the Wyodak-Anderson (WA) seam of the Powder River Basin as having high Fischer Assay yields within certain sections of the coal seam. The upper units of the seam appeared to be particularly rich in oil yields, so a sample from this upper unit of the seam was selected for this study.

The primary use of WA coal is for electricity generation; however, the upper units of the coal seam are not mined because they are unsuitable for electricity generation due to their elevated pyrolysis oil yields and mineral matter. The upper section of the WA coal seam in the Powder River Basin, represents approximately 10% of the entire seam (Warwick and Stanton, 1988b), and is typically discarded with the mineral-rich overburden. The WA coal seam is part of a commercially significant resource in the United States that is estimated to harbor 550 billion short tons of coal in place (Ellis et al., 1999; Flores, 1999) and currently supplies 30% of the U.S. coal needs. Utilizing the discarded 10% of this resource to produce alternative fuels has numerous environmental and economic benefits, and could potentially offer another source for transportation fuels that currently goes unrealized and wasted.

The upper WA coal seam is comprised of low rank lignite rich in the coal maceral
crypto-eugelinite (Warwick and Stanton, 1988b). Crypto-eugelinite is often observed in location of cracks and crevices formally occupied by roots of plants or cell cavities (Taylor et al., 1998), and likely originated from root material. The chemical composition of crypto-eugelinite is not well defined; however, based on its presence in spaces previously occupied by roots, aliphatic moieties from the biopolymer suberan previously present in the roots may be abundant. Certain biopolymers present in plant tissue, cutan and suberan, are selectively preserved during coalification due to their biological and chemical resistance to degradation and become enriched in the coal (Hatcher, 1999). Cutan and suberan are polymethylenic biopolymers with ester functionality that are found in the leaf and root material of terrestrial plants where they act as layers of protection against microbial infection and desiccation (Boom et al., 2005; Kolattukudy, 1980; Nierop, 1998; Tegelaar et al., 1995; Turner et al., 2013). It has been suggested, that these biopolymers are able to survive diagenetic transformations through encapsulation of the ester bonds by the hydrophobic long-chain n-alkyl groups (Hatcher and Clifford, 1997; McKinney et al., 1996; Schouten et al., 1998). Upon coalification these biopolymers can greatly contribute to the coal’s chemical structure (Nip et al., 1986; Tegelaar et al., 1989; Tegelaar et al., 1995), explaining why the crypto-eugelinite-rich coal facies of the WA coal yield high oil contents upon Fischer Assays.

In this study the effectiveness of HTL for the artificial maturation of this coal section of the WA to produce a high quality hydrocarbon-rich oil is demonstrated. Employed are a number of advanced analytical techniques for enhanced characterization of the molecular components of the starting coal material and the expelled oil product. These techniques include cross polarization magic angle spinning (CPMAS)\textsuperscript{-13}C nuclear magnetic resonance
(NMR) (Althaus et al., 2012; Dela Rosa et al., 1992; Hatcher et al., 1994), electrospray ionization-Fourier transform ion cyclotron resonance-mass spectrometry (ESI-FTICR-MS) (Jarvis et al., 2012; Rodgers et al., 2005; Tessarolo et al., 2014), and two dimensional gas chromatography-mass spectrometry (GC X GC-MS) (Frysinger and Gaines, 1999; Sfetsas et al., 2011; Tessarolo et al., 2014). The correlation of several data sets allows for a comprehensive characterization of the expelled petroleum-like product and for a thorough evaluation of the potential this coal offers for the production of alternative fuels.

2. Materials and methods

2.1. Sample description

The coal utilized for this study was a low rank lignite collected from the WA seam of the Powder River Basin. The WA coal is part of the Tongue River Member of the Fort Union Formation and is of Paleocene age (Warwick and Stanton, 1988b). Coal was collected from the upper section of an actively-mined seam near Gillette, WY (Stanton et al., 2005) and is termed Area B by Warwick and Stanton (1988a). This unit is approximately 5 m in thickness. Approximately two 5-gallon containers of the coal section was sampled, sealed and shipped to the laboratory. The containers were subsampled to recover approximately 1 kg of wet coal that was freeze-dried.

2.2. Hydrothermal liquefaction

Samples of (ca. 2.0 g) freeze-dried, milled (20 mesh) coal was prepared for HTL in 22 mL stainless steel autoclaves in the presence of ca. 7.0 grams of milli-Q water. A small Ni-Cr screen (16 mesh) was placed on top of the coal to keep the coal restricted to the lower part of the autoclave and submerged in the water. Prior to heating, all autoclaves’ headspaces were flushed with He gas for approximately 3 min to ensure that all oxygen
was removed. The prepared autoclaves were heated at 360 °C for 72 h. The HTL temperature and time were selected based on previous HTL studies of similar sample types that have demonstrated maximum oil yield between 350-360 °C for 72 h (Lewan et al., 1985; Ruble et al., 2001). Upon completion of the heating time, the autoclaves were immediately placed in an ice bath to terminate the reactions. Products collected after HTL included spent solid residues and expelled oils. The expelled oils were collected using two methods. The first was solvent free where the expelled oils were manually sampled using a Pasteur pipet; the second method involved benzene extraction. This involved rinsing the inside of the autoclave with 5 mL of benzene, shaking extensively, and pouring the contents of the autoclave into a centrifuge tube. The contents were centrifuged to facilitate phase separation, and the organic and aqueous phases were transferred to separate vials and their recovered volumes were recorded. After the aqueous and organic phases had been removed from the autoclaves the remaining spent coal was collected and Soxhlet extracted for 24 h using 3:1 dichloromethane (DCM):methanol (MeOH) as the solvent. This extract was evaporated to dryness using a Büchi Rotovapor R-114 to determine the yields of expelled oils that remain associated with the spent solid. All products were weighed to determine a total mass balance of condensable material. Only gaseous products were not quantified.

2.3. Elemental analysis

The proportions of carbon, hydrogen, nitrogen, and sulfur in the untreated and spent coal and the expelled oil were determined using a Flash 1112 series Elemental Analyzer. Samples were analyzed in triplicate and their response areas were calibrated to a standard curves using nicotinamide for carbon and hydrogen, L-aspartic acid for nitrogen and sulfinamide for sulfur. Sulfur content was conducted in house for the expelled oil and was
quantified by Consol Energy according to ASTM D4239 for the untreated and spent coal. Ash corrected proportions of C, H, N, and S in the untreated coal, spent coal, and expelled oil were recorded. Percent ash was determined from the dry sample weights before and after oxidation in a muffle furnace at 425 °C for 2 h followed by 725 °C for 2 h and cooling in a desiccator. Oxygen content was determined by difference.

2.4. **Dissolved total carbon measurement**

Total dissolved carbon (TC) concentration for the water sample after HTL was determined as both organic and inorganic carbon on a Shimadzu TOC-5000V analyzer. Concentration of TC in the water was calculated using a standard curve of a sodium hydrogen carbonate-sodium carbonate solution. The total carbon concentration was 4996.06 ± 49.36 ppm.

2.5. **Heating value analysis**

Heating values of the untreated and spent WA coal were determined according to ASTM D5865 by Consol Energy. Values are reported on a moisture and ash free basis.

2.6. **Petrographic analysis**

The untreated WA coal was dried, milled to 20 mesh, and impregnated in cold-set epoxy resin for petrographic analysis (macerals analysis and vitrinite analysis) (Mukhopadhyay and Hatcher, 1993). Polished slides were examined using a Zeiss Axioskop microscope with a MPM 03 photomultiplier (Mukhopadhyay et al., 1998). Maceral analyses and vitrinite reflectance studies were carried out following standard procedures (Materials; Stach et al., 1982). Slides were prepared by National Petrographic Service, Inc. and petrographic analysis was performed by Dr. Mukhopadhyay at Global Geoenergy Research Ltd.
2.7. GC-FID

Gas chromatographic (GC) analysis was achieved using a HP6890N series gas chromatograph equipped with a split/splitless injector (HP6890 Injector) coupled with a flame ionization detector (FID). Chromatograms were produced using Agilent 6890 ChemStation software. The chromatographic column used was a Rtx-5 (30 m x 0.25 mm x 0.25 µm of 5% phenyl-95% dimethyl polysiloxane) supplied by Restek (USA). He gas was the carrier gas with a constant flow rate of 0.6 mL min\(^{-1}\). Following a 1 µL injection with a 10:1 split, the temperature program was as follows: 50 °C for 2 min, 10 °C min\(^{-1}\) to 300 °C and held at 300 °C for 10 min. The detector temperature was 250 °C. A standard \(n\)-alkane mixture (Boiling Point Calibration Sample #1, Agilent Technologies) was used to determine the retention times of \(n\)-alkanes observed in the expelled oil.

