Evaluation of Solvent Extraction of Lignite for Production of Transportation Fuels

by

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Abstract

Previous studies on the extraction of liquid products from coals have focused mainly on increasing the yield, with very little emphasis on the quality of the liquid products. The main goal of this study is to achieve a balance between the yield and quality of the coal derived liquids. The first part of the study focused on characterizing four fractions of coal liquid produced from thermal liquefaction, comparing the properties with those of specification fuels, and identifying refining pathways to produce on-specification fuels. The second part of the research focuses on studying the effects of liquefaction conditions on coal liquid quality. The quality was assessed by different analytical techniques including gas chromatography-mass spectrometry, high-performance liquid chromatography, and nuclear magnetic resonance.

In the first part of the study, Coal liquids were produced by solvent extraction of Bienfait lignite at 415 °C and 4 MPa H_2 for 1 h with a hydrotreatedcoal tar distillate in 2:1 solvent to coal ratio. Detailed characterization was performed on four straight run distillation fractions of the coal liquids in the 120-370 °C boiling range. Potential refining challenges were indentified by comparing the properties of the derived liquids with on- specifications of gasoline, jet and diesel fuel. Results indicate that coal-derived naphtha can be refined to an aromatic motor-gasoline blending component by mild hydrotreating to remove the heteroatoms present in the naphtha. Similarly, coal-derived kerosene can be converted into a jet fuel blending component, but does not meet standard specifications for jet fuel. Coal derived distillate; however, is a poor feed material for diesel fuel production.

The second part of the study seeks to understand the impact of liquefaction conditions on the molecular composition of coal derived liquids and in particular on the aromatic hydrocarbon composition. A sensitivity analysis is analysis is carried out to study the effects of temperature and residence time on the quality of the liquid products. Thermal digestion of a Canadian lignite coal was performed in an autoclave reactor. An industrial hydrogenated coal tar distillate was used as solvent with a coal to solvent ratio of 1:2. Digestion was carried out under initial hydrogen pressure of 4MPa at different temperatures and for different lengths of time. The reaction time was divided into two periods: heat-up time; the time required to heat the reactor from 25 ^{o}C to the operating temperature, and hold time; the time at the operating temperature before being cooled down. The tetrahydrofuran (THF)-soluble portion of the product was collected for analysis. The micro carbon residue (MCR) content of the THF-soluble liquids suggest an increases in the concentration of heavier molecules in the liquids as the reaction temperature and hold time increases. High performance liquid chromatography (HPLC) analysis revealed that the mono-aromatic and di-aromatic content decreased as the reaction temperature increased from 350 to 450 ^{o}C. This was accompanied with an increase in heavier polyaromatic hydrocarbons as well as the formation of new species of heavier polyaromatic hydrocarbons. Given that homolytic bond cleavage increases as reaction temperature increases, heavy polyaromatic hydrocarbon content is expected to decrease as reaction temperature increases. However, preliminary results indicate an increase in free radical recombination reactions and hydrogen disproportionation reactions as the liquefaction temperature increased from 350 to 450 ^{o}C. In a typical experiment, a 1.6 wt% reduction liquid yield was observed as the hold time increased from 15 minutes to 30 minutes at 450 ^{o}C. An increase in heavy aromatics content

would be understandable if liquid yield increased, as this will imply a trade-off between yield and quality. However, increasing the severity and time of thermal digestion of lignite coal resulted in lower quality coal liquids, without an increase in liquid yield.

Dedication

This work is dedicated to Dr and Dr Mrs Adesanwo, Oluwaseun, Oluwadamiloa, Anuoluwapo, and Iyanuoluwa Adesanwo; all whose encouragements and love helped me through this work.

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1 INTRODUCTION

There has been an increase in the world energy demand due to the population growth, technological advancement and increase in commercial activities. Crude oil has so far constituted the major energy source. Crude oil is finite in abundance and over the past years, this resource have been increasingly depleted. This has led to concerns over a potential energy crisis – where energy supply fails to meet up with energy demand. Crude oil is employed in the production of transportation fuels. However, there have been efforts to develop other energy sources to supplement crude oil. Coal has been considered a viable supplement to crude oil for transportation fuel. Coal was the source of liquid fuels until the discovery of vast deposit of crude oil. With the huge deposit of coal and the dwindling crude oil reserves, attention is being drifted back to coal for liquid fuel production. There appears to be a collective effort at reducing the reliance on crude oil as the only source of transportation fuels. Producing liquid fuels from coal is not as easy as it was initially. An increasing awareness of the negative impact of automobile emissions has led to more stringent specifications on transportation fuels. It is not any more sufficient just to produce liquid fuels from coal. It has become very crucial whether or not the liquid fuels produced meet specifications.

Conversion of coal to liquid fuel involves two processes namely: conversion of coal to synthetic crude, and refining of synthetic crude to specification fuels. Synthetic crude can be derived from coal either by direct or indirect conversion of coal. Direct conversion involves the use of high temperatures and pressures to break down the complex molecular structure of coal into simpler ones, whilst indirect conversion involves gasifying the coal into carbon monoxide and hydrogen, which are then carefully combined to produce desired synthetic liquids. Direct conversion of coal could be done catalytically (with catalyst) or thermally (without catalyst). Furthermore, thermal conversion of coal can be done in the presence of a solvent (solvent extraction) or in the absence of a solvent (pyrolysis). This study is focused on synthetic liquids produced via solvent extraction of coal.

There are many studies on the production of synthetic crude from coal, while only few exist on the refining of synthetic crude. Most of the studies on conversion of coal have been focused on improving the liquefaction yield and not the quality of the synthetic crude.

Unfortunately, liquids derived from solvent extraction of coal cannot be used as drop-in fuels because of their high aromatic and heteroatom content. This is so because thermal digestion of coal, which involves pyrolysis of coal at elevated temperatures and pressures in the presence of hydrotreated coal liquid as solvent, produces smaller molecules which resemble the parent coal in properties – high aromatic and heteroatom content. For refining to specification fuels, it is needful to characterize the CDLs. Their properties are then compared with those of specification fuels. With this, we then can formulate a refining pathway. However, it is desirable to reduce downstream refining work by ensuring CDLs produced are easy to refine. To accomplish this, an understanding of how digestion conditions influence quality of CDLs is required.

In the first part of this study, CDLs were produced after a Canadian lignite coal was thermally digested at 400°C for 60 minutes under initial hydrogen partial pressure of 4MPa in an autoclave reactor. It is fractionally distilled into different boiling fractions. The different boiling fractions are exhaustively characterized and refining pathways are formulated for each fraction.

Temperature and residence time are two liquefaction conditions that influences liquefaction yield. The effect of these conditions on quality of CDL produced from thermal conversion of lignite coal is also studied.

The present work is comprised of 6 chapters. The first chapter contains the problem statement, and it is followed by the bibliographic review presented in chapter 2. The experimental procedures are presented in chapter 3. Chapters 4 and 5 contain the experimental results of the characterization study and the study of temperature and time effects on coal liquid quality respectively. And finally, chapter 6 presents the conclusions.

Results from this study will hopefully prove to be helpful industrially given the recent interest in seeking alternative sources for the production of transportation fuels. The challenges to be encountered in the refining of thermally produced CDLs will be understood.

1.1 Research Objectives

This research has two main objectives. The first is to understand the suitability of liquids derived from solvent extraction of coal as potential stock for production of transportation fuels. This is hoped to be accomplished by the following tasks:

1. Produce coal liquid and fractionate into four boiling point ranges.
2. Characterize the four fractions.

3. Compare their properties with those of gasoline, jet and diesel fuel, as well as identify potential refining challenges.

The second objective of this research is to study the effects of temperature and residence time in the quality of coal liquids with the aim of arriving at suitable reaction conditions to produce easy-to-refine coal liquid products.

1.2 Limitations

This study is limited to direct thermal digestion, and specifically solvent extraction of a Canadian lignite coal.

2 LITERATURE REVIEW

Transportation is responsible for large consumption of energy derived from oil and gas, and is responsible for about 40% of the total daily oil consumption in the US. This is about 9 million barrels of oil per day. Oil exports in the US as reported, are expected to rise by 60% in 2025. Reducing the dependence on petroleum, by producing liquid fuels from coal, natural gas, oil shale and other carbon based sources, would be beneficial.

Coal plays an important role in meeting energy needs. In 2006, it accounts for 26% of the total world energy consumption. It is also viewed as an attractive alternative source to petroleum in the production of liquid fuels. There are several reasons for coal to be considered as a viable alternative source of liquid fuel. It is estimated that worldwide deposit of coal is ten times larger than that of any other carbonaceous sources, and is more widely located than oil reserves. Countries like the US, China, India, Australia, which are presently relying on oil imports, have large deposits of coal. Moreover, technology required to convert coal to liquid fuels already exist. Pipelines to transport the liquid fuels already exist, as well as refineries to process liquid fuels.

Conversion of coal to liquids can be done directly, also referred as direct coal liquefaction (DCL), or indirectly, also referred to as indirect coal liquefaction (ICL). DCL is a reductive pyrolysis in which coal is converted directly to liquids by reaction with hydrogen. It can be represented in the following reaction: [1]

$$\mathrm{CH_{0.8}S_{0.2}N_{0.01} + xH_2 \rightarrow CH_2 + CO_2, H_2S, NH_3, H_2O}$$

DCL technologies have higher thermal efficiencies (between 65 and 70%) than those of indirect liquefaction (about 55%). This gives DCL a significant advantage over ICL technologies.[1]

Table 2-1: Countries with largest recoverable coal reserves (billion short tons)[1]

Country	Anthracite and Bituminous	Lignite and Subbituminous	Total
USA	126.8	146.8	273.6
Russia	54.1	119	173.1
China	68.6	57.6	126.2
India	90.8	2.2	92.8
Australia	46.9	43.6	90.5
Germany	25.3	47.4	72.7
South Africa	54.6	-	54.6
Ukraine	17.9	19.7	37.6
Poland	22.4	2.0	24.4
Canada	3.8	3.4	7.2
UK	1.1	0.5	1.1

2.1 History of DCL

Direct coal liquefaction was invented by Friedrich Bergius in 1913, while I.G Farben developed the process in Germany in 1930. The direct liquefaction processes required high temperatures and high pressures, due to its inefficiency. These German liquefaction plants were evaluated in the US as well as other countries. Further developments of coal liquefaction technology met with an obstacle, which proved unsurmountable – the discovery of cheap petroleum. Petroleum was discovered in the Middle East in the 1950's, and this halted coal liquefaction developments, except in South Africa. The oil crises in 1973 and 1978 sparked development of alternative technologies for production of liquid fuels mostly using coal as feedstock. These technologies can be categorized into two groups namely: Single stage processes and Two-stage processes.

The single stage processes were developed primarily from the mid 1960's to early 1980's. This technology produces distillates in one primary reactor or set of reactors in series operating at the same conditions. Example of these technology includes Kohleoel (Ruhrkohle, Germany), NEDOL (NEDO, Japan) (Pilot Plant operation late 1990's), H-Coal (HRI, USA), Exxon Donor Solvent (Exxon, USA) and Solvent Refined Coal (SRC-I and SRC-II) (Gulf Oil, USA).

The two-stage DCL process involves the use of two reactors in series operating under different conditions. The first reactor is employed for coal dissolution. It is usually operated with a manufactured catalyst or with a low activity iron-based catalyst which is often disposed after use. The second reactor is employed for hydrocracking and hydrotreating the heavy coal liquids produced from the first reactor. This is carried out in the presence of high activity and more expensive catalyst. Example of this technology includes Brown Coal Liquefaction (NEDO, Japan), Catalytic Two-stage Liquefaction (DOE, HTI, USA), Integrated Two-stage liquefaction (Lummus, USA), Liquid Solvent Extraction (British Coal Corporation, UK) and Supercritical Gas Extraction (British Coal Corporation, UK). The SRC-II, EDS and H-coal processes were successfully developed in the USA, and became a platform for future developments. They were, however, not economically attractive.[1]

Table 2 shows a comparison of process conditions, oil yields and production capacity of different processes.

Table 2-2: Comparison of process parameters and yields of DCL technologies[1]

Process	Single stage DCL				Two-stage DCL		
	NEDOL	H-Coal	EDS	Kohleoel	BCL	CTSL	LSE
Scale/td^{-1}	150	200	250	200	50	1 Mty^{-1}	2.5
R&D step	Pilot	Pilot	Pilot	PDU pilot	Pilot	Commercial	Pilot
Reactor/Catalyst	2-4% Fe	Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3	Non catalytic	Fe catalyst (red mud)	Fe slurry Ca-Ni-Mo	Fe Gelcat-1st stage, 2-stage ebullated reactor Ni-Mo/Al_2O_3	Noncatalytic (1st stage) ebullated-bed reactor (2nd stage)
Temperature (°C)	435-465	435-465	425-450	470	427-448, 360-400	430, 435-440	410-440, 400-440
Pressure (atm)	150-20	200	175	300	150 -200	170	10-20, 200
Yield (%)							
Hydrocarbon gases ($C_1 – C_4$)	16.9	10.5	5	19	13.6	-	15.4
Light oils (C5 - 200°C)	28.8	13.3	14	25.3	36.7	60-65	49.9
Middle oil (200-325°C)	19.3	19.7	10	32.6	15.1	-	12.4
Unreacted Coal and pitch	18.8	37.1	48	22.1	8.1	7-22	24.7
Characteristic	Need upgrading	Reload catalyst during reaction			Using brown coal (moisture 60%)	First DCL plant	

There is an increased selectivity towards distillates with low heteroatom content in the two-stage CTSL compared to the single stage H-Coal process.[1] The low oil prices have prevented the commercialization of any of the two-stage technology. In 2008, however, Shenhua group in Chinabuilt and began operation of the only commercial DCL plant. The plant is designed to produce 778 600 t y^{-1} of liquid fuels, 229 800 t y^{-1} of naphtha and 101 800 t y^{-1} of LPG. The Shenhua DCL plant involves the use of two ebullated reactors in series operated at temperatures of about 450°C. Nano-sized iron catalyst prepared from $Fe(SO)_4$ are used and a hydrogenated recycle solvent is used for a higher hydrogen donor capability.[2]