2.8. GC X GC-MS

GC X GC-MS analysis of the expelled oil was achieved using an Agilent 6890 2D GC coupled to Leco Pegasus IV Time of Flight Mass Spectrometer (TOFMS). LECO ChromaTOF software was used to operate the GC X GC-MS system. The expelled oil sample was injected into a heated (280 °C) split/splitless injector using a 1 µL injection volume with a 20:1 split. The first dimension column was a non-polar Restek Rtx-5 (30 m x 0.25 mm x 0.25 µm 5% phenyl-95% dimethyl polysiloxane). The carrier gas was He at a constant flow rate of 1.0 mL min\(^{-1}\). The temperature program was as follows: 40 °C for 0.5 min, 3.0 °C min\(^{-1}\) to 290 °C and held at 290 °C for 20 min. A quad jet-dual stage cryogenic modulator was used to focus compounds eluted from the first column prior to being separated in the second dimension. The modulator cold jet was dry nitrogen gas, chilled with liquid nitrogen gas and the hot jet air temperature was offset from the main
GC oven by +15 °C. The hot pulse time was 1.3 s with a cold pulse for 0.7 s between stages. The second dimension column was a polar Restex Rxi-17 (1.1 m x 0.1 mm x 0.1 µm 50% diphenyl-50% dimethyl polysiloxane) held at a constant temperature of 310 °C.

The TOFMS transfer line temperature was 280 °C, the electron ionization mode was set to 70 eV, and the MS ion source temperature was 200 °C. The MS detector voltage was set to 1550 V and the data acquisition rate was 200 spectra sec\(^{-1}\) over a mass range of 45-500 Da. The total ion chromatogram (TIC) was processed using LECO ChromaTOF optimized for Pegasus HT software implementing a signal to noise (S/N) of 80. The \(n\)-alkanes were identified using authentic standards (Boiling Point Calibration Sample #1, Agilent Technologies) while other compounds were identified using a NIST spectral database.

2.9. Solid-state CPMAS-\(^{13}\)C NMR spectroscopy

Solid-state \(^{13}\)C NMR analyses of the untreated and spent coal were performed using a 400 MHz Bruker AVANCE II spectrometer equipped with a solid-state MAS probe. Samples were packed into a 4 mm Zirconia rotor and sealed with a Kel-F cap. Samples were spun at the magic angle (54.7°) utilizing two experimental conditions listed in Table V.1. Experimental conditions 1 were chosen to obtain a high S/N spectrum with enhanced separation of the aliphatic peaks; however, the short contact time (0.7 ms) resulted in an underrepresented aromatic region. Experimental conditions 2 were implemented to produce spectra that were semiquantitative. Times listed in Table V.1 were chosen based on the results of variable contact time and recycle delay time experiments conducted on the untreated and spent coal. Spectra of untreated WA coal were obtained using conditions 1 and 2 and a spectrum of spent WA coal was obtained using condition 2 (Fig. V.1). Cross
polarization $^{13}$C NMR spectra were obtained with the basic ramp cross polarization pulse program (cp.av). Chemical shift calibration was performed with a glycine secondary standard and referenced to the carboxyl signal at 176 ppm.

Table V.1. Solid-state CPMAS-$^{13}$C NMR experimental parameters.

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinning speed</td>
<td>11 kHz</td>
<td>14 kHz</td>
</tr>
<tr>
<td>Contact time</td>
<td>0.7 ms</td>
<td>1.5 ms</td>
</tr>
<tr>
<td>Recycle delay</td>
<td>1 s</td>
<td>1 s</td>
</tr>
<tr>
<td>Number of scans</td>
<td>32,000</td>
<td>2,048</td>
</tr>
<tr>
<td>Line broadening</td>
<td>0</td>
<td>25</td>
</tr>
</tbody>
</table>

2.10. CPMAS-$^{13}$C NMR carbon conversion calculation

Utilizing the percent distribution of carbon atoms from NMR measurements and the carbon balance data it was possible to estimate the percent conversion of aliphatic carbon atoms in the untreated WA coal to aromatic functional groups in the spent WA coal or as carbon in expelled oil. The mass attributable to aliphatic and aromatic carbon for the untreated WA coal was determined by multiplying the total carbon mass of WA coal by the percent distribution of aliphatic carbon and aromatic carbon to yield ca. absolute weights of aromatic and aliphatic carbons in the sample. A similar calculation was utilized to determine ca. absolute weights of aliphatic and aromatic carbon masses in the spent WA coal. The mass of aliphatic carbon in the untreated WA coal converted to aromatic carbon
in the spent WA coal was calculated using equation V.1. $C_{aromaticspent}$ is the mass of aromatic carbon in the spent WA coal, $C_{aromaticuntreated}$ is the mass of aromatic carbon in the untreated WA coal, and $C_{ali\rightarrow aromatic}$ is the mass of aliphatic carbon in the untreated WA coal converted to aromatic carbon in spent WA coal. Using equation V.1, the absolute amount of aliphatic carbon in the untreated WA coal converted to aromatic carbon in the spent WA coal was determined.

$$C_{aromaticspent} = C_{aromaticuntreated} + C_{ali\rightarrow aromatic} \quad (V.1)$$

The amount of aliphatic carbon from the untreated WA coal that was lost as expelled hydrocarbons was calculated using equations V.2 and V.3.

$$C_{lostali} = C_{aliuntreated} - C_{alispent} \quad (V.2)$$

$$C_{lostali} = C_{alixpelled} + C_{ali\rightarrow aromatic} \quad (V.3)$$

$C_{lostali}$ is the total mass of aliphatic carbon lost from the untreated WA coal, $C_{aliuntreated}$ is the mass of aliphatic carbon in the untreated WA coal, $C_{alispent}$ is the mass of aliphatic carbon in the spent WA coal, and $C_{alixpelled}$ is aliphatic carbon expelled from the untreated WA coal as hydrocarbon products during HTL. For the calculation of aliphatic carbon lost from the untreated WA coal, the assumption was made that the aliphatic carbon that was not converted to aromatic carbon observed in the spent WA coal was expelled as hydrocarbon products. It is understood there may be other carbon conversions occurring, but for the purpose of this study only aliphatic carbon converted to aromatic carbon or lost as expelled products were considered.

2.11. **ESI-FTICR-MS**

The expelled oil was diluted with 1:1 (v/v) Tetrahydrofuran (THF):MeOH to achieve a final carbon concentration of ca. 30 ppm for analysis by ESI-FTICR-MS. The analyte
solution was infused continuously into an Apollo II ESI source of a Bruker Daltonics 12 T Apex Qe FTICR-MS assisted by nitrogen gas at a rate of 120 µL h⁻¹ by syringe pump (College of Sciences Major Instrument Cluster (COSMIC) facility at Old Dominion University, Virginia). The ESI voltage was 3.6 kV on the spray shield and 4.3 kV on the capillary set at 200 °C. Prior to running the analyte solution a blank solvent solution (1:1 THF:MeOH), was analyzed to avoid contamination or carry over from previous analyses.

The analysis of the expelled oil was carried out in the negative ion mode. Ions were accumulated in the hexapole for 2.0 s before being transferred into the ICR cell, where 300 scans were collected with a 4-Mega Word time domain and were co-added in broadband mode using a m/z range of 200-1200. The summed free induction decay signal was zero-filled once and Sine-Bell apodized prior to fast Fourier transform and magnitude calculation using the Bruker Daltonics Data Analysis software. A polyethylene glycol standard was used to externally calibrate the mass scale prior to analysis and the mass spectrum was internally calibrated using naturally present fatty acids and other homologous series detected within the sample (Sleighter et al., 2008). Only m/z values with S/N > 3 were considered. An in-house MatLab (The MathWorks Inc., Natick, MA) code generated empirical formula matches meeting the criteria: C₀₋∞, H₅₋₁₀₀, O₁₋₃₀, N₀₋₅, S₀₋₂ with an accuracy of < 1 ppm. Additional details of data treatment are described in Stubbins et al. (2010).

A modified solvent subtraction method was implemented to remove solvent contamination peaks without removing real sample peaks. Common peaks observed between the sample peak list and the solvent peak list were compiled and normalized to the smallest solvent peak magnitude. The normalized solvent peaks magnitudes were subtracted from the
normalized sample peak magnitudes yielding solvent free sample peak magnitudes. The corrected sample peaks that agreed with the S/N threshold were added back to the master sample peak list and molecular formulas were assigned using MatLab.

Table V.2. Percent abundance of macerals and sub-macerals observed in the untreated WA coal.