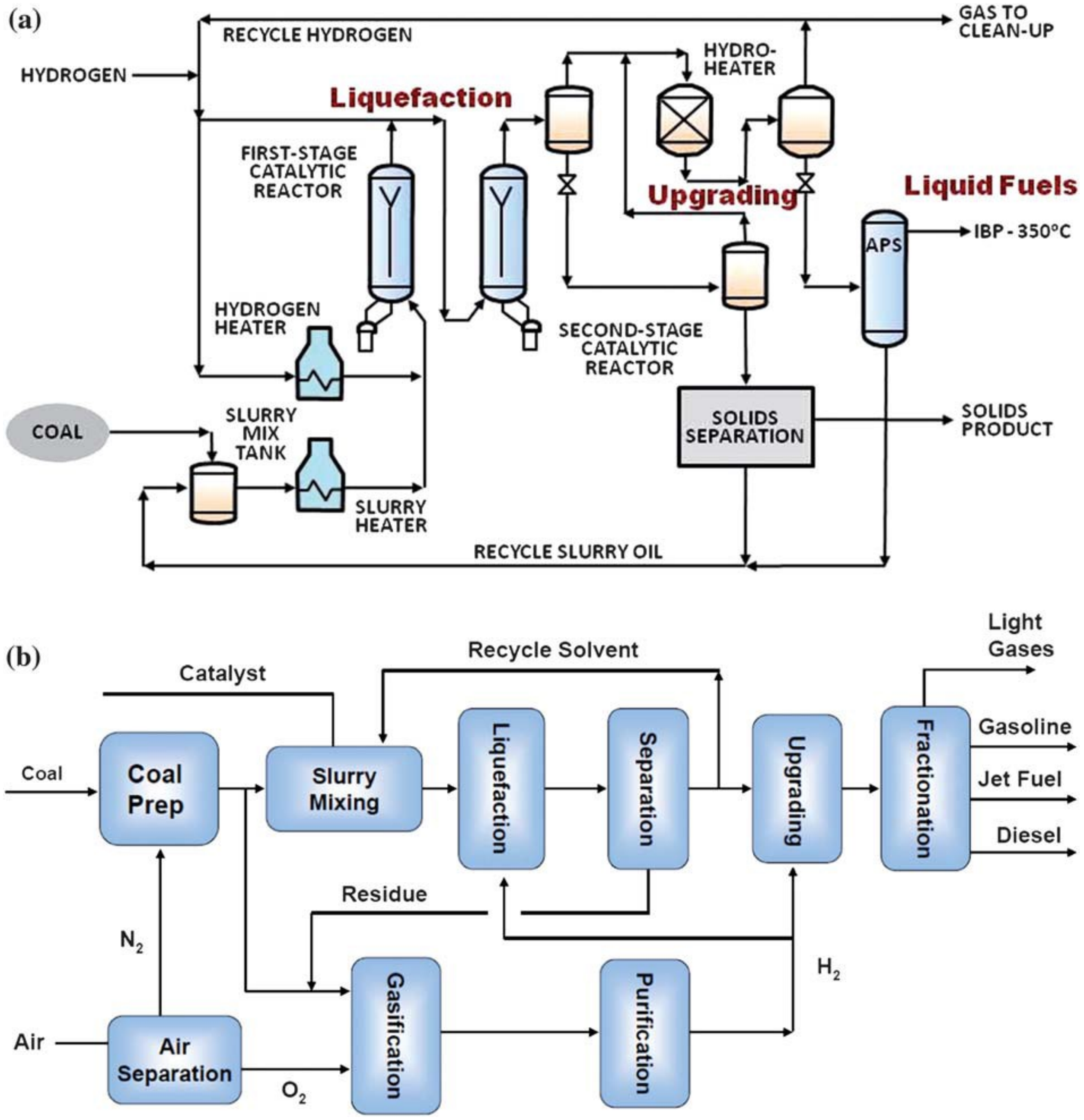


Figure 2-1: (a) Process flow for catalytic two-stage direct liquefaction (CTSL) developed by HTI and DOE in USA. Source: Comolli and Zhou, DOE report under contract no. AC22-92PC92148, January 2000. (b) A flow diagram of the Shenhua Direct Coal Liquefaction plant [2]

2.2 Coal

Coal is physically and chemically a heterogeneous copolymer which mainly consists of organic material made up of large, complex molecules containing mostly cross-linked aromatic ring structures plus varying amounts of inorganic and organically bound sulfur (<1 to 6%), nitrogen (<1 to 2%) and oxygen as structural components. Raw coal also contains moisture and solid particles of mineral matter.[1]

Chemical transformation of coal involves deoxygenation, dehydration, aromatization and oligomerization. The degree of transformation influences the elemental composition of coal. The carbon content of the dry- and ashfree (DAF) coal increases from 60 wt% (peat) to 94 wt% (anthracite), as the coal rank increases from peat to anthracite. Hydrogen content, however, decreases from 6 wt% (peat) to 3 wt% (anthracite) and oxygen decreases from 34 wt% to 3 wt%. Sulfur and nitrogen show less variation with coalification. Aromatic carbon content also increases from 0.5 (mole fraction in peat) 0.98 in anthracite.[3,4]

2.3 Direct Coal Liquefaction

DCL is aimed at breaking down the complex structure of coal into smaller molecules. These smaller molecules can then be further refined to clean fuel products. Refining often involves hydrotreating to remove heteroatoms such as sulfur and nitrogen containing compounds[1,5,6].

2.3.1 General Description of DCL

Direct Coal Liquefaction involves two stages. Primary liquefaction or coal dissolution occurs in the first stage, while and the second stage involves the upgrading of the primary liquid products to synthetic crude oil.

A slurry is made from ground coal and process derived solvent (often recycled) and is exposed to hydrogen at high temperatures of about 400-450°C and pressures of about 15-30 MPa in the presence or absence of catalyst. This produces liquids that can be further upgraded to specification fuels. The macromolecular structure of coal is thermally fragmented to produce free radicals which are capped by hydrogen. This hydrogen donation may be by hydroaromatic solvents, other hydrogen donating species in the coal, in vehicle solvents, and by gas phase H_2. At such high temperatures and pressures, retrogressive reactions can occur leading to heavier products. However, it is believed that rapid heating up to several hundred degrees per minute can prevent retrogressive reactions as well as enhance oil yields. Retrogressive reactions can also be suppressed by the use of hydrogen donor solvents which acts by capping radical moieties, thus, preventing recombination reactions. The amount of hydrogen consumed from solvent is reported to be directly related to the heating rate. The primary liquefaction step produces preasphaltenes, asphaltenes and oil along with C1–C4 hydrocarbons and inorganic gases such as ammonia and hydrogen sulfide.

The crude liquid product is then separated by distillation from solids containing coal residue, mineral matter and catalyst. A fraction of crude liquid is hydrotreated and recycled to prepare the coal slurry. The crude liquid left is further treated in the vapor phase with the hydrogen over fixed bed catalysts, where thermal and catalytic cracking, hydrogenation and hydrocracking reactions take place to produce fuels of various specifications.[1]

2.4 Chemistry of Coal Liquefaction

Coal liquefaction process is the breaking down of macromolecules in coal into smaller hydrocarbon molecules that are distillable. The first step in the liquefaction is the formation of liquid phase by fusing small molecules of coal at above 350°C. At temperatures between 400 and 450°C, bridges linking the cyclical units in coal are ruptured; starting with ether linkages[7-9] and then methylene bridges.[10-12] Radicals are liberated during rupture of bridges or homolysis of bonds. These radicals can be capped by the abstraction of H-atoms from a hydrogen donor molecule, leading to the formation of low molecular weight molecules. It is, however, possible that radicals do not get capped by hydrogen. In such cases, the radicals can repolymerize or recombine in simple coupling reactions or initiate a more complex series of radical reactions to form stable high molecular weight products. Retrogressive reactions are ones that lead high molecular weight product which are insoluble in tetrahydrofuran (THF insoluble). These reactions occur to some extent during liquefaction and are known to be detrimental to liquid yield. [13,14] Oxygen functional groups such as carboxylic acids, ethers, and phenols, which are prevalent in low rank coals are suggested to be major contributors to retrogressive products by crosslinking reactions that inhibit efficient thermochemical processing of low rank coals to liquid fuels. Cross-linking reactions are referred to as repolymerization or recombination reactions between free radicals, coal molecules, or coal molecules and free radicals.

2.4.1 Hydrogen transfer mechanisms

Solvent systems can transfer hydrogen to critical linkages via two different pathways. There could be a transfer of hydrogen atoms from dihydroaromatics in the solvent system through a reverse radical disproportionation (RRD) reaction. On the other hand, solvent derived radicals could transfer H-atoms to closed shell species in a radical hydrogen transfer (RHT) bimolecular step.[15] There is also a competition between cleavages that result from RHT and RRD, and this is influenced by reaction conditions. The efficiency of hydrogen utilization and the distribution of products depend on the competition between the cleavages from RHT and those from RRD[15,16]. The study on hydrogen transfer mechanism by Malhotra and McMillen[16], reveals that different hydrogen transfer pathways are competitive.

In all PAH solvent systems, increasing aromatic content of solvent and lower temperatures favors cleavage by RHT. Hydrogen transfer by addition of free H-atoms is, however, predominant at low concentrations. RHT mechanism involves two molecules, and as such, the solvent must be able to penetrate the coal structure while the coal is still solid. RHT mechanism can also take place with coal radicals formed by thermolysis. Some of these coal radicals are mobile, and might eliminate the need for penetration of coal structure by the solvent. However, the amount of hydrogen within the coal becomes a limiting factor. This limitation can be addressed by an external supply of hydrogen. Hydrogen derived from donor solvent could penetrate the coal structure thought the solvent might not be able to. Hydrogen transfer is known to occur readily between coal, hydroaromatics, and polycondensed aromatics. The quantity of hydrogen available in coal can be increased by the equilibration of H-atoms between donor solvent species and aromatic coal structures. This could propagate cleavage either by free H-atoms or RHT.[1]

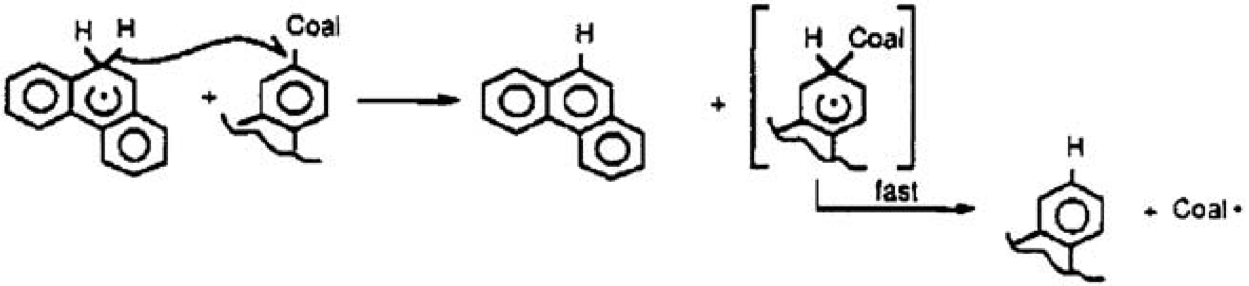
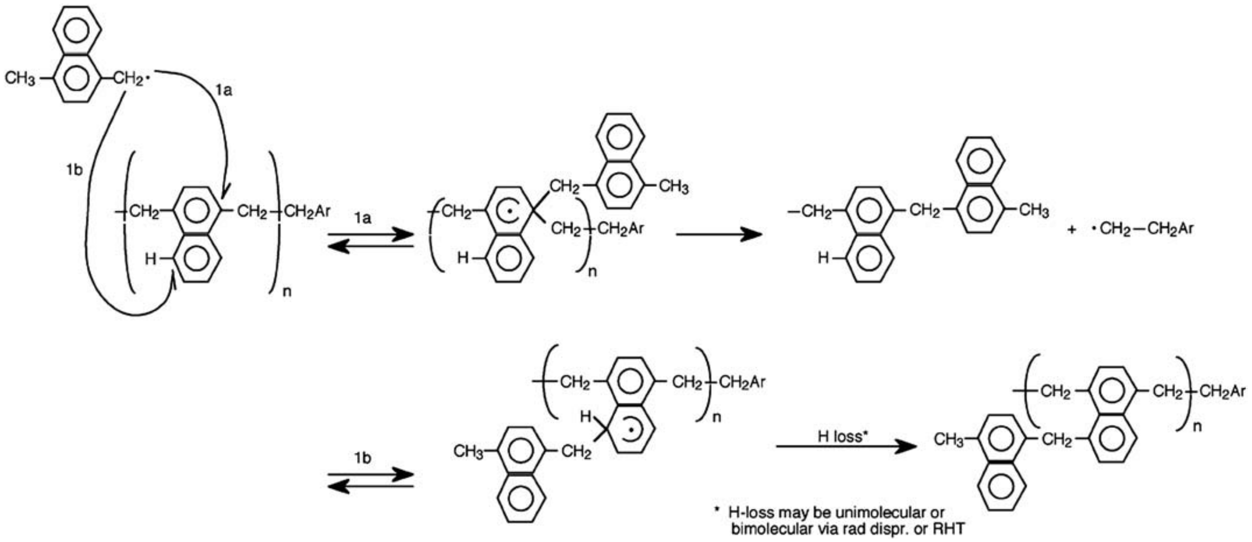


Figure 2-2: Cleavage of strong bonds engendered by H transfer to ipso position.[17]

2.4.2 Retrogressive reactions

It is believed that in coal liquefaction, retrogressive reactions results primarily from the recombination of radicals.[18-21] However, in a system with high PAH content radical addition and displacement reaction on aromatic systems occurs easily, forming retrogressive products. This is illustrated in Figure 2-3



* H-loss may be unimolecular or bimolecular via rad dispr. or RHT

Figure 2-3: Radical Displacement Reactions Leading to Retrogressive Products.[21]

According to thermochemical estimates and numerical modelling by McMillen and Malhotra[21], some of the factors necessary for the occurrence of retrogressive reactions are:

1. The presence of aromatic clusters which are particularly susceptible to radical addition,
2. The presence of readily displaceable radical fragments

3. The presence of aromatic systems or steady-state radical concentrations which are capable of rapid bimolecular reaction with the unstable retrogressive adducts, needed to further accept a hydrogen and stabilize the retrogressive adduct.

Mae *et al.*[14] examined retrogressive reactions monitoring the change in the tetrahydrofuran soluble (THFS) fraction of coal oxidized with nitric acid. It was concluded in the study that two types of retrogressive reactions occur: cross-linking by decomposition of the oxygen functional groups present in the THFS fractions at low temperatures and the recombination or repolymerization of the unit structure in the tetrahydrofuran insoluble (THFI) fractions at above 360°C.

In the study by Wang et al. [22], it was observed that at temperatures below 300°C, cross-linking reactions convert tetrahydrofuran soluble (THFS) fractions into cross-linked solid products. And when the temperature increased, induced cross-linking reactions between large molecular fragments derived from decomposition of oxidized coal and cross- linked solid products took place. This led to retrogressive products. Suppressing retrogressive reactions at low temperatures can be accomplished by selecting proper solvent based on its physiochemical properties in addition to the hydrogen donating ability, such as solubility parameters and vapor pressure. These properties will enable the solvent have a high contact with the coal surface and retrogressive becomes limited by donation of hydrogen by the solvent to the nascent radicals. [1]

2.5 Factors Affecting Coal Liquefaction

2.5.1 Effect of preheat treatment

The efficiency of coal liquefaction has been found to improve with pretreatment coal before liquefaction. Pretreatment results in a net reduction on retrogressive reactions and this help improve process economics at mild operating conditions of liquefaction. One of the pretreatment methods is heat treatment.[23-26] Solvent penetration and hydrogen transfer could be enhanced by a low temperature treatment. It has been shown that conversions for thermal (noncatalytic) liquefaction of bituminous coals increased with pretreatment at 200°C[24] and 277–322°C[25] , while high yields for the catalytic hydroliquefaction of subbituminous and bituminous coals were reported after preheat treatment at 350°C.[26] The increase in liquefaction yield for coal that is pretreated at 350°C could be as result of the loss of the carboxyl functional groups usually responsible for crosslinking.[1]

2.5.1.1 Effects of heating rate

Reducing the rate of formation of free radicals by controlling the temperature program appropriately, rate of hydrogenation could match with the rate of radical formation, consequently preventing retrogressive reactions. This is another means to preventing retrogressive reactions other than the use of high hydrogen donor solvent.[27] There are different modes of operation of liquefaction. A single stage liquefaction (SSL) is one in which there is only one reaction temperature. In the single stage liquefaction mode, reactants can be heated up slowly or quickly to the desired temperature. Another mode of operation is the temperature staged (TSL) and temperature programmed liquefaction (TPL). In this mode of operation, there are two temperature levels namely the low temperature and the high temperature level. The low temperature level (usually between 200 and 350°C) is designed for pretreatment, while the high temperature level (between 400 and 500°C) is used for liquefaction. While there is a rapid heating to the high temperature level in the TSL, a slow heat up (30 minutes or longer) to the high temperature level follows the pretreatment step in the TPL.

At high temperatures, thermal cracking can occur quickly leading to retrogressive reactions. The TPL mode of operation allows for a reduction in the rate of thermal cracking of the coal structures. Liquefaction in the SSL mode, though it is the simplest, may result in problems particularly for low rank coals. Bond cleavage at high reaction temperature can occur so rapidly that hydrogenation can become too slow to cap the radicals formed, leading to coupling reactions that reduce liquefaction yield. However, cleavage of other bonds may occur so slowly and no significant reaction may occur within the reaction time. It has been suggested that conversions and yields of low distillate products can be improved by operating in the TSL mode than in the SSL mode.[27-30]

2.5.2 Effect of Hydrothermal treatment

Hydrothermal treatment is another pretreatment method used in coal liquefaction.