<table>
<thead>
<tr>
<th>Maceral</th>
<th>Sub-maceral</th>
<th>Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitrinite</td>
<td>Telocollinite</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Gelocollinite</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Desmocollinite</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Corpocollinite</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>25</td>
</tr>
<tr>
<td>Inertinite</td>
<td>Fusinite</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Semifusinite</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Macrinite</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Micrinite</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Inertodetrinite</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Sclerolinite</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>34</td>
</tr>
<tr>
<td>Liptinite</td>
<td>Sporinite</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Cutinite</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Resinite</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Suberinite</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Alginite</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Liptodetrinite</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Amorphinite</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>41</td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Organic petrography

Petrographic analysis of the untreated WA coal indicate that the random vitrinite reflectance in oil (R₀) of the coal is 0.43% ± 0.06%. The main maceral groups vitrinite, inertinite, and liptinite contribute 25, 34, and 41% of the organic components, respectively. Based on the abundant liptinite content that produces abundant bitumen and amorphinite the reflectance is suppressed and the coal is therefore considered to be closer to the characteristics of subbituminous coal. The lipinite group is composed of several sub-macerals including sporinite, cutinite, resinite, suberinite, alginites, liptodetrinite and amorphinite. The percent contributions of each maceral and sub-maceral are listed in Table V.2. It is quite surprising that the sub-maceral suberinite is observed in the WA coal as previous work by Warwick and Stanton (1988b) on a similar Wyodak-Anderson coal sample indicated no suberinite present. Suberinite is known to be transformed readily to bitumen at low rank and was likely more prevalent during early coalification. As maturation increases and the R₀ value increases above 0.5%, suberinite loses its hydrocarbon characteristics and eventually undergoes transformations to corpocollinite, while the more resistant sub-macerals, such as sporinite and cutinite, remain because they are more refractory. A photomicrograph in Figure V.1 displays various sub-macerals observed in the untreated coal.
3.2. Elemental composition of coal and expelled oil

Upon completion of the HTL treatment three layers were observed within the autoclave. The neat oil produced from the treatment was collected from the topmost layer and exhibited a red-brown color. Elemental (C, H, N, O, S) and ash contents for the untreated WA coal, the spent coal, and the expelled oil are displayed in Table V.3. The elemental composition of the untreated coal changes significantly after the HTL treatment, demonstrated by a significant increase in the percent carbon from the untreated coal, 57.64%, to the spent coal, 93.07% as well as a decrease in the molar H/C ratios from 1.46 to 0.54. The molar proportions of C and H in spent coal is consistent with a low volatile bituminous coal (Solum et al., 1989). Low H/C molar ratios of the solid materials that remain after the HTL treatment indicate that the remaining solids have a higher degree of aromaticity, which is expected with increased thermal maturation (Durand, 1980). The expelled oil from the HTL treatment of the coal displays an H/C molar ratio of 1.76, which
is consistent with what would be expected for oils rich in \( n \)-alkanes.

**Table V.3.** Proportions of C, H, N, O, S and ash present in the untreated WA coal, the spent WA coal and expelled oil product produced after subjecting the WA coal to HTL. CHNO and S are reported on a dry, ash free basis (DAF).

<table>
<thead>
<tr>
<th></th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% O</th>
<th>% S</th>
<th>% ash</th>
<th>molar H/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated Wyodak-</td>
<td>57.64 ± 1.21</td>
<td>7.08 ± 0.16</td>
<td>0.39 ± 0.05</td>
<td>32.52 ± 2.34</td>
<td>1.87</td>
<td>12.40 ± 2.00</td>
<td>1.46 ± 0.03</td>
</tr>
<tr>
<td>Anderson coal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>spent Wyodak-</td>
<td>93.07 ± 1.41</td>
<td>4.20 ± 0.08</td>
<td>1.46 ± 0.04</td>
<td>0.33 ± 1.41</td>
<td>1.22</td>
<td>24.05 ± 1.40</td>
<td>0.54 ± 0.01</td>
</tr>
<tr>
<td>Anderson coal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>expelled oil (neat)</td>
<td>73.44 ± 1.65</td>
<td>10.85 ± 0.21</td>
<td>0.39 ± 0.03</td>
<td>15.32 ± 1.67</td>
<td>N/A</td>
<td>1.14 ± 0.17</td>
<td>1.76 ± 0.06</td>
</tr>
</tbody>
</table>

The expelled oil exhibits a low heteroatom content as inferred from low contents of O, N, and S; although, a deoxygenation process may be required for direct use as a fuel in a spark engine (Yakovlev et al., 2009). It is well known that NSOs present in crude oil can be troublesome to refining operations. To meet EPA standards, sulfur has to be removed from crude oil during refining; however, catalysts used for sulfur removal can become deactivated by the presence of alkaline nitrogen-containing molecules (La Vopa and Satterfield, 1988). Another potential problem with NSOs in crude oil is the presence of acidic molecules that can lead to corrosion (Jayaraman and Saxena, 1995; Turnbull et al., 1998). Catalytic removal of O, N, and S in bio-oils has been extensively reviewed (Bridgwater et al., 1999; Bridgwater, 2012; Elliott, 2007). The oxygen content of the expelled oil from HTL of the coal, 14%, is much lower than the oxygen content of other alternative fuels such as bio-oils from fast pyrolysis methods, typically ranging from 35-
40% (Bridgwater, 2012; Oasmaa and Czernik, 1999; Scholze and Meier, 2001; Zhang et al., 2007) suggesting that HTL is a more appropriate method for the production of high quality petroleum-like products (Furimsky, 2000; Gandarias et al., 2008; Landau, 1997).

Using elemental analysis data along with the recovered masses (spent coal, expelled oil, and water) the carbon mass balance was determined (Table V.4). The total recovery of carbon was 98% and the unaccounted 2% is attributed to the gases that were not collected. The yield of oil based on total carbon is 21%.

Table V.4. Carbon balance of the starting dried untreated WA coal and recovered dried products and the carbon percent distributions (TC%) of the recovered products.

<table>
<thead>
<tr>
<th>Sample</th>
<th>grams of C</th>
<th>TC %</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated Wyodak-Anderson coal</td>
<td>1.3442</td>
<td>100%</td>
</tr>
<tr>
<td>spent Wyodak-Anderson coal</td>
<td>0.9887</td>
<td>74%</td>
</tr>
<tr>
<td>expelled oil (neat)</td>
<td>0.2842</td>
<td>21%</td>
</tr>
<tr>
<td>water after HTL</td>
<td>0.0352</td>
<td>3%</td>
</tr>
<tr>
<td>sum of products</td>
<td>1.3081</td>
<td></td>
</tr>
<tr>
<td>recovery</td>
<td></td>
<td>98%</td>
</tr>
</tbody>
</table>
Figure V.2. CPMAS-$^{13}$C NMR spectra of the untreated WA coal and the thermally altered spent coal residue utilizing experimental parameters listed in Table V.1. Spectra A and B display the untreated WA coal and spectrum C displays the spent coal. Spectrum A was run using experimental conditions 1, which consisted of a spinning speed of 11 kHz and 32,000 scans. The large number of scans results in a spectrum with enhanced S/N. Spectra B and C were run using conditions 2 which implemented a spinning speed of 14 kHz and 2048 scans. For comparison purposes, spectra B and C were run with the same number of transients and plotted on the same absolute scale. Peaks labeled with a circle have been identified as spinning sidebands (SSB).
3.3. CPMAS-$^{13}\text{C}$ NMR of untreated and spent coal

Both the untreated WA coal and the thermally spent residue remaining after the HTL treatment were analyzed by CPMAS-$^{13}\text{C}$ NMR and their spectra are displayed in Figure V.2. The untreated WA coal was analyzed utilizing two experimental conditions (Table V.1); condition 1 employed a lower spinning speed (11 kHz) and a large number of scans (32,000) which increases the S/N and provided a qualitative spectrum with enhanced resolution of peaks in the aliphatic, aromatic, aryl-O and carboxyl regions. Experimental condition 2 employed a higher spinning speed (14 kHz) and a lower number of scans (2048) and was used for a semi-quantitative comparison between the untreated and the spent WA coal. The untreated coal is primarily composed of aliphatic carbons, accounting for 55% of the total relative peak area, and is consistent with the molar H/C ratios presented earlier (Table V.3). The aliphatic region in the WA coal is dominated by two intense peaks at 30 ppm and 33 ppm characteristic, respectively, of amorphous and crystalline polymethyleneic carbons. These peaks have been previously associated with terrestrial biopolymers cutan and suberan (Hu et al., 2000; Turner et al., 2013). It is well known that these biopolymers are biologically and chemically resistant and able to survive early diagenetic transformations (Nip et al., 1986; Tegelaar et al., 1989; Tegelaar et al., 1995) and become incorporated into coals (Hatcher and Clifford, 1997; Scott, 2002). Based on the knowledge that crypto-eugelinite, an abundant submaceral in the WA coal sample, is found in peats and originates in the cracks and crevices formally occupied by roots (Taylor et al., 1998), it is likely that the 30 and 33 ppm signals are associated with suberan.