An increase in pyridine extraction yield from 17% to 30% was reported for of Illinois No 6 after treatment in steam at 50 atm and 340–500°C. However, the extraction yields decreased to the levels of raw coal after the treated sample was exposed to air for minutes.[31,32] it was concluded that during hydrothermal (steam) pretreatment new hydroxyl groups are introduced, resulting in a decrease in covalent cross-links in coal. This yields a partially depolymerized coal, which is potentially, an improved feedstock for coal liquefaction.[31]

Study by Ivanenko et al.[33] showed that the quality of liquid product in coal slurry liquefaction improved and the oil yield is doubled under low severity conditions after steam pretreatment. Their study concluded that the benefits of steam pretreatment can be realized only if the pretreated coal is then rapidly heated to liquefaction temperature. This will ensure that the pretreated coal can pass quickly through the temperature region where retrogressive effects occur. There is need to protect the pre-treated coals from oxygen to preserve the benefits of pretreatment.

The enhancements of extraction and liquefaction yields after hydrothermal treatment of coal has been explained to occur by the rupture of weak covalent bonds, such as ether bonds,[34] the breaking of hydrogen bonds,[35] loosening of π-π interaction and breaking of hydrogen bonds,[36] the removal of minerals by sulfuric acids formed during the treatment with H_2O[37] and the decrease in oxygen functional groups,[38] which are thought to be responsible for cross-linking reactions. The suppression of metal carboxylate-induced retrogressive reactions in liquefaction by the association of metal cations with water was also suggested as possible mechanism through which hydrothermal pretreatment increased liquefaction yields.[38,39]

Hydrothermal treatment at proper conditions, as reported in the study by Shui et al., can increase the extraction yields of bituminous coals and especially for higher ranks of coal. They attributed this to the decrease of total oxygen and hydroxyl oxygen during treatment by water, which can act more effectively as an acid or a basic catalyst. The hydrogen bonds in macromolecular network of coal are broken because loss of oxygen and hydroxyl oxygen leads to the formation of smaller molecules. These molecules are immediately solvated by water and are stabilized by incipient hydrogen obtainable either through the interplay of carbon and water, or from water alone. [40]

2.5.3 Effects of drying and oxidation

Pretreatment by drying can improve the liquid yields, particularly for the low rank coals. Direct liquefaction conversion and kinetics depend heavily on the partial pressure of hydrogen in the liquefaction reactor. Therefore, the removal of moisture in the coal allows the partial pressure of hydrogen to be increased without increasing the total operating pressure.[41] Removal of the steam partial pressure in the reactor increases the partial pressure of hydrogen and other gaseous components if the reactor pressure is held constant.

Drying of coals before liquefaction has an added benefit of reducing the cost of both separating water from the coal and wastewater treatment because of the prior water removal. When a drying process has minimal effect on the reactivity of coal, it becomes important in coal liquefaction.[42-44]

Some studies[43-45] have shown that drying of coal has negative impacts on its reactivity, while here is also contradicting evidence in non-catalytic liquefaction. [42] The negative impacts of drying on liquefaction can be due to irreversible changes in the pore structure such as collapse of pores. [46] This could limit the accessibility of the reacting components during liquefaction and thus limit the rate of reaction. It is also reported that oxidative drying has a detrimental effect on the coal conversion. [43-45] Oxidation significantly increased oxygen functionality which enhances the cross-linking reactions in the initial stages of liquefaction. This is thought to be responsible for the negative impact of severe oxidation on coal liquefaction.

In the study of the effect of non-oxidative drying and drying in the presence of air at 100–150°C on catalytic and non-catalytic liquefaction of Wyodak subbituminous coal at 350°C by Song et al.,[47] fresh raw coals gave higher conversion and higher oil yield than the dried coals, regardless of the solvent in thermal liquefaction. It was observed that coal dried in air showed no apparent negative effect while vacuum dried coal showed better conversion and oil yields. While Miknis et al. [41] observed that thermal and microwave-drying appeared to collapse pore structure, and prevent donor solvents from reaching reactive sites inside the coals leading to lower conversions and lower liquid yields (in the case of low rank coals) compared to pre-moisturized coals. Chemically dried coals show high conversions (up to 18%) and liquid yields (low rank coals) between 11 and 60% greater suggesting that pore structure did not collapse.

2.5.4 Effect of coal swelling in solvents

Organic solvents in contact with coal often become incorporated in the structure and swell the coal. The degree of swelling depends on solvent chemistry and coal rank. Subsequent liquefaction of solvent swollen coals has shown improved conversion and product quality.[48-53] It is postulated that solvent swelling of a coal selectively disrupts hydrogen bonds and increases the mobility of small molecules associated with the macromolecular network of the coal.[48] Solvent swelling may facilitate self-donation reactions of indigenous hydrogen, and suppress the initial retrogressive reactions while enhancing reactivity. Improved contact of coal with liquefaction solvents increases the liquefaction efficiency and reduces the severity of liquefaction conditions by improving mass transfer and reaction rates. Solvent swelling may cause coal molecules to be dissociated, rearranged, and re-associated in lower free energy conformations.[54] Swelling may also break weaker non-covalent bonds, forming more active reaction sites and increasing macropores in the coal structure. Increased porosity would increase diffusion[55] and may also facilitate the roles of catalysts.[56]

2.5.5 Effect of coal rank

Among other factors like petrographic composition and inorganic constituents,[57] rank of coal is the most crucial parameter which control coal behavior during liquefaction. Similarly, the macerals of the vitrinite (>80 vol% of the organic content of most coals) and liptinite groups are generally accepted to be the major reactive groups during coal liquefaction (compared to the inertinite group macerals). [58,59] Higher oil yields were observed with high rank coals than with low rank coals[60,61]. Kabe et al.[63] examined the hydrogen exchange reactions between tritium labeled gaseous hydrogen and three different ranks of coal (Datong – bituminous coal, Wandoan – subbituminous coal, and Morwell – brown coal) to estimate the hydrogen mobility under coal liquefaction conditions. They observed that the hydrogen exchange reaction between these three coals and gaseous hydrogen proceeded even at 300 ^{o}C and increases rapidly with temperature from 350 to 400 ^{o}C. The hydrogen exchange ratio increased in the order of Datong < Wandoan < Morwell. The yields of coal liquids increase with temperature and decrease with coal rank. The rate of liquefaction decreased in the order of Morwell > Wandoan > Datong, which shows that coals with higher carbon content are more difficult to liquefy. Lower rank coals require an additional H_2 source to attain high conversion levels. Although low rank coals, lignites, brown coals and subbituminous coals liquefy more readily, the hydrocarbon yield is limited because of the increasing oxygen content, which forms water and carbon oxides.[62] Also, the liquefaction of low rank coals yield high viscosity of the residual products, which has caused pumping difficulties. This challenge can be prevented by increasing the liquefaction residence time[1] or adding disposable catalysts. The presence of Ca (e.g. as humic acid salts) accounts up to 3 wt% in low rank coals. Ca converts to CaO during liquefaction and reacts with CO_2, leading to the deposition of $CaCO_3$ on the reactor walls. This is one reason that low rank coals are not attractive feedstocks for liquefaction. Although the total liquid yield tends to decrease with decreasing rank, the fraction of low boiling distillates increases.[64] The subbituminous coal products are more volatile, contain more saturated hydrocarbons, are less aromatic, and have higher hydrogen content and fewer heteroatoms.

2.6 Process yield of coal liquefaction

Coal liquefaction produces C_1−C_3 gaseous hydrocarbons, naphtha, and middle distillates (kerosene and gas oil) as petroleum substitutes. These products are generally called the total distillate. Additionally, gaseous nonhydrocarbons (such as CO, CO_2, H_2S, and NH_3) and residual oils (including vacuum gas oil, vacuum residue or heavy tar), and solid products such as unliquefied coal and coke (char), are found in the product. The vacuum gas oil is recycled as the solvent after hydrogenation to regenerate the hydrogen donor activity. The residual oil can be used as a coal tar substitute, which is useful as a carbon source in the coking process (blast furnace, binder and impregnation pitches, and delayed coker feed after the solid/liquid separation and pretreatment; see section 8 for details). The yields of naphtha, middle distillate, gas oil, and total distillates were approximately 20%, 22%, 5−8%, and 50% respectively in liquefaction during the 1980s. The yields improved in the 1990s by using two-stage liquefaction, that is, about 15−20%, 20−40%, 12−30%, and 65−73%, respectively. This resulted in the increased yield of the total distillate, particularly of the middle distillate and gas oil fractions. The latter two are equivalent because gas oil is converted into middle distillates during hydrotreatment. A significant decrease in hydrocarbon gases and a decrease in naphtha yield improved the hydrogen consumption in the liquefaction process and the overall hydrogen efficiency for the distillate production. Such improvement and the slight moderation of liquefaction conditions improved the economic competiveness of coal liquids. Post-hydrotreatment improves the quality of coal liquids and makes them comparable to those of petroleum products.

2.7 Chemical composition of the coal liquefaction products

Kobe Steel[65] reported details of the products from Indonesian brown coal, Mulia, obtained through their two-stage liquefaction process. The yield of the total distillate was 63.5%, which comprises light oil (C_5, bp 220 °C, 31.2%), middle oil (bp 220–300 °C, 26.2%), and heavy oil (bp 300–420 °C, 6.1%). The yield of distillation bottoms (>420 °C) was 7.3%, while the yields of H_2O, $CO + CO_2$, C_1–C_2, and LPG were 16.3%, 10.7%, 5.4%, and 3.9%, respectively, at the hydrogen consumption of 7.1%. [66] Ultimate analyses and ^{1}H NMR, gives the properties of the naphtha and gas oil. High aromatic, nitrogen, and oxygen contents are characteristic of primary coal liquid. The hydrotreatment in the second step significantly reduced the N, S, and O contents, and increased the hydrogen content. Aromatic and olefin contents are significantly reduced by increasing the amount of saturates. The H/C ratios of naphtha, kerosene, and gas oil were 2.01, 1.83, and 1.76, respectively, and suggest high degrees of saturation.[66] Their nitrogen and sulfur contents were less than 10 ppm except for the naphtha, which suggests a high degree of refining. The coal-derived naphtha has high octane number due to its aromatic content. Octane number is a standard measure of the performance of a motor or aviation fuel. The higher is the octane number, the more compression the fuel can withstand before detonating. Fuels with a higher octane rating are used in high-compression engines that generally have higher performance. The kerosene and gas oil contained saturates above 88.3% and 80. 0%, respectively,[66] with small amounts of total aromatic hydrocarbons (11.7%) and 1– ring (17.9%), 2– ring (1.4%), and 3– ring (0.1%) aromatic hydrocarbons. Nevertheless, the cetane index of the gas oil was 38.6, which is lower than that of the petroleum derived one. Hence, improvement of cetane number is one of the critical issues for the coal liquefaction products. Aromatic ring-opening is required.

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3 Chapter III – Experimental Methods

The following chapter outlines the methodology that was followed in order to achieve the proposed specific objectives. The chapter also includes the materials, instruments and analytical methods used for this study purpose

3.1 Materials

Tetrahydrofuran (THF)

THF is a colorless solvent (liquid), was employed during the filtration process of the coal liquid products after digestion in an autoclave reactor. Fresh solvent as provided by Sigma-Aldrich, ACS reagent, purity > 99 % was used.

Hexane

This is a colorless liquid used as a mobile phase during high performance liquid chromatography (HPLC). It has a purity of 99.9 % (HPLC grade) and was supplied by Fisher Scientific.

Chloroform

This is also a colorless liquid used as a mobile phase during high performance liquid chromatography (HPLC). It has a purity of 99.9% (HPLC grade, stabilized with 0.75% ethanol) and was supplied by Fisher Scientific.

Carbon Disulfide

Carbon disulfide (anhydrous) with a purity of > 99 % was used as provided by Sigma Aldrich, to dilute the samples that were analyzed with the GC/MS.

o-Xylene

This colorless liquid (purity 98%) was used in the calibration mixture for qualitative and quantitative HPLC analysis, and was supplied by Sigma Aldrich.

1,3,5-Trimethylbenzene

This colorless liquid (purity 97%) was used in the calibration mixture for qualitative and quantitative HPLC analysis, and was supplied by Sigma Aldrich.

Toluene

This colorless liquid (purity >99.9%) was used in the calibration mixture for qualitative and quantitative HPLC analysis, and was supplied by Fischer Scientific.

Naphthalene

This white solid (purity 99%) was used in the calibration mixture for qualitative and quantitative HPLC analysis, and was supplied by Sigma Aldrich.

Methylnaphthalene

This colorless liquid (purity 95%) was used in the calibration mixture for qualitative and quantitative HPLC analysis, and was supplied by Sigma Aldrich.

Bi-Phenyl

This white solid (purity ≥99%) was used in the calibration mixture for qualitative and quantitative HPLC analysis, and was supplied by Sigma Aldrich.

Anthracene

This white solid (purity 97%) was used in the calibration mixture for qualitative and quantitative HPLC analysis, and was supplied by Sigma Aldrich.

Phenanthrene

This white solid (purity 98%) was used in the calibration mixture for qualitative and quantitative HPLC analysis, and was supplied by Sigma Aldrich.

Pyrene

This white solid (purity 98%) was used in the calibration mixture for qualitative and quantitative HPLC analysis, and was supplied by Sigma Aldrich.

Chrysene

This golden-yellowish solid (analytical grade) was used in the calibration mixture for qualitative and quantitative HPLC analysis, and was supplied by Supleco.

Fluoranthene

This yellowish solid (analytical grade) was used in the calibration mixture for qualitative and quantitative HPLC analysis, and was supplied by Supleco.

1,3,5-Triphenylbenzene

This solid (purity 97%) was used in the calibration mixture for qualitative and quantitative HPLC analysis, and was supplied by Sigma Aldrich.

Perylene

This solid (purity ≥99.5%) was used in the calibration mixture for qualitative and quantitative HPLC analysis, and was supplied by Sigma Aldrich.

Benzo[a]pyrene

This solid (purity ≥96%) was used in the calibration mixture for qualitative and quantitative HPLC analysis, and was supplied by Sigma Aldrich.

Coronene

This solid (purity 97%) was used in the calibration mixture for qualitative and quantitative HPLC analysis, and was supplied by Sigma Aldrich.

Hydrogen gas

The gas employed in the autoclave reactor during the digestion of coal is hydrogen gas (purity 99.999%) supplied by Praxair.

Helium

The carrier gas employed for gas chromatography was helium (purity 99.999 %) supplied by Praxair.

Industrial hydrotreated coal tar distillate (HT-1006)

This is a hydrodrotreated solvent (dark brown viscous liquid) derived from coal liquid, and it contains a mixture of hydrocarbons. It was used as provided by Sherritt Technology Inc. as a solvent for the digestion of coal. It's proximate and ultimate analyses are presented in Table 3-1.

A trace metal analysis of the solvent was performed by an external laboratory using inductively coupled plasma mass spectrometry (ICP-MS) (Appendix). The main metal impurities present in the solvent were: 20 μg/g Al, 190 μg/g Ca, 34 μg/g Fe, and 17 μg/g Zr. These are listed, because it is indicative of the metals load that must be dealt with during downstream refining. The metals load may affect refinery technology selection and affect operation. The carbon residue obtained when the solvent was heated to 950 °C under inert conditions was 2.43 ± 0.18 wt%.

3.2 Coal Characterization

Canadian Bienfait lignite was employed as coal feed for the solvent extraction process to produce coal liquids. A lignite coal was chosen because coal-derived liquids have an increasing content of low molecular weight compounds as the rank of the parent coal decreases. This is reported to related to the lower ring-cluster sizes in the lower rank coals[1] The coal was crushed and the size fraction of < 150 μm was employed for the solvent extraction to prepare the coal liquids. Representative sampling was accomplished using an aleatory sampler.