Other signals in the untreated coal are attributed to alkyl-O carbons (6.7%) from either carbohydrates, ethers, or esters. Aromatic signals account for 31% of the carbons with 6.3%
attributed to aryl-O carbons such as those associated with phenolic groups probably derived from lignin components that have undergone maturation (Hatcher and Clifford, 1997). The remainder, 25%, are mainly protonated, carbon-substituted, and catechol-like carbons. The weak shoulder at 145 ppm is most likely associated with the catechols typically found in low-rank coals due to transformations of lignin (Hatcher and Clifford, 1997). Carbonyl groups constitute 6.7% of the total carbons and both carboxyl carbons (175 ppm) and aldehyde/ketone carbons (210 ppm) comprise these functionalities.

After subjecting the untreated coal to HTL, the most apparent change observed between the untreated coal and the remaining spent coal was the loss of aliphatic carbons and the gain of aromatic carbons. The increase in aromatic carbons is consistent with the changes in the aforementioned elemental composition (H/C ratio) and other studies of artificial maturation of coals and biomass (Behar and Hatcher, 1995; Orem et al., 1996). The decrease in aliphatic carbon is attributed to the cracking of aliphatic C-C bonds (Leif and Simoneit, 2000; Lewan, 1997) that lead to the production of hydrocarbon-rich liquid products. It is possible to estimate the amount of aliphatic carbon that is converted to aromatic carbon or lost as expelled carbon utilizing the recovered masses (Table V.5), the total carbon data (Table V.3) and the percent distribution of carbon atoms observed in CPMAS-\(^{13}\)C NMR spectra (Table V.6) with equations V.1, V.2 and V.3. The ca. total absolute weight of aliphatic carbon lost from the untreated WA coal as either conversion to aromatic carbons or expelled products is 0.6 g and the ca. absolute weight of aliphatic carbon lost as expelled products is 0.3 g. These results are listed in Table V.5 along with
Table V.5. Estimates of carbon masses of various types of carbon observed in the untreated and spent WA coal as well as the corresponding total carbon percent (TC %).

<table>
<thead>
<tr>
<th>Type of carbon</th>
<th>grams of C</th>
<th>TC %</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated WA coal</td>
<td>0.7</td>
<td>54%</td>
</tr>
<tr>
<td>aliphatic carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>untreated WA coal</td>
<td>0.3</td>
<td>25%</td>
</tr>
<tr>
<td>aromatic carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>spent WA coal</td>
<td>0.2</td>
<td>17%</td>
</tr>
<tr>
<td>aliphatic carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>spent WA coal</td>
<td>0.6</td>
<td>61%</td>
</tr>
<tr>
<td>aromatic carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>aliphatic carbon lost from untreated WA coal</td>
<td>0.6</td>
<td>42%</td>
</tr>
<tr>
<td>aliphatic carbon converted to aromatic carbon in</td>
<td>0.3</td>
<td>20%</td>
</tr>
<tr>
<td>spent WA coal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>aliphatic carbon lost from untreated WA coal as</td>
<td>0.3</td>
<td>22%</td>
</tr>
<tr>
<td>hydrocarbon products</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table V.6. Distribution (%) of carbon atoms in untreated WA coal and WA coal that has been subjected to HTL. Distribution of samples determined from solid-state CPMAS-\(^{13}\)C NMR spectroscopy spectra B and C in Figure V.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(^{13})C Chemical Shift (ppm)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated Wyodak-Anderson coal</td>
<td>54</td>
<td>6.7</td>
</tr>
<tr>
<td>spent Wyodak-Anderson coal</td>
<td>17</td>
<td>8.9</td>
</tr>
</tbody>
</table>
the corresponding total carbon percentages. The percent aliphatic carbon conversion of the coal before and after HTL is 42%. The estimated conversion of the aliphatic carbons to liquid and gas products is 22%, which is consistent with the carbon recovery yields (Table V.4), and to aromatic carbon is 20%. The increase in aromatic carbon is caused by aromatization reactions of the aliphatic carbon during the HTL treatment.

3.4. Heating value of untreated and spent coal

To maximize the economic feasibility of the HTL treatment, it would be economically beneficial to use the spent coal as an energy source to power the HTL treatment. Initially the WA coal has a heating value of 14,773 dry and ash free basis (DAF) Btu/lb and after HTL has a heating value of 15,100 DAF Btu/lb. The heating value of the spent WA coal is comparable to Pocahontas #3 coal (Durand, 1980) and suggests it will be suitable for combustion in coal fired electric plants. Additionally, due to the 1990 Clean Air Act Amendments, the relatively low sulfur content (1.22%) of the spent WA coal makes it a desirable energy source (Ruppert et al., 2002).

3.4. Non-polar, volatile characterization of expelled oil

Aside from the spent residue, expelled oil was the main product observed after the coal was subjected to HTL. A benzene extract of the expelled oil was analyzed with GC-FID for quantification and characterization purposes. The GC-FID chromatogram (Fig. V.3A) reveals the presence of a homologous series of n-alkanes extending from C₈-C₃₂ that dominate the chromatogram. To confirm that the observed n-alkanes are products of HTL and are not intrinsic to the coal, the untreated coal was Soxhlet extracted with a 3:1 mixture of DCM:MeOH and analyzed using GC-FID. From the GC-FID chromatogram (Fig. V.3B) there does not appear to be a significant amount of hydrocarbon content that is inherent to
the coal and it can therefore concluded that the \( n \)-alkanes observed in the expelled oil are produced from the HTL treatment. The distribution of \( n \)-alkanes observed in the expelled oil is rather similar to that of waxy crude oils from coals especially those associated with low-rank coals in the Gippsland Basin, Australia and the Mahakam Delta, Indonesia (Peter et al., 2005; Tran et al., 2006).

Oils that have relatively high \( n \)-alkane contents, such as the oil examined in this study, are often referred to as “high wax crude oils” and are generally considered to be derived from terrestrial organic matter (Tissot and Welte, 1978). These types of waxy oils can be further refined to produce high value fuel products.

Two dimensional GC-MS was applied to the WA expelled oil, a technique that has

**Figure V.3.** GC-FID chromatograms of A) the expelled oil after subjecting the WA coal to HTL where \( n \)-alkanes have been labeled with a triangle and B) a 3:1 DCM:MeOH Soxhlet extract of the untreated WA coal.
Figure V.4. TIC and EIC GC X GC-MS chromatograms of expelled oil. A) TIC, B) alkanes (m/z 57), C) alkylbenzenes (m/z 91+106+120+134), (continued)
Figure V.4. (continued) D) ketones ($m/z$ 58), E) indanes ($m/z$ 117), F) phenols ($m/z$ 94+108+122), G) naphthalenes ($m/z$ 128+142+156+170). Compound classes have been circled and classified. The classification codes are listed in Table V.7. Peaks have been identified with relative bubble markers which are proportional to the peaks’ intensity within the displayed window. Alphanumeric designations indicate the number of alkyl substituents.

Table V.7. GC X GC-MS compound classes’ classification codes, total area percentage and peak count percentages as shown in Figure V.4A-G.

<table>
<thead>
<tr>
<th>Classification Code</th>
<th>Compound Class</th>
<th>Area %</th>
<th>Peak Count %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Alkanes</td>
<td>30.6</td>
<td>11.3</td>
</tr>
<tr>
<td>II</td>
<td>Cycloalkanes and Alkenes</td>
<td>19.8</td>
<td>28.1</td>
</tr>
<tr>
<td>III</td>
<td>Bicyclic alkanes and Cycloalkenes</td>
<td>2.2</td>
<td>4.4</td>
</tr>
<tr>
<td>IV</td>
<td>Alkyl benzenes, Ketones and Thiophenes</td>
<td>23.0</td>
<td>26.1</td>
</tr>
<tr>
<td>V</td>
<td>Indanes</td>
<td>3.7</td>
<td>3.6</td>
</tr>
<tr>
<td>VI</td>
<td>Phenols</td>
<td>11.3</td>
<td>4.7</td>
</tr>
<tr>
<td>VII</td>
<td>Naphthalenes</td>
<td>9.4</td>
<td>22.0</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

demonstrated its ability to separate complex mixtures such as petroleum and bio-oil samples (Frysinger and Gaines, 1999; Marsman et al., 2007; Parastar et al., 2011) and is well suited for characterizing the volatile compounds in the expelled oil collected in this
study. Figure V.4 displays the TIC and several extracted ion chromatograms (EIC) of the GC X GC-MS analysis of the expelled oil and demonstrates the complexity of the sample. The first dimension of the chromatogram displays separation based on volatility and the second dimension is a polarity-based separation. The use of two columns with different retention mechanisms provides the effective separation of coeluting analytes.

The most intense peaks are from \(n\)-alkanes ranging from \(C_9\text{--}C_{31}\) consistent with the GC-FID data (Fig. V.3A). This region contains 11.3\% of the total peaks and accounts for 30.6\% of the total peak area (Table V.7). Of all the petroleum-like products, \(n\)-alkanes are the least polar and have the weakest interaction with the secondary column resulting in a short retention time in the second dimension. The distribution of \(n\)-alkanes’ peak intensities are displayed in Figure V.5. In the low-carbon number range (\(C_8\) to \(C_{19}\)), there is a gradual decrease in concentration indicated by the peaks’ intensities (Fig. V.5), and there appears to be no preference of odd-over-even carbon numbers. However, there is a clear odd-over-even carbon number preference in the \(C_{20}\text{--}C_{30}\) range as the Carbon Preference Index (CPI) is 1.26 using the formula proposed by Bray and Evans (1961). An odd-over-even \(n\)-alkane preference is indicative of hydrocarbons that are derived from cuticular waxes from higher order plant material which is consistent with the NMR spectrum (Fig. V.1). It has been suggested that these \(n\)-alkanes are derived from early diagenetic transformations of fatty acids (Tissot and Welte, 1978) having a predominance of even-over-odd carbon numbers that would yield a predominance of odd-over-even numbered alkanes upon decarboxylation.
Figure V.5. Distribution of peak intensities of $n$-alkanes observed in GC X GC-MS chromatogram (Fig. V.4A) of the expelled oil from HTL treatment of WA coal.

Other compounds that are located in the alkane region of the chromatogram include mainly branched alkanes. These compounds have similar polarities as the $n$-alkanes but have slightly different volatilities resulting in their elution between the $n$-alkanes. Further examination of Figure V.4A indicates that in addition to the alkanes there are complex series of compounds of increasing polarity that separate along the vertical dimension. These include, cycloalkanes/alkenes, bicyclic alkanes/cycloalkenes, alkyl benzenes/ketones/thiophenes, indanes, phenols, alkyl naphthalenes, and various hydroaromatic structures. Other than the oxygenated aromatic compounds like the ketones and phenols, the occurrence of aromatics, cyclic, and hydroaromatic compounds in the expelled oil is quite desirable as these components are important to refining the oils for production of high octane fuels (Schobert, 1990).
The resolving power of 2D GC is best demonstrated through the separation of \(n\)-alkanes and ketones (Fig. V.4 A, B and D). In one dimensional GC these compound classes would likely coelute resulting in compromised peak shape and incomplete assessment of the sample; however, with the use of 2D GC these compounds classes are clearly resolved providing an enhanced characterization of the sample that would not be possible with 1D GC techniques. The alkyl benzenes/ketones/thiophenes compound class exhibits the second largest peak total area percent at 23.04% and accounts for 26.10% of the total number of peaks (Table V.7). Within this region, alkyl benzenes with 2, 3, or 4 alkyl substituents account for the majority of the total peak area (11.63%) and total number of peaks (6.18%), whereas the ketones account for 0.44% of the total peak area and 2.83% of the total number of peaks (Table V.8). Thiophenes are also present in this region, and account for a small percentage of the total number of peaks and peak area, 1.47% and 2.68% respectively (Table V.8). The incorporation of sulfur, specifically thiophenes, into petroleum has been extensively reviewed by Cai et al. (2003) and references within. The presence of thiophenes and other heterocyclic compounds is problematic as they are difficult to remove during fuel refining.
Table V.8. GC X GC-MS sub-compound classes’ classification codes, total area percentage and peak count percentages as shown in Figure V.4A-G.

<table>
<thead>
<tr>
<th>Classification Code</th>
<th>Sub-Compound Class</th>
<th>Area %</th>
<th>Peak Count %</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV</td>
<td>Alkyl benzene C2</td>
<td>4.9</td>
<td>0.7</td>
</tr>
<tr>
<td>IV</td>
<td>Alkyl benzene C3</td>
<td>3.6</td>
<td>2.1</td>
</tr>
<tr>
<td>IV</td>
<td>Alkyl benzene C4</td>
<td>3.1</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>11.6</td>
<td>6.2</td>
</tr>
<tr>
<td>IV</td>
<td>Ketones</td>
<td>0.4</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>0.4</td>
<td>2.8</td>
</tr>
<tr>
<td>IV</td>
<td>Thiophenes</td>
<td>2.7</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>2.7</td>
<td>1.5</td>
</tr>
<tr>
<td>V</td>
<td>Phenol C0</td>
<td>2.4</td>
<td>0.1</td>
</tr>
<tr>
<td>V</td>
<td>Phenol C1</td>
<td>3.5</td>
<td>0.9</td>
</tr>
<tr>
<td>V</td>
<td>Phenol C2</td>
<td>2.3</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>8.2</td>
<td>1.8</td>
</tr>
<tr>
<td>VII</td>
<td>Naphthalene C1</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>VII</td>
<td>Naphthalene C2</td>
<td>1.3</td>
<td>0.9</td>
</tr>
<tr>
<td>VII</td>
<td>Naphthalene C3</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>2.9</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Aromatic compounds, compounds containing only aromatic rings and chains, and cycloalkanes are important constituents of crude oil as they increase the octane number of transportation fuels. The principal aromatic compounds of crude oil are benzene, toluene, and isomers of xylene (Schobert, 1990; Tissot and Welte, 1978); the latter compounds are observed in Figure V.4. Toluene is the largest observed peak in Figure V.4A with a retention time of 472 s and 0.855 s while isomers of xylene are observed in the C2 region of Figure V.4C. The solvent delay prevented the observation of benzene. Based on total area percent (Tables V.7 and V.8), the main compounds classes of aromatic compounds
were alkylbenzenes (11.63%), naphthalenes (2.87%) and indanes (3.70%). The presence of aromatic and cycloalkane compounds in the expelled oil may be refractory components of the original coal material or produced through reactions that occur during HTL such as, cyclization of unsaturated molecules, thermal breakdown of alkyl chains on aromatic rings, or aromatization reactions.

Conversely, oxygenated compounds, such as phenols and ketones, present in crude oils are undesirable as they lower the heating value. Phenolic compounds account for 11.25% of the total peak area, where the majority of the phenolic compounds’ peak area is attributable to phenol, mono-alkyl substituted phenols (C1) and dialkyl substituted phenols (C2). It has been previously suggested that ketones, phenols and esters observed in bio-oils are the result of decomposition of lignin, proteins and cellulose present in the starting material (Cai et al., 2003; Schobert, 1990; Shuping et al., 2010; Toor et al., 2011; Zhou et al., 2010). The untreated WA coal contains small ketone, phenolic, and lignin signals in the NMR spectrum (Fig. V.1A) and minimal, if any, signals from carbohydrates or proteins. This is consistent with the GC X GC-MS analysis of the expelled oil where small amounts of ketones and phenols are observed.

3.5. Polar, non-volatile characterization of expelled oil

Two dimensional GC-MS provides excellent characterization of the non-polar, volatile compounds, but for a thorough molecular understanding of the expelled oil it is necessary to analyze the polar, non-volatile fraction of the oil as well. ESI-FTICR-MS is compatible with the higher molecular weight polar species present in oil samples and is complementary to results obtained through GC methods. The ultrahigh mass resolution and mass accuracy of the FTICR-MS has the capability to assign exact masses to thousands of compounds.
present in an oil sample (Fernandez-Lima et al., 2009; Jarvis et al., 2012; Marshall and Rodgers, 2008) and as a result provides a vast amount of sample information. ESI-FTICR-MS operates in either positive or negative mode, depending on the functional groups present in the sample. Positive ionization mode is suitable for basic compounds that readily gain a proton, mainly basic nitrogen containing compounds (Marshall and Rodgers, 2004; Sleighter and Hatcher, 2011). Conversely, negative ionization mode is appropriate for functional groups that easily lose a proton, such as carboxylic acids and alcohols (Hughey et al., 2002; Sleighter and Hatcher, 2011). Since a focus of this study was on the relationship between \( n \)-alkanes and fatty acids the expelled oil was analyzed using negative mode.

Over 2300 molecular formulas were identified in the expelled oil sample, of which approximately 1700 were assigned a unique formula with a mass range \( m/z \) 200-800. The majority of the formulas were CHO compounds, accounting for 79% of the formula assignments and 96% of the relative peak magnitude (Table V.9). The expelled oil also contained CHON, CHOS, and CHONS accounting for 9%, 10% and 2%, respectively, of the assigned molecular formulas (Table V.9). The distribution of the molecular formula assignments of the expelled oil is consistent with elemental analysis data (Table V.3), which shows that the majority of the expelled oil, based on weight, is C, H, and O.
Table V.9. FTICR-MS heteroatom content and compound classes’ relative peak magnitudes and peak count percentages. Relative peak magnitudes were calculated by dividing the sum of the peak magnitudes of interest (e.g. CHO, CHON, CHONS, etc.) by the summed total peak magnitude of the sample (Table V.8).