3.2.1 Ultimate Analysis

An Elementar Vario MICRO Cube was used to carry out the elemental analysis of the coal, and industrial solvent as well using the standard test method ASTM D3176.[2] The tests were performed in triplicates with samples between 2 to 4 mg. The coal used for this analysis was previously dried. Oxygen content was determined by difference using equation 3.1

$$W_o = 100 - W_c - W_H - W_S - W_N \tag{3.1}$$

Where each term is oxygen, carbon, hydrogen, sulphur and nitrogen weight percent (daf), respectively. This is presented in Table 3-1

Table 3-1: Ultimate analysis of the Canadian Bienfait lignite and the hydrotreated coal tar distillate that was employed as solvent

Composition	Analysis (wt %, maf) [a,b]			
	lignite		solvent	
	x	s	X	s
carbon	54.26	0.03	90.57 [c]	0.16
hydrogen	3.92	0.06	5.83[d]	0.01
nitrogen	1.23	0.02	1.44	0.04
sulfur	1.15	0.01	0.09	0.00
oxygen [e]	24.86	0.10	2.07	0.14

[a] maf = moisture and ash-free basis: ash = 14.6wt%

[b] Average (x) and sample standard deviation (s) of triplicate analyses

[c] ^{13}C NMR analysis indicated that the carbon was 84.5 % aromatic and 15.5 % aliphatic

[d] ^{1}H NMR analysis indicated that the hydrogen was 58.3 % aromatic and 41.7 % aliphatic

[e] Oxygen content was calculated by difference

3.2.2 Proximate Petrographic analysis

Proximate analysis of coal (dried) and industrial solvent was performed using the standard test method ASTM D 7582[3] using electric Barnstead Thermolyne 6000 muffle furnace with airflow of 20 slpm. The lignite coals were dried overnight in a vacuum oven at temperature of 80 °C and vacuum pressure of -14 inHg for four hours before its utilization. Coal samples sent for petrographic analysis were kept in sealed containers after being dried. The maceral composition was determined by an external laboratory using reflectance microscopy. The proximate and petrographic analytical results are presented in Table 3-2 and Table 3-3 respectively.

Table 3-2: Proximate analysis[a] of Canadian Bienfait lignite[b]

Composition	Analysis (wt %)	
	X	s
moisture	5.2	0.03
ash	14.6	0.04
volatile matter	38.6	0.37
fixed carbon	41.6	0.38

[a] Average (x) and sample standard deviation (s) of triplicate analyses

[b] Proximate analysis were performed on dried coals

Table 3-3: Petrographic Analysis of Canadian Bienfait lignite[c]

Maceral composition [d]	
vitrinite	53.2
inertinite	36.4
liptinite	7.0
bright minerals	0.9
dark minerals	2.5

[c] Petrographic analysis were performed on dried coals

[d] The maceral composition includes associated minerals

3.3 Equipments:

High Pressure, High Temperature Stirred Reactor (HP/HT Autoclave reactor)

The HP/HT Autoclave reactor (Figure 3-1), designed and manufactured by Parr instruments was used for the liquefaction of coal. All coal liquefaction experiments were performed in this 500 ml reactor supplied with a control panel for temperature profile programming and adjustment of stirring speed. Reactor has a maximum operating temperature of 500 °C and maximum operating pressure of 5000 psi (344 bar). Heat is supplied using a programmable resistant-heater and an automatic valve is used to pump cooling water into cooling loop for the purpose of maintaining temperature during reaction.

Figure 3-1: High Pressure, High Temperature Stirred Reactor

Vacuum filtration

Vacuum filtration was used to separate the liquid from the solid phases after the reaction. Whatman fibre glass filter media with 0.5 μm pore diameter and a Welch Dryfast vacuum pump were used. The filtration flask set-up is shown in Figure 3-2

Figure 3-2: Coal Liquid Filtering Flask Set-up

Vacuum oven

After filtration, solid samples were dried overnight in a Stable Temp Cole-Parmer vacuum oven, to remove the remaining solvent. Temperature was kept at 80 ^{o}C, and vacuum at -14 in Hg (-47.4 kPa).

Roto-evaporator

A Büchi Roto-vapor R210 was used to separate the washing solvent (THF) from the reaction solvent and the coal liquids.

3.4 Procedures

3.4.1 Coal Preparation

The coals were supplied in crushed form, but were sieved to obtain fractions <150 µm. Samples of approximately 50 g were obtained using an aleatory sampler to ensure that the sample was representative of the whole coal. The samples were then dried for 4 hours in a vacuum oven at 80 °C and -14 in Hg before liquefaction.

3.4.2 Coal Liquefaction

Reactor Charging

Solvents and coal were separately weighed using a Mettler-Toledo PR 5002 scale. A solvent to coal ratio of 2:1 was used for all experiments. The solvent was first loaded into the reactor to prevent any caking effect on the coal at the bottom of the reactor. After the reactor was fully loaded with coal and solvent, the bottom part was raised to close the gap between the upper and lower compartments. Graphite gaskets were places in the space provided in the upper part for sealing. Final sealing was performed using a flange the bolts of which were tightened using a torque wrench. The reactor was then purged 3 times with nitrogen. After purgingthe reaction gas (hydrogen) or inert gas nitrogen was loaded in the reactor and pressurized to 40 bars and then left for fifteen minutes to monitor possible pressure release due to leakage. The above steps were performed for each of the liquefaction runs.

Liquefaction

When no pressure drop was observed nor any leak detected, the desired temperature and heating rate are set using the controller software of the reactor and the impeller speed kept at 1000 RPM. The reactor is then heated up to the desired reaction temperature. At the end of reaction time, the heater was turned off and the impeller was left on while the reactor cooled down. Liquefaction experiments were carried out at temperatures of 350, 400, 415 and 450 °C, residence times of 0, 15 and 30 minutes with an initial H_2 pressure of 4 MPa. Table 3-4 shows experimental conditions for all liquefaction runs.

Table 3-4: Experimental Conditions for all Liquefaction Runs

Exp Number	Temperature/ °C	Hold time/ minutes	Initial Reactor Pressure/MPa	Gas Atmosphere
1	350	0	4	H_2
2	350	0	4	H_2
3	383	0	4	H_2
4	400	0	4	H_2
5	415	0	4	H_2
6	415	0	4	H_2
7	415	0	4	H_2
8	415	0	4	H_2
9	450	0	4	H_2
10	350	15	4	H_2
11	400	15	4	H_2
12	450	15	4	H_2
13	350	30	4	H_2
14	450	30	4	H_2
15	350	30	4	N_2

Reactor Washout

The reactor is allowed to cool to 100 ^{o}C, and the pressure was released by the gas release valve after which the reactor was opened carefully by loosening the bolts. The product gases were released through an exhaust pipe into the vent The liquid product was transferred to a filtration unit immediately and the reactor was washed with THF (measured amount) including the impellers several times to collect almost at the coal liquid. Some of the THF got vaporized, thus contributed to errors in mass balance.

Filtration and Solvent Recovery

A 0.5 μm filter paper was used to separate the dissolved products form mineral matter and unreacted coal. The THF – product mixture was poured on the upper part of the filtration unit and vacuum was used to suck the mixture through the filter, the dissolved products were collected in the bottom flask and the residue over the filter paper. The dissolved products were stored in a separate flask and the filter paper was dried at 80°C under vacuum overnight. The filtrate was then transferred to the rotatory evaporator where the washing solvent (THF) was recovered for reuse. The water bath in the rotatory-evaporator was set to 60 ^{o}C and the vacuum to 260 mbar. The separation took place over a period of about 2 hours.

Liquid Distillation

The solvent-free liquid was then distilled into four boiling fractions: 120-250, 250-300, 300-343, and 343–370 ^{o}C. A bench-top vacuum distillation unit (BR instruments) was employed to prepare the distillation fractions following the ASTM D 1160 method.[4] The distillation unit was equipped with a 3 L reboiler and the column had the equivalent of 8 stages. A reflux ratio of 5 was employed to obtain sharper cuts.

A coal liquefaction process flow diagram for the experiment is shown in Figure 3-3.

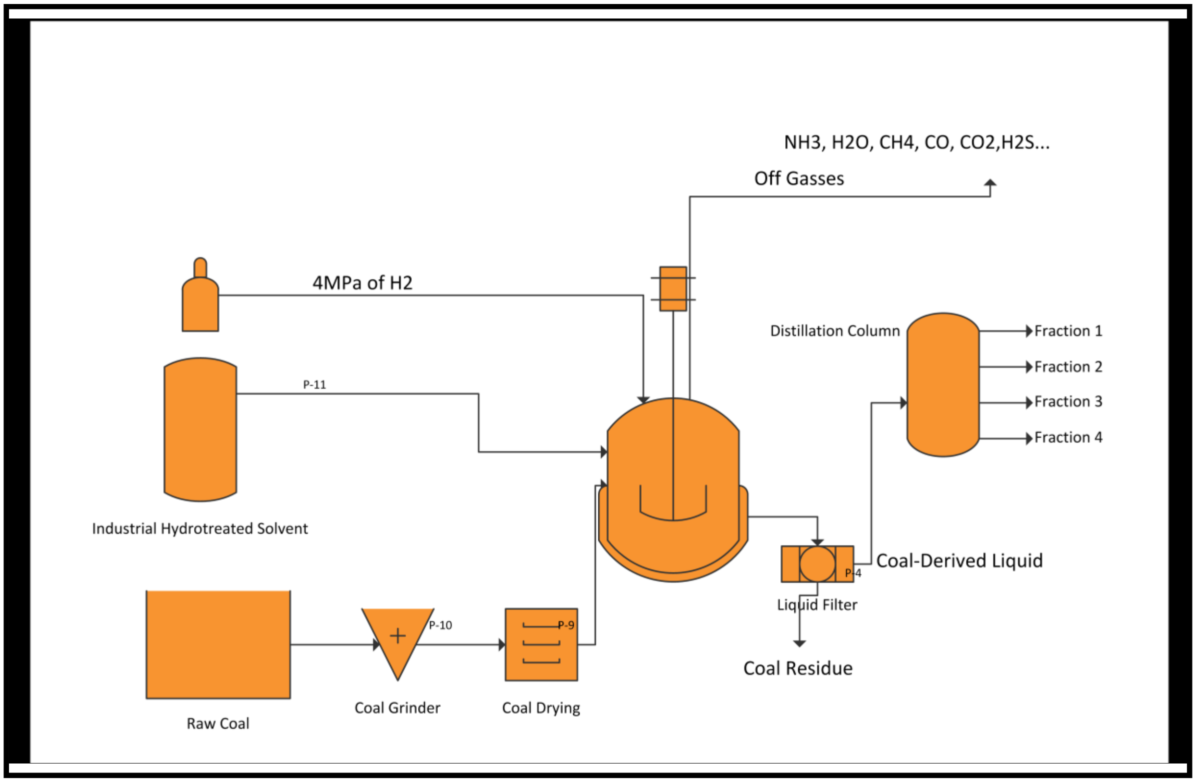

Figure 3-3: Coal Liquefaction Process Flow Diagram

3.5 Coal Liquid Characterization

3.5.1 Elemental analysis

Elemental compositions (CHNS) of the coal liquids were determined using Elemental Analyser (Model: Vario Micro, USA). The mass fractions of carbon, hydrogen, nitrogen and sulfur were determined directly, while that of oxygen was determined by difference.

3.5.2 Nuclear magnetic resonance (NMR) spectrometry

Quantitative ^{1}H NMR and ^{13}C NMR analyses were performed using a Varian Inova-400 NMR spectrometer operating at 399.794 MHz for proton and 100.54 MHz for carbon. The solvent, deuterated chloroform ($CDCl_3$), was used to dissolve the samples for ^1H NMR. The sample concentration was maintained approximately at 20 mg/3.5 mL $CDCl_3$. All the ^1H NMR data were acquired using a 2.5 s acquisition time, 4799 Hz sweep width, a 45º pulse flip angle and a recycle delay of 0.10 seconds. The proton spectra were recorded by performing 16 scans and were referenced to the residual chloroform ($CHCl_3$) peak resonance at 7.26 ppm. The ^{13}C NMR spectra were recorded at a sweep width setting of 26990.6 Hz. Each solvent was maintained at a concentration of 0.16g/3.5 mL of $CDCl_3$ in the presence of tetramethylsilane (TMS) in chloroform (15 μL/100g) as an internal reference. The ^{13}C NMR spectra were recorded performing around 1000 scans and were referenced to the $CDCl_3$ resonance peak at 77.06 ppm.

3.5.3 Gas Chromatograph and Mass Spectrometer

The major compounds present in the samples were identified using gas chromatography coupled with mass spectrometry (GC-MS). For this purpose a Varian CP3800 gas chromatograph with flame ionization detector (FID) and Saturn 2200 GC/MS ion trap spectrometer (Varian) were employed. The samples were separated using a FactorFour™ capillary column (30 m × 0.25 mm internal diameter), which has a fused silica stationary phase. Helium was employed as carrier gas. Samples (1 μL) were injected into the column at an injector temperature of 320 °C and a 20:1 split ratio was used. The column was heated to 50 °C and was held at 50 °C for 10 minutes. It was afterwards ramped from 50 °C to 320 °C at 10°C/min and then held for a further 10 minutes a 320 °C.

The relative abundance of the different species in each boiling fraction was quantified based on the peak area of the flame ionization detector. This may have introduced some quantification errors, because no FID response factor corrections were made. Nevertheless, most of the compounds were aromatic and with the exception of the heteroatom containing compounds that may have been under-reported, little bias in the results was anticipated[5,6]

3.5.4 Micro Carbon Residue (MCR) Analyses

MCR content of coal liquids was determined using the ASTM D4530 method.

3.5.5 High performance liquid chromatography (HPLC)

A Waters Alliance e2695 HPLC separation module was employed, which was equipped with a photodiode array detector (Waters Model 2998) for ultraviolet-visible spectrometry and a refractive index detector (Waters Model 2414). The system included an electronic back flush valve and it was capable of gradient-elution. The separation was performed using three columns connected in series. The columns employed were µBondapak™-NH_2 (3.9 × 300 mm) 10 µm particle diameter and 12.5 nm pore size. The mobile phases were *n*-hexane and chloroform. The combined flow rate of the mobile phases was kept constant at 1 mL/min throughout the analysis. The method used for separation of the hydrocarbon fraction of the coal liquids is summarized in Table 3-5. The back flush was necessary to remove polar compounds from the columns.

Table 3-5: HPLC separation method

Period (min)	Mobile phase (%)		Comments
	hexanes	chloroform	
0 - 40	100	0	Elution of hydrocarbon fraction
40 - 45	100 → 60	0 → 40	Back flush started, constant gradient [a]
45 - 75	60	40	Removal of polar compounds
75 - 80	60 → 100	40 → 0	Back flush stopped, constant gradient [a]
80 - 95	100	0	Re-equilibration of columns

[a] Solvent concentration was changed at a constant rate over the period indicated

Calibration of HPLC for aromatic hydrocarbon analysis

Identification

A model mixture of aromatic hydrocarbons was prepared for calibration purposes (Table 3-7). The aromatic compounds in this calibration mixture were commercially obtained. Compound identification during HPLC analysis of the coal liquid distillation fractions was made by comparison of retention times and UV-Vis spectra of the coal liquid components with that of the compounds in the calibration mixture[7]. Retention times of different classes of hydrocarbons are presented in Table 3-6. The following observations were made:

1. Aliphatic compounds, including decahydronaphthalene, eluted before mono aromatics. These were detected using the refractive index detector.
2. Aromatic compounds eluted in the order of the number of rings regardless of the substituent groups. Compounds with one aromatic ring all eluted at similar times. As such, tetralin (tetrahydronaphthalene) is considered a mono-aromatic.
3. Toluene and o-xylene co-eluted.

Table 3-6: Retention time of Model Compounds

Compounds		Retention Time/ Mins
Aliphatics		
	Hexene	8.88
	Heptane	9.02
	Hexadecane	8.97
	Decahydronaphtalene	9.02
Aromatics		
# Rings	Sample	
1	M-Xylene	10.15
	1,2,4-Tmb	10.46
	P-Cymene	10.37
	Tetralin	10.33
2	Acenaphthene	13.40
	Biphenyl	14.32
	Naphthalene	13.81
	Methylnaphthalene	14.03
3	Phenanthrene	15.15
	Anthracene	15.17
4	Pyrene	18.89
	Chrysene	25.01
	Triphenylbenzene	22.50
	Perylene	26.00
	Fluoranthene (Three Rings Though)	20.00
5	Benzo[A]Pyrene	30.00
6	Coronene	32.00

Quantification

An external standard method was employed for quantification. A mixture of the model compounds was prepared at five (5) different concentrations (Table 3-7). The mixtures were analyzed with the HPLC, and the peak heights were correlated to the concentration. Peak height was chosen for quantification rather than peak area because there was a greater repeatability in the response factors derived from peak heights than from peak area. Response factor here refers to:

$$\text{Response Factor} = \frac{\text{Peak Height}}{\text{Concentration}} \text{ or } \frac{\text{Peak Area}}{\text{Concentration}}$$

A plot (comprising of 5 data points) of peak height versus concentration was made for all the individual compounds in the mixture. The data points were fitted to generate a straight line with the smallest Y-intercept value and greatest R square value. All these were accomplished with the HPLC software.