<table>
<thead>
<tr>
<th>Compound Class</th>
<th>Relative Peak Intensity %</th>
<th>Peak Count %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHO</td>
<td>96%</td>
<td>79%</td>
</tr>
<tr>
<td>CHON</td>
<td>1%</td>
<td>9%</td>
</tr>
<tr>
<td>CHOS</td>
<td>3%</td>
<td>10%</td>
</tr>
<tr>
<td>CHONS</td>
<td>&lt;1%</td>
<td>2%</td>
</tr>
<tr>
<td>total</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Lipid</td>
<td>96%</td>
<td>65%</td>
</tr>
<tr>
<td>Unsaturated Hydrocarbon</td>
<td>1%</td>
<td>15%</td>
</tr>
<tr>
<td>Condensed Aromatic</td>
<td>&lt;1%</td>
<td>0%</td>
</tr>
<tr>
<td>Lignin</td>
<td>2%</td>
<td>18%</td>
</tr>
<tr>
<td>Protein</td>
<td>&lt;1%</td>
<td>1%</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>&lt;1%</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>total</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

In an attempt to simplify the complex nature of the FTICR-MS data, visualization techniques are often applied. A visualization diagram commonly used to elucidate structural information from the thousands of molecular formulas present in a sample is a van Krevelen plot (Kim et al., 2003; Van Krevelen, 1950). The location of a molecular formula on the van Krevelen diagram can be correlated to major biochemical classes (Marshall and Rodgers, 2008; Sleighter and Hatcher, 2011). Figure V.6 displays the van Krevelen diagram of all the assigned molecular formulas from the expelled oil with the
Figure V.6. A van Krevlen diagram using all assigned molecular formulas from the expelled oil collected after HTL of the WA coal. CHO compounds are identified as blue circles, CHON compounds are red circles, CHOS compounds (continued)
Figure V.6. (continued) are green circles, and CHONS compounds are purple circles. The size of the bubble is proportional to the magnitude of the molecular formula peak. Boxes overlain on the plot indicate molecules having structural similarity to the molecular group listed and were adapted from Hockaday et al. (2009). The 100 most intense peaks have been reduced by an order of magnitude to allow for the visualization of the lower intensity peaks. A pie chart displays the relative peak intensities of the molecular formulas as lipid- (blue), unsaturated hydrocarbon- (red), condense aromatic-(green), lignin- (purple), carbohydrate- (teal) and protein-like (orange) compounds.

The majority (65%, Table V.9) of the molecular formulas plotting in the lipid region. Additionally, this region accounts for 96% of the relative peak magnitude. The molecular formulas are denoted using magnitude weighted bubbles relative to each other. To enhance the resolution of the lower intensity peaks in Figure V.6, the 100 most intense peaks were reduced by an order of magnitude. A high H/C molar ratio and low O/C molar ratio is consistent with other petroleum studies (Corilo et al., 2010) as well as with the elemental analysis data (Table V.3). There are not many molecular formulas that fall in the protein and carbohydrate region (1.6%, Table V.9), which is expected since the starting material coal is void of many of these types of structures in NMR (Fig. V.1).

Another visual diagram that can be used to discern trends is a plot of H/C vs. number of carbon atoms as utilized by Salmon et al. (2011) (Fig. V.7). One may also utilize plots of double bond equivalents (DBE) vs carbon number as employed in many crude oil studies (Jarvis et al., 2012; Marshall and Rodgers, 2008; Tessarolo et al., 2014). The
Figure V.7. H/C ratio versus number of carbon atoms per molecule for A) CHO compounds, B) CHOS compounds, C) CHON compounds and D) CHONS compounds. Molecules that are part of the same series fall along the same transect, several series have been identified and labeled within the plots. Peaks have been identified with bubble markers, relative to peaks within the specified family, which are proportional to the peaks’ magnitude. CHO peaks with a magnitude greater than E8 had to be reduced by an order of magnitude to allow for the visualization of the lower magnitude peaks.
molar H/C ratios plotted vs carbon number were chosen for this study, and using this approach results in formulas that are part of the same homologous series falling along the same transect. Molecular formulas have been designated by peak magnitude weighted bubbles and the sizes of the bubbles are relative to other compounds within the same family. CHO compounds display the greatest number of long, continuous homologous series (Fig. V.7A), containing 21 total series (6 have been traced and labeled) containing varying degrees of unsaturation ($C_nH_{2n}-0O_x$, $C_nH_{2n}-2O_x$ up to $C_nH_{2n-38}O_x$). Saturated compounds, such as fatty mono-acids and fatty di-acids, present in the expelled oil can be observed in Figure V.7A along the transects labeled $C_nH_{2n-0}O_x$ and $C_nH_{2n-2}O_x$. These series dominate the CHO compounds containing the largest peak, $C_{30}H_{60}O_2$, a mono-saturated fatty acid. Based on DBE/C and the modified aromaticity index (Koch and Dittmar, 2006), CHO compounds exhibit high aliphaticity and low aromaticity. The other compound families also exhibit homologous series. The CHON and CHOS compounds (Fig. V.7B and C) contain aliphatic and alkylaromatic series, with the majority of the CHOS formulas containing 1-3 oxygens and CHON containing primarily 2, 3, or 5 oxygens.

The CHO family is the most abundant, relatively based on peak magnitude, with 96% (Table V.9) of the relative peak magnitude belonging to this family. Fatty acids are responsible for the majority of the relative peak magnitude, specifically saturated fatty mono-acids and saturated fatty di-acids. The peak magnitude distribution of the saturated fatty mono-acids and saturated fatty di-acids are displayed in Figure V.8. As mentioned in the introduction, certain biopolymers can be preserved and incorporated into coals and it is hypothesized that upon thermal maturation ester linkages present in preserved
Figure V.8. Distribution of peak magnitudes of saturated fatty mono-acids (blue) and saturated fatty di-acids (red) observed in FTICR-MS analysis of the expelled oil from HTL treatment of WA coal.

biopolymers crack resulting in the formation of fatty acids. Further maturation of these fatty acids can result in decarboxylation to yield \( n \)-alkanes (Stach et al., 1982; Tissot and Welte, 1978).

The coal utilized for this study is believed to have originated from terrestrial material and it is likely that the fatty acids observed in the expelled oil originated from the biopolymers such as cutan and suberan. Suberan’s structure is predominantly crystalline with alkyl chain lengths C\(_{18}\), C\(_{20}\), and C\(_{22}\) connected with glycerol linkages (Turner et al., 2013). If a decarboxylation reaction of fatty acids present in the WA coal is occurring during HTL to yield the observed \( n \)-alkanes, there should be an observable relationship
between the distribution of \( n \)-alkanes (Fig. V.5) and the distribution of saturated fatty mono-acids and saturated fatty di-acids (Fig. V.8). The CPI value between C\(_{24}\)-C\(_{34}\) of the saturated fatty mono-acids and saturated fatty di-acids were calculated as 3.8 and 1.7, respectively. Due to the lack of a C\(_{28}\) peak magnitude for the saturated fatty di-acids, the peak magnitude of the neighboring C\(_{26}\) saturated fatty di-acid was used for the CPI calculation. The CPI values as well as the observed distribution (Fig. V.8) of the saturated fatty mono-acids and saturated fatty di-acids indicated there is a clear even-over-odd predominance. An even-over-odd distribution of acids is representative of higher order plant waxes (Chaffee and Johns, 1985; Tissot and Welte, 1978).

If decarboxylation of fatty acids is occurring during the HTL treatment of the WA coal, the even-over-odd predominance of saturated mono- fatty acids should yield an odd-over-even predominance of \( n \)-alkanes. Similarly, the even-over-odd predominance of saturated fatty di-acids should yield an odd-over-even predominance of mono-acids with loss of the first carboxyl group and then an even-over-odd predominance of \( n \)-alkanes. While there was an observable odd-over-even predominance of \( n \)-alkanes (Fig. V.5), it was only apparent in the high molecular weight compounds (\( \geq C_{20} \)). This suggests that while some decarboxylation of the fatty acids is occurring, it is a first step reaction followed by additional random cracking of the carbon-carbon bonds to yield the lower molecular weight \( n \)-alkanes with no apparent predominance (Leif and Simoneit, 2000; Lewan, 1997).

4. Conclusions

This work is the first detailed characterization of a petroleum-like product from HTL treatment of coal from the upper region of the WA basin. The complex nature of the collected expelled oil required the use of several advanced analytical techniques to achieve
a comprehensive molecular level understanding of the sample. Results from this study indicate that the WA coal can generate a high value petroleum-like product that is rich in \(n\)-alkanes and contains a lower heteroatom content than bio-oils produced using HTL.

These results suggest that during HTL, the aliphatic components of the coal undergo thermal alteration and lead to the formation of liquid hydrocarbon products. This hypothesis is supported by results obtained from CPMAS-\(^{13}\)C NMR. Analyses of the untreated and spent WA coal indicate that the majority of the aliphatic character is removed, and likely contributes to the formation of the expelled oil. Estimates of percent carbon conversions from the EA and CPMAS-\(^{13}\)C NMR reveal that a consistent fraction, ca. 22\%, of the aliphatic carbon observed in the untreated coal is converted to liquid and gas hydrocarbons.