With the use of the photodiode array detector, response factors of the model compounds were determined at maximum absorbance across the UV-Vis range. Response factors were assigned to the same compounds, as well as compounds with the same number of aromatic rings that were detected in the coal liquid samples[8].

The use of a single response factor per number of aromatic rings was also necessitated by the ability to resolve the aromatic hydrocarbons. It was possible to separate the coal liquid distillation fractions in clusters with the same number of aromatic rings in each cluster, but it was not possible to achieve a compound-level separation.

The polar compounds were removed from the column by back flushing and were not analyzed, i.e. did not pass through the detectors. Figure 3-4 shows the HPLC chromatogram of the calibration mixture. There was a good repeatability in the chromatograms of the model compounds.

Table 3-7: Five Different Concentrations (ppm) of HPLC Calibration Mixture

S/N	Compounds	C1 /ppm	C2 /ppm	C3 /ppm	C4 /ppm	C5 /ppm
1	Coronene	885	475	296	206	129
2	Benzo[a]pyrene	1162	624	388	270	169
3	Perylene	608	327	203	141	89
4	Fluoranthene	1549	832	518	360	225
5	Chrysene	940	505	314	218	137
6	1,3,5-Triphenylbenzene	885	475	296	206	129
7	Pyrene	2987	1604	999	694	435
8	Anthracene	1936	1040	647	450	282
9	Phenanthrene	2932	1574	980	681	427
10	Naphthalene	1715	921	573	398	250
11	Methlnaphthalene	1659	891	555	385	242
12	Bi-Phenyl	1991	1069	666	462	290
13	Toluene	1936	1040	647	450	282
14	Mesitylene	2213	1188	740	514	322
15	o-Xylene	1328	713	444	308	193
16	Toluene + o-Xylene*	3263	1753	1091	758	475

* Toluene and o-xylene co-eluted

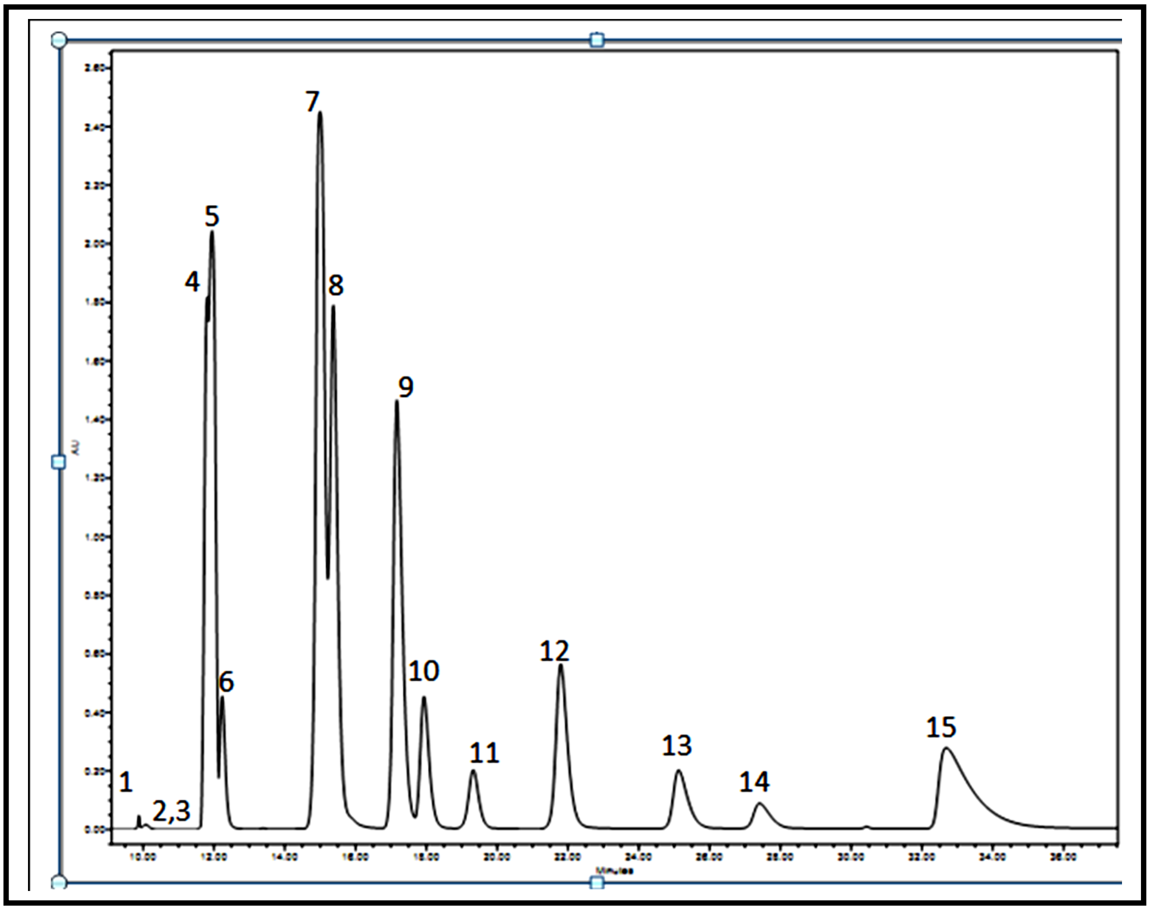

Figure 3-4: HPLC Chromatogram of Calibration Mixture

1 =1,3,5-Trimethylbenzene, 2,3 = o-xylene, Toluene, 4 = methylnaphthalene, 5= naphthalene, 6 = bi-phenyl, 7 = Anthracene, 8 = Phenanthrene, 9 = Pyrene, 10 = Fluoranthene, 11 = Chrysene, 12 = 1,3,5 –Triphenylbenzene, 13 = Benzo[a]pyrene, 14 = Perylene, 15 = Coronene

3.5.6 Titration

Total Acid number was determined by titration using a Mettler Toledo titrator according to the standard test method ASTM D 664.[9]

3.5.7 Infrared spectroscopy

An ABB MB3000 Fourier Transform Infrared spectrometer was employed. Samples were placed directly on a Pike MIRacle™ Reflection Attenuated Total Reflectance (ATR) attachment to the spectrometer. Spectra were collected at a resolution of 4 cm^{-1} as the average of 120 scans.

3.6 Extraction of Naphthalene and Acenaphthene from the 120-250 °C fraction

A thin layer chromatography (TLC) of the 120-250 °C fraction was performed using hexane as an eluent. The nonpolar components were observed to separate under an ultraviolet light into three different clusters. The second cluster was suspected to be due to naphthalene, as it appeared to be the major spot indicating that it constituted major portion of the 120-250 °C cut sample.

Separation of the components was performed using a silica gel chromatographic column and hexane was used as the solvent. 2.0 grams of dissolved in hexane and was gradually emptied into the column until almost totally adsorbed unto the silica bed, after which hexane was poured into the column gradually. Elution of components was monitored with a thin layer chromatographic (TLC) plate. The presence of a dark spot under the UV light showed elution of coal liquid component. Similar eluted fractions identified by TLC plate were mixed together. GC-MS of the separated fractions was performed and two fractions appeared to consist of mostly one major compound which was confirmed to be Naphthalene and Acenaphthene. Other fractions consisted of mixture of three or more compounds. Hexane was distilled off from the solution using a rotary evaporator. The concentrated extract was then washed with pentane and left to dry in a fume hood. The column chromatography set up is shown in Figure 3-5

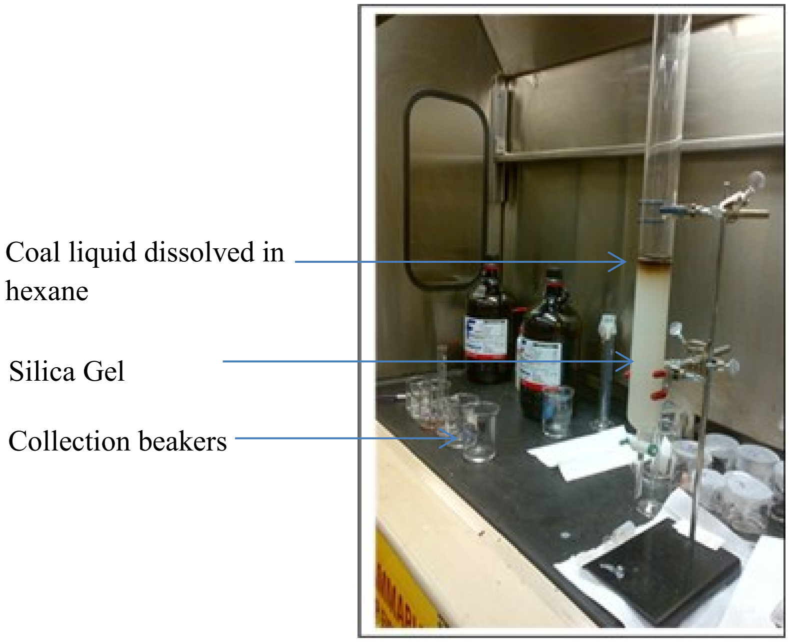

Figure 3-5: Silica gel Chromatography Set up

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4 CHARACTERIZATION OF COAL LIQUID FRACTIONS

Excerpted from 'Characterization and Refining Pathways of Straight-Run Heavy Naphtha and Distillate from the Solvent Extraction of Lignite'[1]

Coal liquid derived from thermal liquefaction of lignite coal at 415°C and for 1 hour under initial hydrogen partial pressure of 4MPa was distilled into four boiling fractions 120-250°C, 250-300°C, 300-343°C and 343-370°C.

4.1 Boiling Distribution

The percentage by volume of each boiling fraction in the whole liquid product was determined by simulated distillation. The results are shown below.

Table 4-1: Liquid yield in 120-370 °C range of the coal liquid from solvent extraction of Bienfait lignite at 415 °C and 4 MPa for 1 hour

Boiling fraction (°C)	Yield (vol %) [a]
120-250	7
250-300	17
300-343	18
343-370	20

[a] Representative yields determined by simulated distillation analysis

4.2 Elemental composition

The ultimate analyses of the different coal liquid distillation fractions were performed (Table 4-2: Elemental composition of coal liquid distillation fractions). The elemental composition of the coal liquids was important primarily for two reasons. First, it indicated the heteroatom content in each fraction that had to be removed during coal liquid refining. Second, it provided the hydrogen to carbon ratio of each fraction, which was an indicator of the aromaticity and the anticipated H_2 consumption during coal liquid refining.

Table 4-2: Elemental composition of coal liquid distillation fractions

Description	Elemental composition (wt %) [a]							
	120-250 °C		250-300 °C		300-343 °C		343-370 °C	
	x	S	x	s	x	s	x	s
carbon	87.94	0.31	91.75	0.25	92.62	0.20	93.19	0.04
hydrogen	7.63	0.18	6.69	0.04	6.22	0.03	5.62	0.10
nitrogen	0.45	0.02	0.39	0.03	1.00	0.01	0.49	0.02
sulfur	0.11	<0.01	0.06	<0.01	0.09	<0.01	0.04	<0.01
oxygen [b]	3.88	0.51	1.11	0.31	0.07	0.22	0.65	0.04
H:C ratio [c]	1.03		0.87		0.80		0.72	

[a] Average (x) and sample standard deviation (s) of triplicate analyses

[b] Oxygen content is calculated by difference

[c] Molar ratio

The results showed a monotonous decrease in the H:C molar ratio with increasing boiling point of the distillation cut. Yet, no specific trend was observed with respect to the heteroatom content distribution.

4.3 HPLC Analyses of Coal Liquid Fractions

From the elemental analyses (Table 4-2) it was clear that the coal liquids produced by solvent extraction was hydrogen deficient and likely aromatic in nature. HPLC analysis was performed on the coal liquids to determine the distribution of aromatic hydrocarbons in each of the distillation fractions. It was possible to differentiate between mono-nuclear, di-nuclear, tri-nuclear, tetra-nuclear and penta-nuclear aromatic hydrocarbons (Table 4-3).

Table 4-3: Concentration of aromatic hydrocarbons in each of the coal liquid distillation fractions

Aromatic hydrocarbons	Concentration by HPLC (wt %) [a]			
	120-250 °C	250-300 °C	300-343 °C	343-370 °C
mononuclear aromatics	1.8	0.0	0.0	0.0
dinuclear aromatics	24.5	21.6	3.4	0.6
trinuclear aromatics	0.0	5.0	35.3	3.9
tetranuclear aromatics	0.0	0.0	8.2	54.4
pentanuclear aromatics	0.0	0.0	0.3	0.1
Σ	26.3	26.6	47.2	59.0

[a] Excludes heteroaromatics and aromatics with polar substituents

The retention times of the aromatic hydrocarbons depended strongly on the number of aromatic rings in the compound. Compounds with the same number of aromatic rings were eluted in a cluster. It was observed that the compounds within each cluster were not necessarily fully resolved, but groups of compounds with the same number of aromatic cores were differentiated and quantified. The polar compounds were removed from the column by back flushing and were not analyzed.

The aromatics containing heteroatoms could not be differentiated based on the number of aromatic rings and were eluted as a single cluster of polar compounds. The composition in Table 6 therefore refers strictly to aromatic hydrocarbons, i.e. it excludes polar heterocyclic aromatics and it excludes aromatic compounds with polar heteroatom containing substituents. As indicated before, the polar fraction was not eluted and was removed by back flushing of the column.

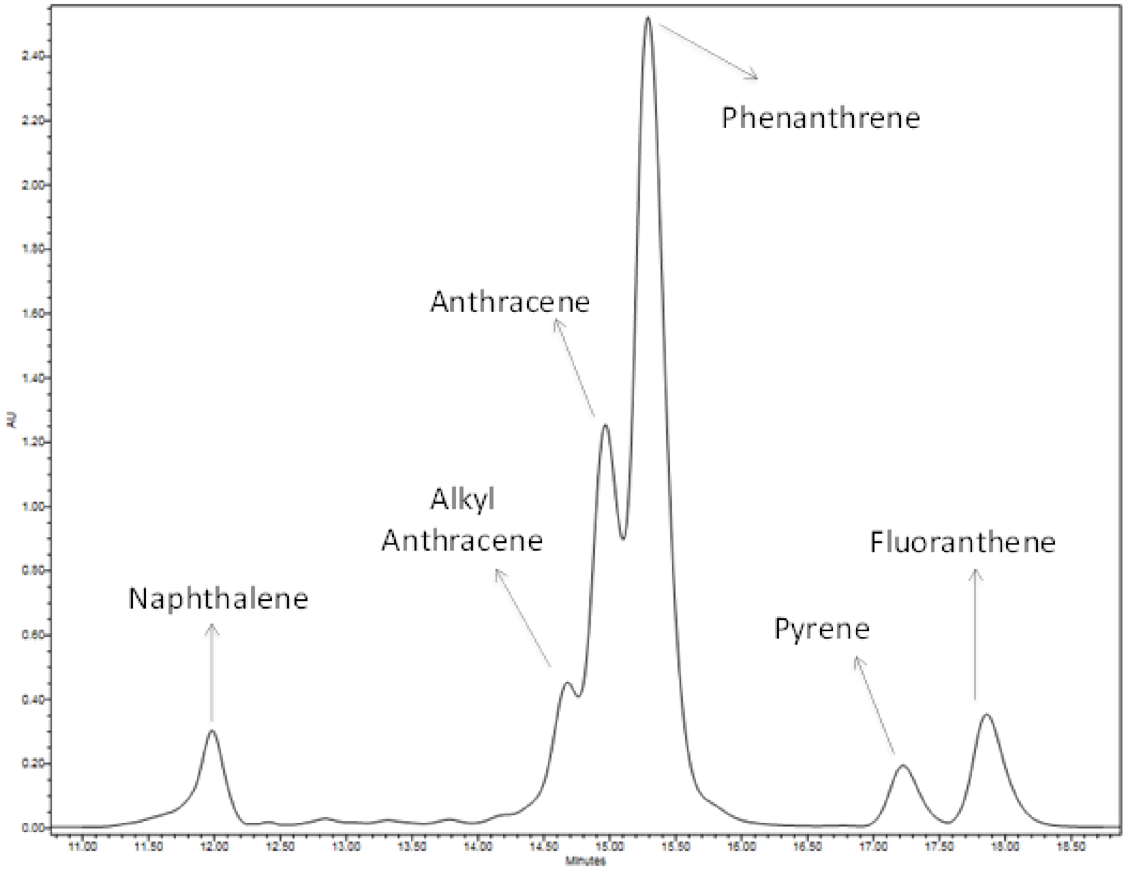


Figure 4-1: Chromatogram of the HPLC analysis of the 300-343 °C distillation fraction of the coal liquids.

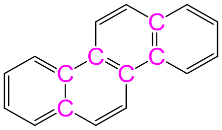
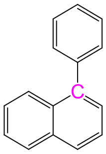
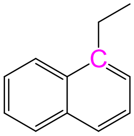
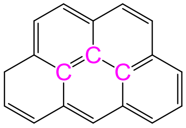
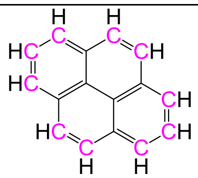
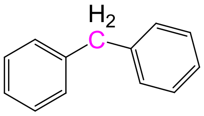
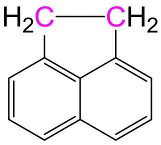
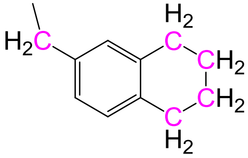
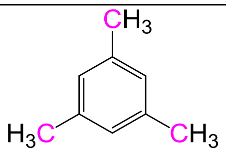
4.4 ^{1}H and ^{13}C NMR Measurements of Coal Liquid Fractions

The HPLC analyses provided information only about the aromatic hydrocarbons and not the total aromatics content. In order to quantify the total fraction of carbon that was present as aromatic carbon, as well as how hydrogen was distributed between aromatic and aliphatic carbon, ^{13}C and ^{1}H NMR analyses were performed.

4.4.1 ^{13}C NMR shift-values

In the work by Díaz and Blanco,[2] coal tar pitches were analyzed with the objective of extracting additional information from the ^{13}C NMR spectra. The assignment of structural features to specific shift-ranges of mixtures cannot yield absolute numbers devoid of uncertainty. It was noted that many aspects affect the shift-range cutoffs, including the concentration of the analyte. A summary of the ^{13}C NMR shift-assignments by Díaz and Blanco is given (Table 4-4). We used this classification for interpretation. Qualitatively this is likely to provide a good indication of the nature of the coal liquids, even though the quantitative values are associated with some uncertainty that was not quantified for our materials.

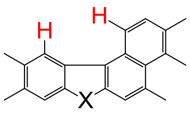
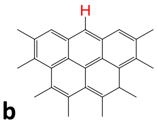
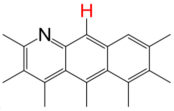
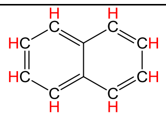
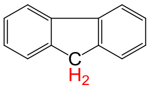
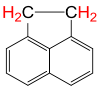
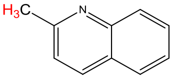
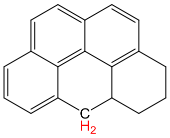
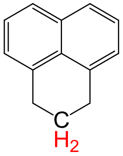
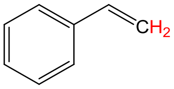
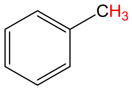
Table 4-4: 13C NMR shift-assignments by Díaz and Blanco[2] for coal tar pitches at 20 wt% concentration of the analyte in CS2.

Symbols			Description	δ ppm	Examples
C_{ar}	$C_{ar1,2}$	C_{ar2}	(a) catacondensed aromatic carbons, (b) aromatic carbons both with heteroatomic or aromatic substituents	160 - 129.5	**(a)**  **(b)** 
		C^{s}_{ar}	Aromatic carbons joined to aliphatic chains		
	$C_{ar1,3}$	C_{ar3}	Pericondensed aromatic carbons	129.5 - 108	
		CH_{ar}	Protonated aromatic carbons		
C_{al}	$C_{\alpha 2}$		Bridge/hydroaromatic structures (methylene carbons in α position to two aromatic rings)	49.3 - 34	
	CH_2		All the rest of methylene carbons (CH_2 different from $C_{\alpha 2}$)	34 - 23	 
	CH_3		Methyl carbons	23 - 17	

4.4.2 ^{1}H NMR shift-values

A chemical shift classification of ^{1}H NMR spectra of coal tar pitches was developed by Guillen, Díaz and Blanco.[3] A summary of the ^{1}H NMR shift-assignments is given (Table 4-5). Unlike pitches, some longer aliphatics and alkyl chains were anticipated in the coal liquids and therefore the sub-classification between $H_{\beta1}$ and $H_{\beta2}$ was not considered (e.g. see aliphatic ^{13}C NMR shift-ranges).[4] The comments made in relation to the ^{13}C NMR shift-assignments (Section 4.4.1) is equally applicable to the assignments based on the ^{1}H NMR spectra. Qualitatively it is likely to yield good information, but the uncertainty associated with the quantitative measurements of the coal liquids was not quantified for our materials.

Table 4-5: 1H NMR shift-assignments by Guillen, Díaz and Blanco[3] for coal tar pitches in CS2

Symbols				Description	δ ppm	Examples
H_{ar}		H_{ar2}		(a) Aromatic hydrogen sterically hindered: in angular polyaromatic hydrocarbons (PACs), (b) Aromatic hydrogen in very pericondensed PACs or (c) next to heteroatoms	9.5 - 8.36	a  b  c 
		H_{ar1}		All other aromatic hydrogen	8.36 - 6.3	
H_{al}	H_{α}	$H_{\alpha 2}$	H_F	Aliphatic hydrogen in methylene groups α to two aromatic rings (fluorene type)	4.5 - 3.69	
			H_A	(a) Aliphatic hydrogen in methylene groups α to an aromatic ring and β to another (acenapthene type) (b) Aliphatic hydrogen in methyl groups placed in the same zone as H_{ar2}	3.69 - 3.0	a  b 
		$H_{\alpha 1}$		Aliphatic hydrogen in methyl or methylene groups α to an aromatic ring which can moreover be attached in γ position or further to another or the same aromatic ring	3.0 - 2.0	
	H_{β}	$H_{\beta 2}$		Alicyclic hydrogen in β position to two aromatic rings (naphthenic methylenes)	2.0 - 1.6	
		$H_{\beta 1}$		Aliphatic hydrogen in methyl or methylene groups β to an aromatic ring.	1.6 - 1.0	
	H_{γ}			Aliphatic hydrogen in methyl or methylene to an aromatic ring.	1.0 - 0.5	

The ^{13}C and ^{1}H NMR results are tabulated in Table 4-6.

Table 4-6: Aromatic and aliphatic distribution of carbon and hydrogen in coal liquid distillation fractions

Description	Concentration based on ^{13}C NMR and ^{1}H NMR (wt %) [a]			
	120-250 °C	250-300 °C	300-343 °C	343-370 °C
Carbon distribution				
aromatic	80.2	83.2	88.7	93.9
aliphatic	19.8	16.8	11.3	6.1
Hydrogen distribution				
aromatic	53.1	55.2	77.1	81.6
aliphatic	46.9	44.8	22.9	18.4

[a] Sample standard deviation of triplicate analyses was 0.4 wt %

The differentiation between aromatic and aliphatic carbon was based on the ^{13}C shift. Carbon shift-values of $\delta \geq 90$ ppm were taken as aromatic and lower shift-values were taken as aliphatic.[4] This type of differentiation is only possible in the absence of alkenes. The ^{13}C shift-values of the alkenes largely overlap with that of the aromatics. A similar approach was employed for the differentiation between aromatic and aliphatic hydrogen. The ^{1}H shift-values of $\delta \geq 6.3$ ppm were taken as aromatic hydrogen and lower shift-values were taken as aliphatic hydrogen. In the case of hydrogen this type of classification is more error-prone, because the shift-values for hydrogen in some heteroatom containing functional groups, such as carboxylic acids and amides, overlap with the shift-values of aromatic hydrogen.[4] The possible presence of carboxylic acids and amides was determined separately and it was confirmed that these compounds did not affect the NMR analyses in a measurable way, if at all. In fact, even when dealing with pure acids and amides, the fraction of hydrogens in the aromatic shift-range is small. For example, in the case of pure decanoic acid, the acidic hydrogens constitute only 5 %.

The ^{13}C NMR shift-values (Table 4-7) provided additional information on the likely chemical character of the carbon. The ranges employed for integration were taken from the work of Díaz and Blanco.[2] The error associated with the quantitative values based on this assignment was not determined. Care must therefore be taken not to over-interpret the quantitative values.

Table 4-7: Distribution of carbon types based on the 13C NMR shift-values of the coal liquids

Description	δ (ppm)	Symbol	Concentration based on ^{13}C NMR (wt %)			
			120-250 °C	250-300 °C	300-343 °C	343-370 °C
aliphatic, CH_3 groups	17.0-23.0	CH_3	5.1	2.4	2.0	1.2
aliphatic, CH_2 groups	23.0-34.0	CH_2	12.0	11.7	7.6	2.5
aliphatic, C bridge α-position to 2 aromatics	34.0-49.3	$C_{\alpha 2}$	2.7	3.1	2.0	2.4
aromatic, CH or pericondensed	108.0-129.5	$C_{ar1,3}$	54.8	51.3	62.0	67.6
aromatic, edge-C without H attached	129.5-160.0	$C_{ar1,2}$	25.5	31.6	26.3	26.2

In an analogous fashion the ^{1}H NMR shift-values (Table 9) provided additional information on the likely chemical character of the hydrogen in the coal liquids.

Table 4-8: Distribution of hydrogen types based on the 1H NMR shift-values of the coal liquids

Description	δ (ppm)	Symbol	Concentration based on ^{1}H NMR (wt %)			
			120-250 °C	250-300 °C	300-343 °C	343-370 °C
aliphatic, CH_3 on aromatic	0.5-1.0	H_γ	2.6	1.1	1.0	0.6
aliphatic, acyclic or an alkyl / naphthenic on β-position from aromatic	1.0-2.0	H_β	13.7	9.6	8.1	5.4
aliphatic, CH_2 on aromatic	2.0-3.0	$H_{\alpha1}$	26.4	9.9	9.2	7.0
aliphatic, CH_2 on aromatic and β-position from aromatic / heteroatom	3.0-3.69	$H_{\alpha2,A}$	3.5	21.9	3.1	4.0
aliphatic, CH_2 in aromatic bridge	3.69-4.5	$H_{\alpha2,F}$	0.8	2.3	1.1	1.4
aromatic, all H except H_{ar2}	6.3-8.36	H_{ar1}	52.6	53.8	66.2	77.1
aromatic, crowded, very condensed, next to or attached to heteroatom	8.36-9.5	H_{ar2}	0.5	1.4	10.9	4.6

The interpretation and shift-ranges employed for integration of the ^{1}H NMR spectra were taken from the work of Guillén, Díaz and Blanco.[3] The classification was simplified for H_β, because coal liquids were anticipated to be richer in aliphatic, alkyl aromatic and hydroaromatic compounds than pitches for which the classification was originally developed. All of the hydrogen in acyclic aliphatics, or in alkyl or naphthenic groups at β-positions or further away from aromatics, is lumped in H_β.

4.5 Acid Titration

The acid content of the different coal liquids was determined by titration (Table 10). There were little acids present and the acid content displayed the same trend as the oxygen content (Table 5) of the coal liquids. The lighter fractions seem to contain two classes of compounds with some acidic character, for example carboxylic acids and phenolics, because two inflection points can be seen on the potentiographs (Figure 4-2).

Table 4-9: Acid content of coal liquids

Acid number (mg KOH/g)			
120-250 °C	250-300 °C	300-343 °C	343-370 °C
1.6	0.5	0.2	- [a]

[a] No measurable acidity.

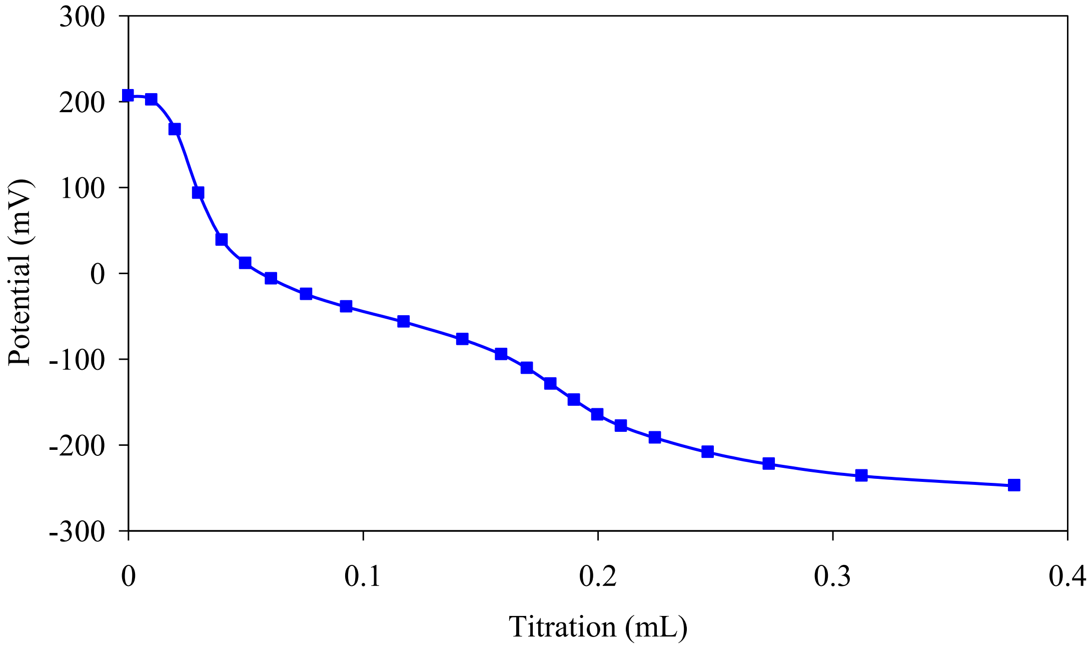


Figure 4-2:Potentiograph from the KOH titration of the 120-250 °C fraction of coal liquid

4.6 Infrared spectroscopy

Infrared spectroscopy was employed to look for specific heteroatom functional groups to better understand the change in composition with boiling point (Figure 4-3). The main observations that were made from the infrared spectra are:[5]

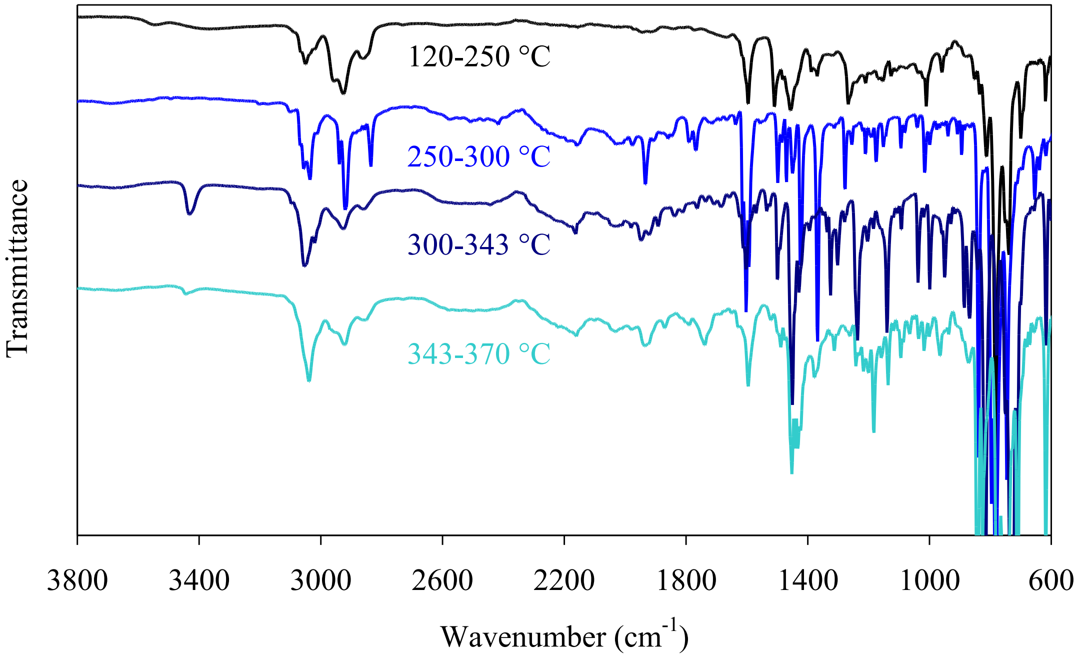


Figure 4-3: Infrared spectra of the coal liquid boiling fractions

(a) The oxygen contained in the lighter fractions was mainly present as ethers. The 120-250 °C and 250-300 °C coal liquid fractions exhibited the two distinctive ether absorption bands at 1267-1279 cm^{-1} and 1011-1016 cm^{-1}. The 250-300 °C fraction had a clear methoxy (–OCH_3) absorption at 2835 cm^{-1}, which may also have been present as a shoulder in the infrared spectrum of the 120-250 °C fraction. The oxygen in the 343-370 °C fraction seemed to be present mainly as esters, with a prominent carbonyl absorption peak at 1738 cm^{-1}. Surprisingly the infrared spectra did not indicate a strong presence of phenolic and carboxylic acid functional groups.