GC techniques as well as (-) ESI-FTICR-MS provided a molecular understanding of the non-polar, volatile and polar, non-volatile fractions of the oil. Two dimensional GC analysis of the expelled oil was able to successfully separate the complex mixture of volatile compounds present in the expelled oil and showed evidence of desirable crude oil components such as cycloalkanes, alkyl benzenes, and naphthalenes, which are important constituents for refining to high octane value fuels. Negative mode ESI-FTICR-MS analysis provided thousands of molecular formulas, primarily CHO compounds. Comparing the distribution of \(n\)-alkanes, obtained using GC methods, and saturated fatty mono-acids and saturated fatty di-acids, observed from the (-) ESI-FTICR-MS data, provides complementary data sets yielding valuable insight regarding the formation of \(n\)-alkanes. The results of this study suggest that upon thermal maturation of the coal, the expelled oil is produced through first cracking of preserved esters to fatty acids, followed
by decarboxylation of fatty acids, and finally random breaking of C-C bonds to yield the lower molecular weight \( n \)-alkanes.

These results confirm that HTL is an effective technique to generate petroleum-like products from coals, and possibly other organic materials. The artificially generated petroleum produced in this study would be an effective alternative to crude oils. While the focus of my work reported here was to examine the chemistry of oils produced, it is noteworthy to mention that the eventual commercial utility of this HTL approach will depend on assessment of energy balances and economics. Such assessments are impractical from laboratory-scale experiments and require pilot-scale systems for more appropriate evaluation. However, I can make some assumptions to provide a general sense of the net energy production of the process. If it is assumed that the heat content of the water can be recovered with a 50% efficiency and that a commercial-scale system would be large enough to render the heat loss from a well-insulated reactor vessel negligible, then it can be calculated that the fossil energy ratio (Xu et al., 2011) of the products vs energy content of feed materials would be greater than 2 indicating that there would be a favorable gain in energy from the process.

Evaluating the economic feasibility of upscaling HTL examined in this study is challenging; however there are studies that have investigated the potential costs utilizing biomass materials (Zhu et al., 2014; Zhu et al., 2011). As a means to minimize costs and waste produced during HTL, it is proposed here to repurpose the spent WA coal as an energy source for HTL and to recycle the aqueous phase for multiple HTL treatments (Elliott et al., 2014; Zhu et al., 2015). There are several observations that lead one to believe that the technology presented in this work would be economically feasible. First, the coal
is wasted and not utilized as an energy resource and there is a cost incurred for just burying with the overburden. Second, the fossil energy ratio is very favorable and this translates into an economic gain. Third, most coal mining operations employ water for various activities and this water as well as well water sources can be employed and recycled for HTL. Also, coal mining companies have on-site licenses for use, disposal, and/or remediation of water used in mining operations. The waste water from HTL could be made compliant with those ongoing activities.
1. Conclusions

The primary focus of the studies outlined in this dissertation was to provide an enhanced chemical understanding regarding the fate of vascular plant material in coals, kerogens, and eventually the oils produced when these substances are subjected to thermal maturation. Utilizing the artificial maturation approach, hydrothermal liquefaction (HTL), it was demonstrated that the polymethylenic terrestrial biopolymers, cutan, cutin, and suberan, yield high quality petroleum-like products when heated at temperatures and pressures that mimic the oil production zone in deeply buried sediments, the oil window. The results obtained are particularly valuable as they not only shed light on the geological transformations that occur to plant materials during maturation, but also reveal the potential application these biopolymers have as alternative transportation fuel sources.

To obtain an enhanced chemical understanding of both the feedstock materials and the expelled oil products, several advanced analytical techniques were utilized and, when appropriate, correlated several data sets to obtain a comprehensive characterization that had not been previously reported. In order to characterize the feedstock and spent materials I relied heavily on cross polarization magic angle spinning (CPMAS)-$^{13}$C nuclear magnetic resonance (NMR) and flash pyrolysis-gas chromatography-mass spectrometry (py-GC-MS). The complex nature of the expelled oil products, commonly referred to as bio-oils, often required the application of several analytical techniques to obtain the desired in-depth molecular level characterization of the samples. These include electrospray ionization-
Fourier transform ion cyclotron resonance-mass spectrometry (ESI-FTICR-MS), gas chromatography coupled to flame ionization detection (GC-FID), and one and two dimensional gas chromatography-mass spectrometry (GC-MS, GC X GC-MS). Many of the conclusions presented throughout this dissertation would not have been possible without the use of the aforementioned instrumentations.

The studies of this dissertation began by examining the oil generating potential of suberan. Modern and ancient samples of the aliphatic biopolymer present in the bark and root material of certain terrestrial plants were subjected to HTL conducted at 360 °C for 72 h. I hypothesized that suberan would provide coal, specifically coal containing the maceral crypto-eugelinite, the aliphatic structural entities necessary for oil production. By examining both a modern, bark of Yellow Birch (YB), and ancient, lignite rich in crypto-eugelinite collected from the Wyodak-Anderson (WA) coal seam, the striking similarities between the untreated, spent, and expelled oil products collected from the modern and ancient samples was shown. Based on results obtained from CPMAS-\textsuperscript{13}C NMR the presence of suberan in the bark and coal was confirmed from the characteristic crystalline and amorphous peaks at 33 and 30 ppm. Additionally, a homologous series of \textit{n}-alkanes was observed when the samples were analyzed by py-GC-MS, further confirming the presence of suberan.

Upon subjecting the YB bark and the WA coal to HTL, high quality petroleum-like products were produced containing minimal amounts of heteroatoms (NSO). From the GC-MS chromatograms it was observed that the petroleum products were dominated by homologous series of \textit{n}-alkanes ranging from C\textsubscript{8}-C\textsubscript{31} for the YB bark and from C\textsubscript{8}-C\textsubscript{33} for the WA coal. It is obvious that the aliphatic C-C bonds present in the bark and coal are
cracking during the HTL treatment to yield the observed hydrocarbons. From these results it was concluded that aliphatic biopolymers, such as suberan, can explain the existence of waxy crude oils typically associated with coals and Type III source rocks. Another additionally important conclusion is that excellent quality liquid fuels can be obtained from HTL of these feedstocks making it feasible to engage in commercialization of this approach. Moreover, the WA coal rich in crypto-eugelinite is currently being discarded in the overburden being removed from the deposit and wasted as an economically viable source of fuel.

To further examine the ability of polymethylenic plant biopolymers to generate desirable petroleum-like products, samples containing cutin and/or cutan were subjected to HTL and their corresponding bio-oils were examined. Cuticular samples from Agave americana and Capsicum annuum were selected for this study for two primary reasons: 1) they contained differing amounts of cutin and cutan and 2) they represented cuticles found in a large segment of plants and fruits used in commercial operations. From CPMAS-\textsuperscript{13}C NMR and elemental analysis data it was observed that these cuticular materials were largely comprised of polymethylenic carbons and less than 30\% of their weights were attributed to N, S, and O. Since bio-oils often closely resemble their feedstock materials, these inherent molecular characteristics are ideal for producing high quality bio-oils that can be considered renewable potential fuels.

The bio-oils produced from A. americana and C. annuum cuticles contained less than 12\% by weight of N, S, and O resulting in higher heating values (HHV) of 40 MJ kg\textsuperscript{-1}. In an attempt to lower the oxygen content of the bio-oils a two-step HTL treatment was implemented and resulted in the oxygen weight percent of the A. americana bio-oil
decreasing by 40% and increased the HHV by 9%. The results of the two-step HTL process demonstrates HTL’s versatility to produce bio-oils and remove unwanted oxygen compounds from feedstock materials.

To obtain a complete molecular understanding and thoroughly evaluate the potential application of the *A. americana* and *C. annuum* bio-oils as an alternative fuel, it was necessary to couple data sets obtained from GC techniques and FTICR-MS analyses. Two dimensional GC-MS analyses, compatible with the non-polar, volatile fraction, displayed the complexity of the bio-oils samples and along with their striking differences. The *A. americana* bio-oil was predominantly composed of *n*-alkanes whereas the *C. annuum* bio-oil was dominated by cycloalkanes and alkenes. The FTICR-MS data revealed that the polar, non-volatile fractions of the bio-oils were largely lipid-like in character, accounting for 82% and 72%, of the total peaks in the *A. americana* bio-oil and the *C. annuum* bio-oil, respectively. From the results of all the biopolymer studies, it is concluded that cutin, cutan, and suberan are ideal feedstocks for the production of high quality bio-oils.