(b) The nitrogen in the lighter fractions is likely present as pyridinic compounds, but is difficult to unambiguously identify within the aromatic matrix using infrared spectroscopy. The two heavier fractions, 300-343 °C and 343-370 °C, definitely contained some pyrrolic nitrogen, with the N–H stretch being clearly visible at 3432-3443 cm^{-1}. The N–H stretch in the infrared spectrum of the 300-343 °C fraction was particularly prominent.

(c) The sulfur content in all of the coal liquids was too low to make use of infrared spectroscopy to identify functional groups.

4.7 Compound identification

The major compounds present in each of the coal liquid fractions were identified using GC-MS (Figure 4-4 to Figure 4-7). Since the compounds were identified from their electron impact mass spectra, the structures should be seen as representative of the isomers shown, rather than a specific isomer. There may also have been some compound overlap, since the complexity of the coal liquids was less than shown by more advanced chromatographic analyses.[6-8]

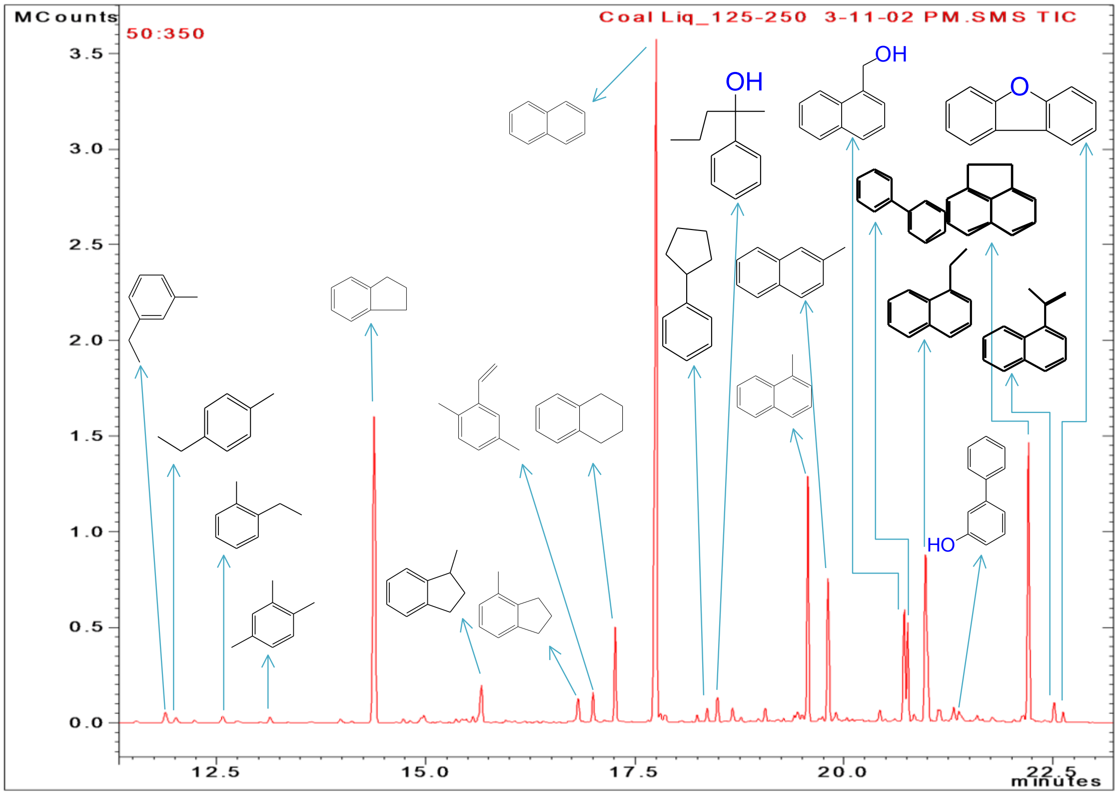


Figure 4-4: Compounds in the 120-250 °C boiling fraction of the coal liquid

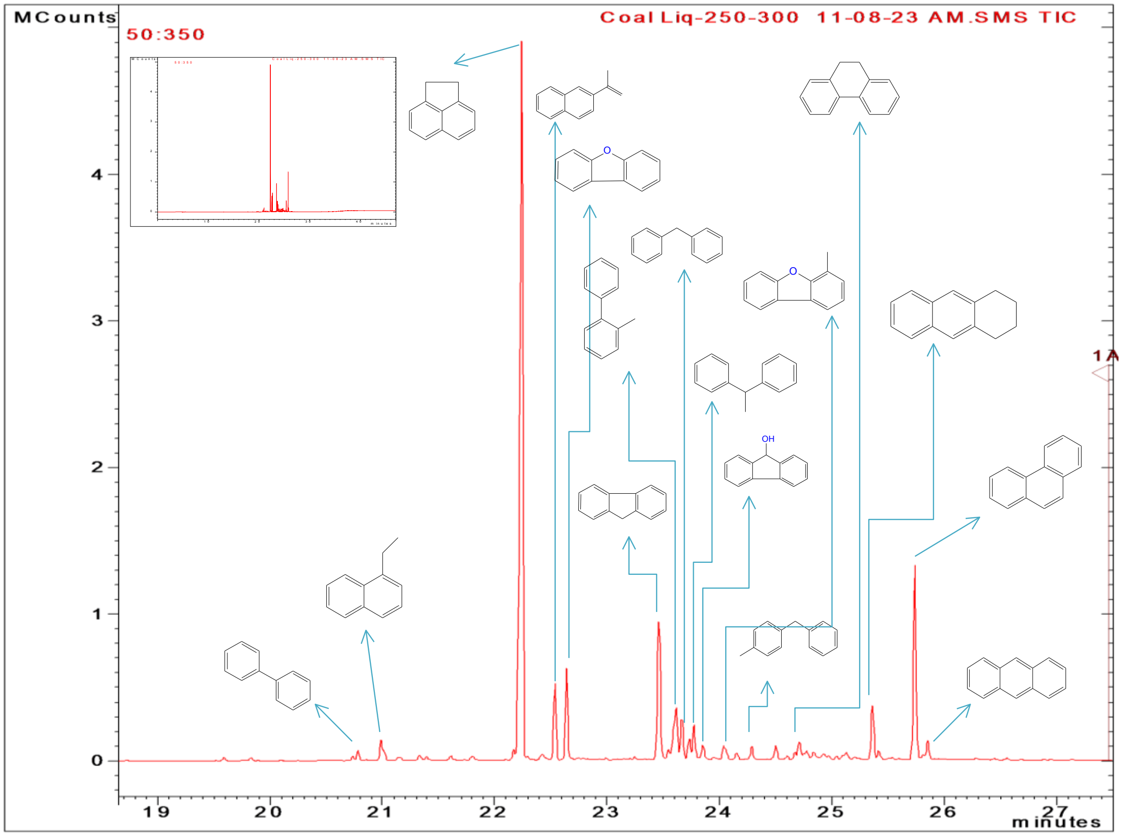


Figure 4-5: Compounds in the 250-300 °C boiling fraction of the coal liquid

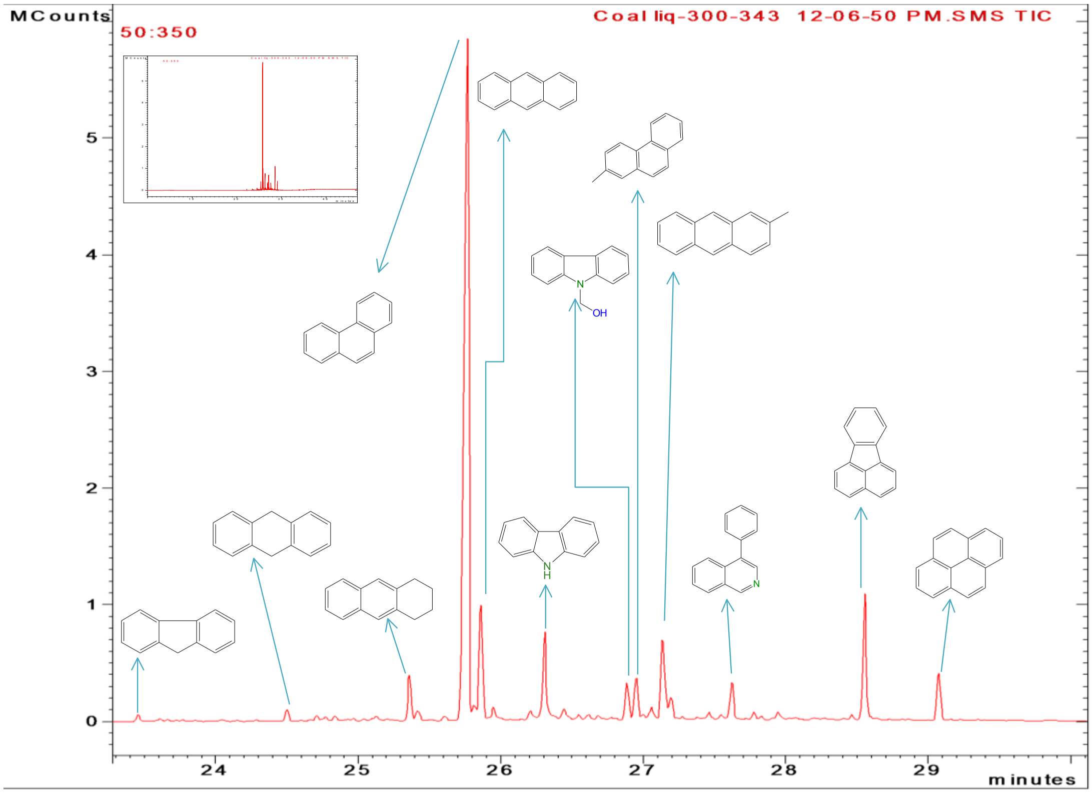


Figure 4-6: Compounds in the 300-343 °C boiling fraction of the coal liquid

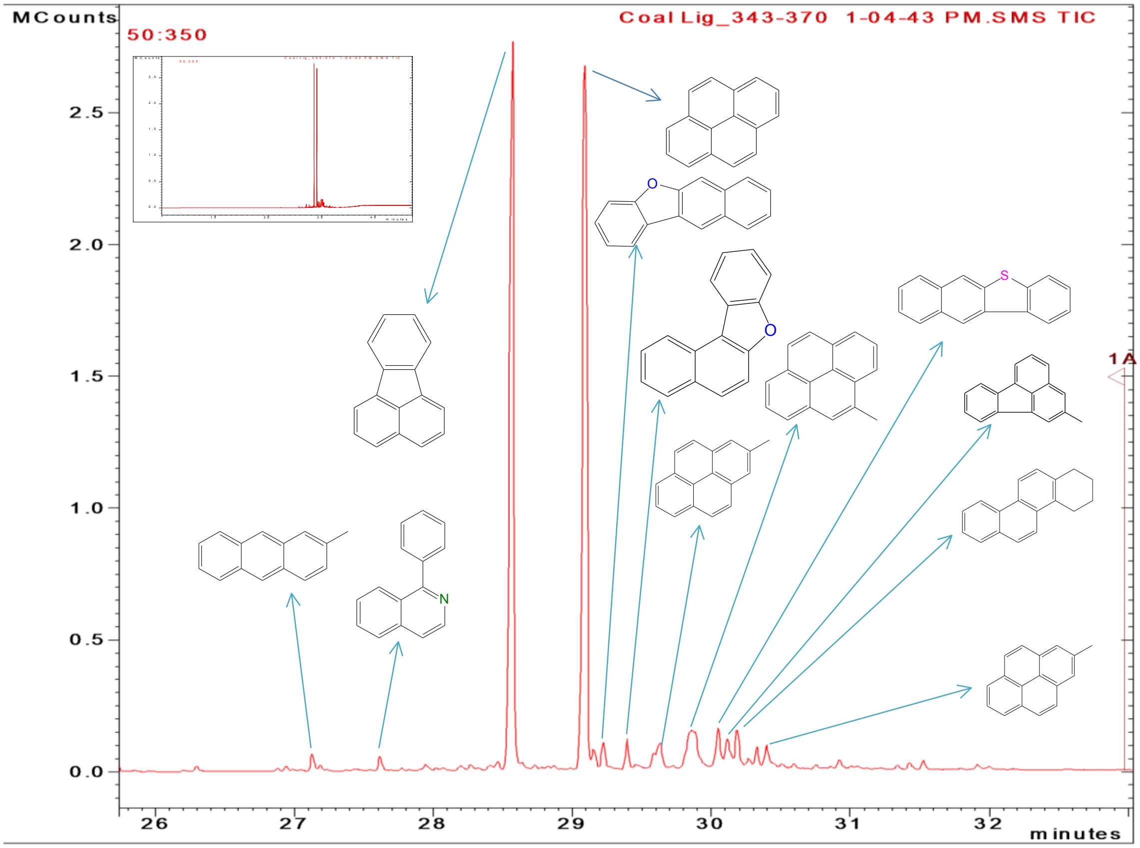


Figure 4-7: Compounds in the 343-370 °C boiling fraction of the coal liquid

Quantification of the compounds that were identified was based on the FID peak areas obtained during gas chromatography. No FID response factor corrections were made. Since most of the compounds were aromatic little bias in the results was anticipated, with the exception of the heteroatom containing compounds that may have been slightly under-reported.[9] The concentrations of the most abundant compounds are summarized in Table 11. Tables showing the abundance, retention times, and structure of compounds identified by the GCMS are presented in the appendix.

Table 4-10: Concentration of most abundant compounds in the coal liquids

Compound [a]	Concentration (wt %) [b]			
	120-250 °C	250-300 °C	300-343 °C	343-370 °C
Indane	9.6			
naphthalene	21.9			
methylnaphthalene	11.2			
ethylnaphthalene	7.1	1.2		
acenaphthene	7.6	47.5		
dibenzofuran		5.0		
Fluorine		8.3		
phenanthrene		11.3	58.4	
anthracene		1.2	6.9	
Carbazole			5.6	
methylanthracene			6.0	0.8
fluoranthene			8.8	39.5
Pyrene				40.3

[a] Only compounds with a concentration of more than 5 (wt %) in any one fraction are listed.