Because an overarching goal of this dissertation was to understand the geological preservation of terrestrial plant biopolymers within coals and kerogens, it was logical to study the chemical alterations that occur to organic matter in peat swamps. It was hypothesized that photochemical alterations of peat swamp dissolved organic matter would result in the formation of carboxyl-containing alicyclic (photoCCAM) and black carbon (photoBC) molecules and could explain the occurrence of petrographically distinct submacerals of the inertinite maceral groups in coal. This hypothesis was proven by examining humic acids samples isolated from peat samples collected from coal forming localities across the United States and from a low-rank coal of the Gippsland Basin,
Australia. Using ultra high resolution mass spectrometry and multiple cross polarization (multiCPMAS) $^{13}$C NMR. The FTICR-MS analysis confirmed the presence of photochemically produced formulas in the three peat samples and the coal sample. Quantitative analyses by multiCPMAS-$^{13}$C NMR complemented the results obtained by FTICR-MS, indicating that the peat and coal humic acid samples were primarily composed of aliphatic and aromatic carbons. These results lead to the conclusion that photoCCAM and photoBC account for a significant amount of the signal observed in these regions. The presence of photoCCAM and photoBC formulas in the peat and coal has significant implications in the fields of organic geochemistry, geology, and petroleomics as the findings of this study suggest a new source of organic matter to ancient deposits and could be a primary precursor material to oil. This conclusion was derived from the observations made in Chapter V where significant quantities of high-quality oil was generated from HTL of the WA coal which likely contains organic matter like that derived from photoCCAM in addition to the suberan biopolymers.

Finally, although the WA coal sample was originally chosen to represent suberan in an ancient form, it became apparent that in addition to its geological value it may also be economically profitable as an alternative fuel feedstock. Due to the high aliphatic content of the coal located in upper section of the WA coal seam, it is typically discarded along with the overburden as it cannot be used in traditional boilers in coal-fired power plants. Utilizing the upper section to generate alternative fuels through HTL has numerous environmental and economic benefits. Therefore, a more extensive study was conducted on the WA coal and the products produced after HTL to evaluate its application as an alternative fuel source. Based on the results discussed in Chapter V, it was apparent that
HTL of the WA coal generates a high value petroleum-like product that would be effective as an alternative fuel.

Similar to the study of the cuticular materials, GC techniques and FTICR-MS analyses were coupled to obtain a comprehensive characterization of the expelled oil. Two dimensional GC-MS analyses indicated that the WA coal expelled oil was primarily comprised of \( n \)-alkanes, displaying an odd-over-even preference. Additionally, through the use of 2D GC-MS it was observed the occurrence of aromatics, cyclic, and hydroaromatic compounds which are desirable components in petroleum products. The polar, non-volatile oil fraction was analyzed using FTICR-MS and revealed an abundance of saturated fatty mono-acids and saturated fatty di-acids displaying an even-over-odd predominance. Comparing the distribution of \( n \)-alkanes with the distributions of saturated fatty mono/di-acids, I was able draw the conclusion that during thermal maturation ester bonds present in the coal are being cracked to yield fatty acids, which upon additional heating are decarboxylated to yield the desired \( n \)-alkanes.

2. **Future work**

Upon completing the research outline in this dissertation there are many research directions that would be logical extensions. The most intriguing expansion would be to continue the work that focuses on the contribution photochemically produced particulate organic matter (photoPOM) has to ancient sediments, specifically, Type II kerogen. It is currently accepted by Organic Geochemists that Type II kerogen originates from marine autochthonous organic matter (Durand, 1980; Tissot and Welte, 1984); however, based on the findings outlined in Chapter IV, it is likely that photoPOM also contributes to the formation of Type II kerogen. It was observed that this photoflocculating phenomenon
originally observed by Chen et al. (2014) in the Dismal Swamp is not a unique occurrence and is likely also occurring in other aquatic systems, such as riverine systems. It would be valuable to collect transect water and sediment samples from a riverine system to an oceanic basin to investigate the occurrence of photoPOM compounds and their eventual fate in off-shore sediments known to be the main producers of Type II kerogen. This study would provide valuable insight regarding the fate of terrestrial matter in the ocean and potentially alter our understanding of Type II kerogens and their associated expelled oils.

In addition to examining the occurrence of photoPOM formulas in Type II kerogens, it is also necessary to obtain structural information regarding the photoPOM formulas observed by Chen et al. (2014). Currently, the structures of these compounds are hypothesized to be carboxyl containing alicyclic and condensed aromatic based on their placement within van Krevelen diagrams; however, a more thorough investigation using techniques such as 2D NMR and ion mobility mass spectrometry needs to be conducted in order to confirm the proposed structures. These compounds could potentially explain a significant amount of the aliphatic and condensed aromatic carbon found in the open ocean and therefore it is imperative to obtain structures that accurately represent photoPOM. Once structures are confirmed, photoPOM could readily explain the origin of certain compounds of expelled oils associated with Type II source rocks.

Another research aspect to pursue is conducting hydrothermal liquefaction experiments on triglyceride model compounds to provide mechanistic information regarding the formation of expelled oils from aliphatic biopolymers. It is likely that esters and fatty acids present in the aliphatic biopolymers play a central role in the formation of hydrocarbons. Furthermore, it is often observed that ancient oils contain no odd-over–even predominance
of \( n \)-alkanes while in modern oils an odd over even predominance of \( n \)-alkanes is observed. It is unclear why ancient and modern oils differ in their \( n \)-alkane predominance. By utilizing triglyceride compounds that contain both odd and even carbon chain lengths that have similar chain lengths to those found in cutan, cutin, and suberan and conducting variable temperature and timed experiments, it may be possible to propose a mechanism through which hydrocarbon formation occurs from cracking of esters and acids.
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APPENDIX A

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Author: Blaine E. Hartman and Patrick G. Hatcher

Publication: Energy & Fuels

Publisher: American Chemical Society

Date: Dec 1, 2014

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APPENDIX B

ABBREVIATIONS AND ACRONYMS

AI_FI  modified aromaticity index
BC  black carbon
C  carbon
CCAM  carboxyl-containing aliphatic molecules
CDS  Chemical Data Systems
COSMIC  College of Sciences Major Instrument Cluster
CPI  carbon preference index
CPMAS  cross polarization magic angle spinning
CRAM  carboxyl-rich alicyclic molecules
DAF  dry, ash free
DBE  double bond equivalent
DCM  dichloromethane
DOM  dissolved organic matter
EA  elemental analysis
EIC  extracted ion chromatogram
ESI-FTICR-MS  electrospray ionization-Fourier transform ion cyclotron resonance-mass spectrometry
GC-FID  gas chromatography-flame ionization detector
GC-MS  gas chromatography-mass spectrometry
GC X GC-MS  two dimensional gas chromatography-mass spectrometry
H  hydrogen
H_3O^+  hydronium ion
HA  humic acid
HHV  higher heating value
HTL  hydrothermal liquefaction
photoBC  photochemically produced black carbon
photoPOM  particulate organic material
photoCCAM  photochemically produced carboxyl-containing aliphatic molecules
MeOH  methanol
MMM  Molecular Mixing Model
multiCPMAS  multiple cross polarization magic angle spinning
$M_w$  mass of the water at room temperature
$m/z$  mass to charge
N  nitrogen
ND  not determined
NMR  nuclear magnetic resonance
O  oxygen
OH$^-$  hydroxide ion
P  phosphorus
py-GC-MS  flash pyrolysis-gas chromatography-mass spectrometry
$R_D$  random vitrinite reflectance
S  sulfur
S/N  signal-to-noise
SSB  spinning sidebands
T  tesla
TC  total dissolved carbon
TC$\%$  carbon percent distributions
THF  tetrahydrofuran
TIC  total ion chromatogram
TOFMS  time of flight mass spectrometer
$V_{wT}$  volume of water at the experimental temperature
$V_R$  reaction autoclave volume
$v/v$  volume-to-volume
WA  Wyodak-Anderson
YB  Yellow Birch
YOC  Yallourn Open Cut
\( \rho_v^T \) specific volume of the vapor phase at the experimental temperature

\( \rho_w^T \) specific volume of the liquid phase at the experimental temperature
VITA

Blaine Elizabeth Hartman
bhart020@odu.edu

Department of Chemistry and Biochemistry
Old Dominion University
Norfolk, VA 23529

Education

August 2015 ........................................ Ph.D. Chemistry, Old Dominion University
Norfolk, VA

May 2010 ...................................... B.S. Environmental Chemistry, Florida State University
Tallahassee, FL

Presentations


Awards

Lee Entsminger Outstanding Ph. D. Dissertation Award from the College of Sciences at Old Dominion University, Spring 2015.

CIBA Fellowship from the Department of Chemistry and Biochemistry at Old Dominion University, Summer 2014.

Graduate Student Travel Award from the Division of Student Engagement & Enrollment Services at Old Dominion University, Fall 2013.