[b] Concentration is expressed on the basis of the total mass in each boiling fraction.

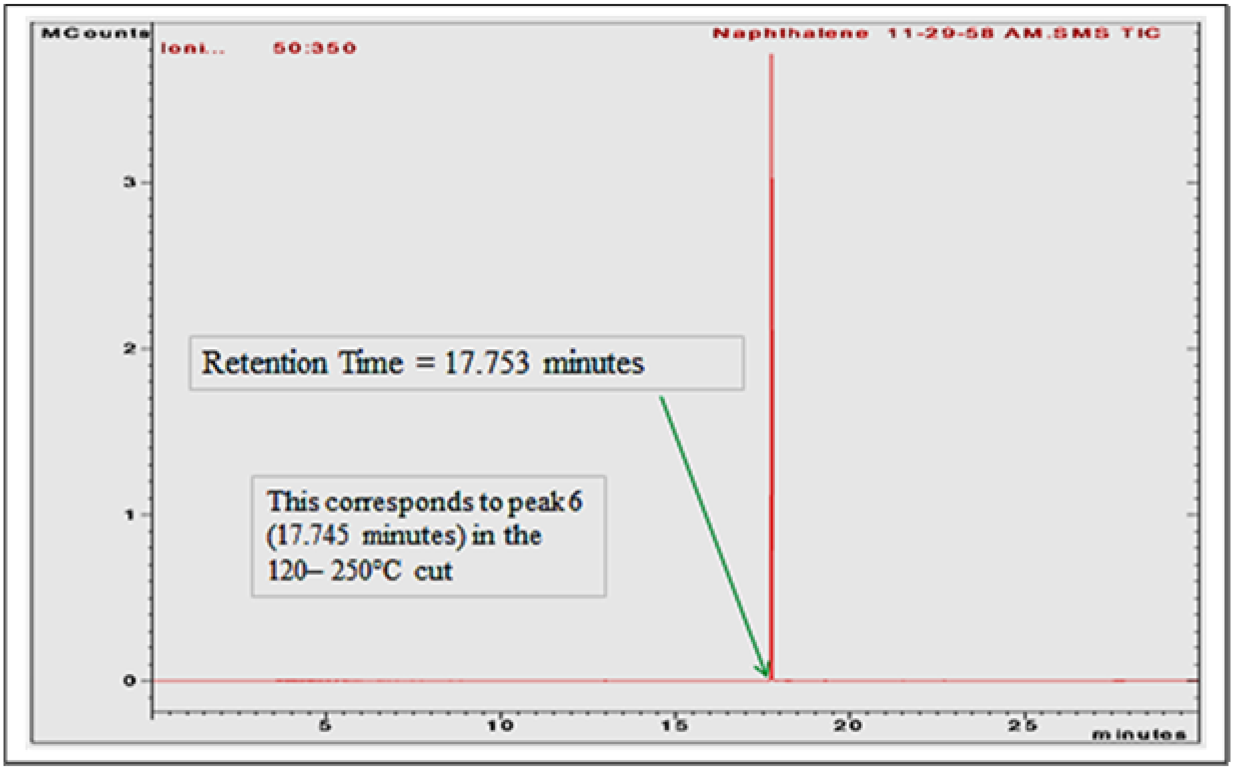
The most abundant compounds in the 120-250 °C boiling fraction (Figure 2) were indane, naphthalene and alkyl derivatives of indane and naphthalene. In the 250-300 °C boiling fraction (Figure 3) acenaphtene was the major compound, with smaller amounts of dibenzofuran, fluorene and anthracene derivatives. The 300-343 °C boiling fraction (Figure 4) was dominated by phenanthracene, with lesser amounts of various anthracene derivatives, carbazole and fluoranthene. The high concentration of carbazole explained the higher than average nitrogen content of this fraction (Table 5). Fluoranthene and pyrene were the two major constituents of the 343-370 °C boiling fraction (Figure 5). Various compounds containing four fused rings made up the rest of this fraction.

Due to the importance of sulfur species in the refining of oil to transportation fuels, the main sulfur compound classes were identified. In the 120-250, 250-300 and 300-343 °C boiling fractions, the most abundant sulfur class was the thioethers (sulfides). In the 343-370 °C boiling fraction the most abundant sulfur class was the thiophenes. However, in all boiling fractions the sulfur content was low (Table 5), typically less than 0.1 (wt %).

Taken collectively, two specific observations regarding the compound identification stand out. First, the products are almost exclusively aromatic in nature, with none of the main compounds being aliphatic. Second, despite the diversity of compounds, the composition of the coal liquids was dominated by a limited number of compounds rather than compound classes, which were present in high concentration. Acenaphtene, phenanthracene, fluoranthene and pyrene were particularly abundant and comprised 62 (wt %) of combined coal liquid product in the 120-370 °C boiling range.

4.8 Chemical Extraction from 120-250 °C Fraction

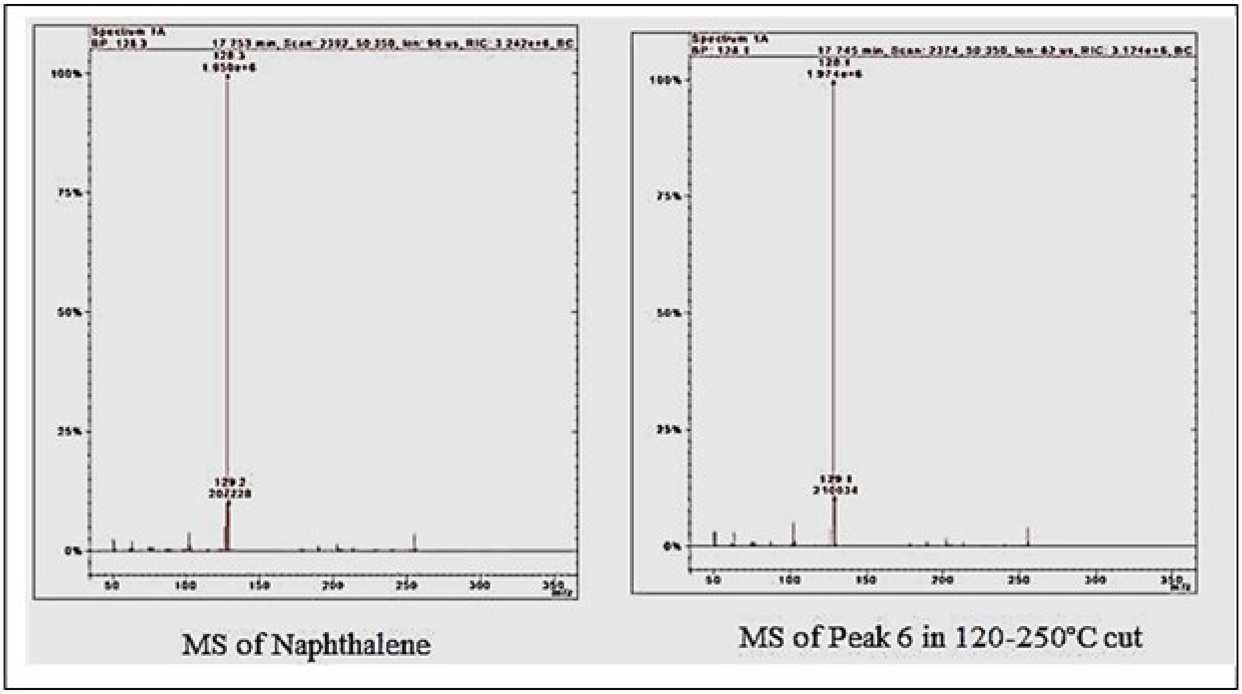
Naphthalene is one of the value added products that is of significant economic value. Therefore attempt was made to identify and confirm the presence of naphthalene in the coal liquid cuts. First of all, GC-MS of pure Naphthalene was performed with the same conditions as those of coal liquids. The retention time was observed, which was 17.75 minutes (Figure 4-8). The Mass fragmentation spectrum was also observed. The retention time was matched with those of the coal liquids, and it was observed that the sixth peak in the first cut had a retention time very close to that of pure naphthalene. The Mass spectrum was also compared to that of pure naphthalene, and the fragmentation patterns appeared very similar as shown in Figure **4-9**. This peak appeared as the major peak in the 120-250 °C cut. Extraction as well as further confirmatory analysis was also carried out.



Retention Time = 17.753 minutes

This corresponds to peak 6 (17.745 minutes) in the 120– 250°C cut

Figure 4-8: GC of Pure Naphthalene



MS of Naphthalene

MS of Peak 6 in 120-250°C cut

Figure 4-9: Mass spectra of Naphthalene and Peak 6 in 120-250 ℃ Fraction

White crystals were observed in one of the beakers while the other beaker showed a needle type solid crystal in it (Figure 4-10 and Figure 4-11).

Figure 4-10: White crystals of extracted Naphthalene

Figure 4-11: Rod-like crystals of extracted Acenaphthene

4.8.1 Confirmatory Analysis:

Three tests were carried out to confirm the identity of the extracted compounds, namely:

1. Melting Point determination
2. GC-MS and
3. ^{1}H NMR analysis

4.8.1.1 Melting Point Determination:

Melting points of the extracted crystals were determined and compared to that of literature. These are reported in Table 4-11. There were some deviations from those reported in literature. The presence of other compounds, though minute, resulted in a melting point depression. There were more compounds present in the acenaphthene crystals as shown in the GC-MS (Figure 4-12) and consequently greater melting point depression.

Table 4-11: Melting Points of Naphthalene and Acenaphthene

Compound	Literature Melting Point	Experimental Melting Point
Naphthalene	78 – 79 °C	79 – 82 °C
Acenaphthene	86 – 88 °C	93 – 95 °C

4.8.1.2 GC-MS analysis:

The extracted solids were analysed with the GC-MS. The well pronounced peaks in the chromatograms were identified as Naphthalene and Acenaphthene. The GC-MS of Naphthalene and Acenaphthene are shown in Figure 4-12 and Figure 4-13.

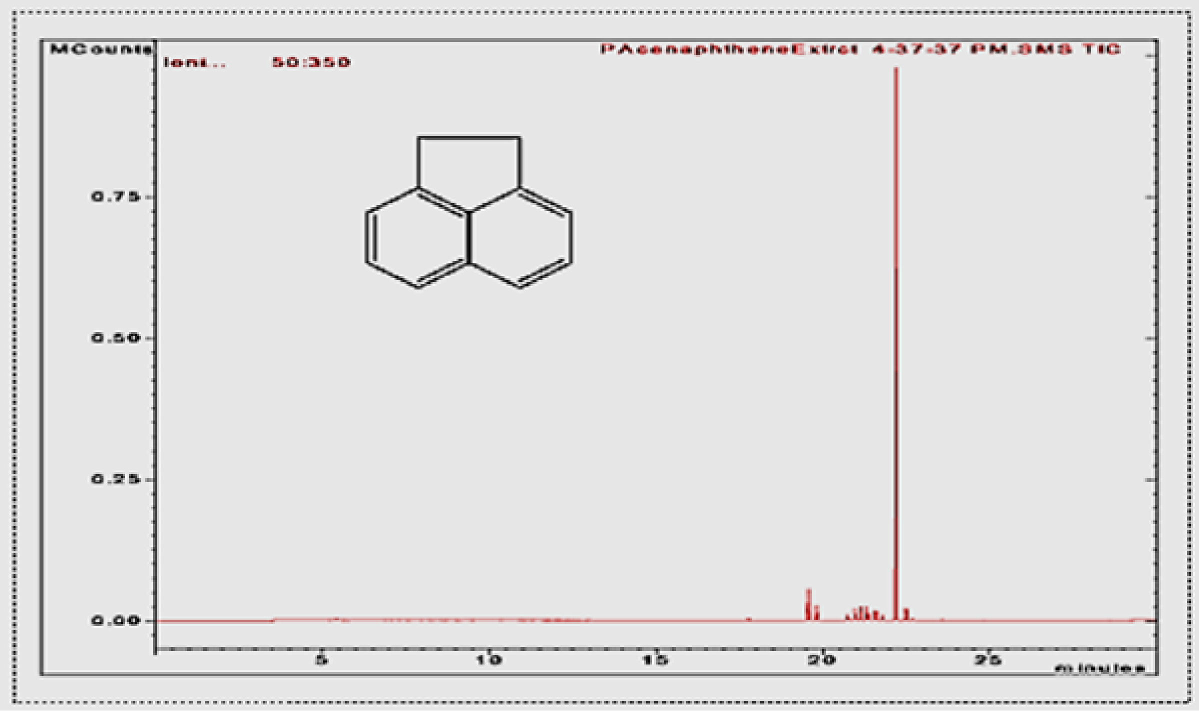


Figure 4-12: GC of Acenaphthene

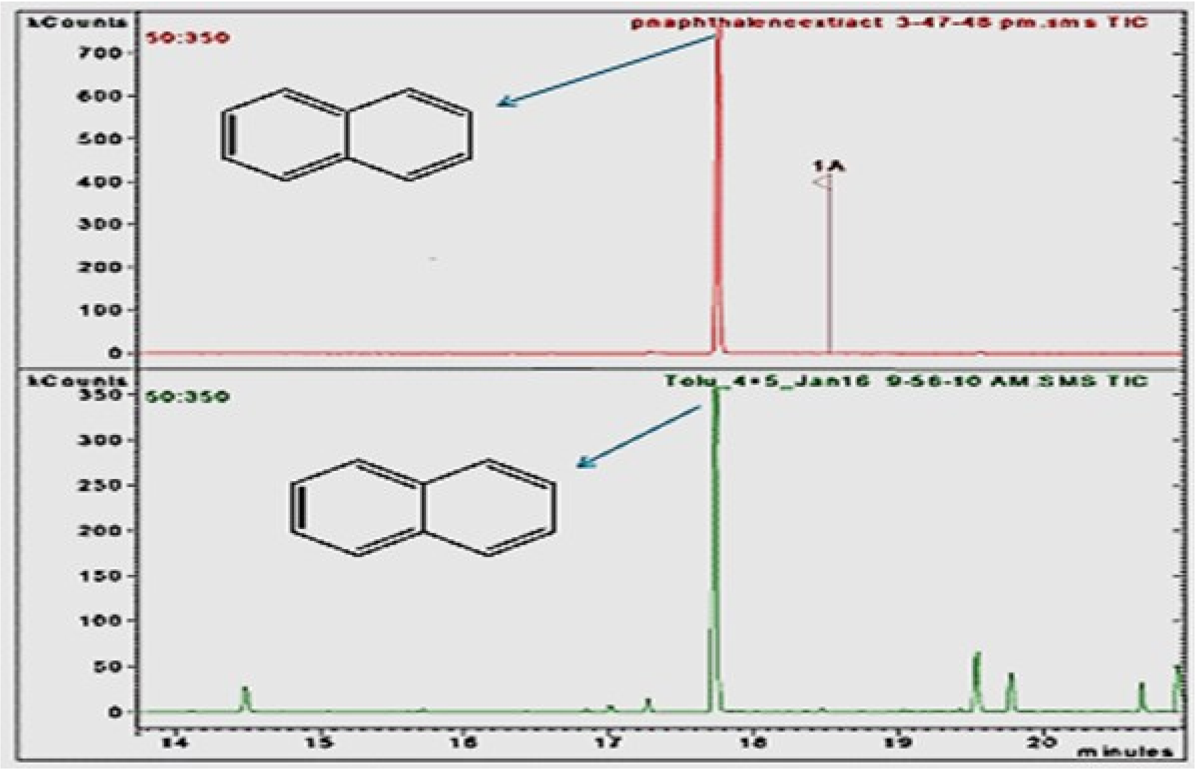


Figure 4-13: Naphthalene before (lower) and after (upper) pentane wash

4.8.1.3 ^{1}H NMR Analysis:

^{1}H NMR analysis was also performed on the solid crystals and results confirmed these compounds to be Naphthalene and Acenaphthene. The ^{1}H NMR of Naphthalene and Acenaphthene are shown in Figure 4-15 and Figure 4-17. The ^{1}H NMR shows the different protons present in the compound as well as the percentages in which they are present. Naphthalene has two different types of aromatic proton as shown in Figure 4-14.

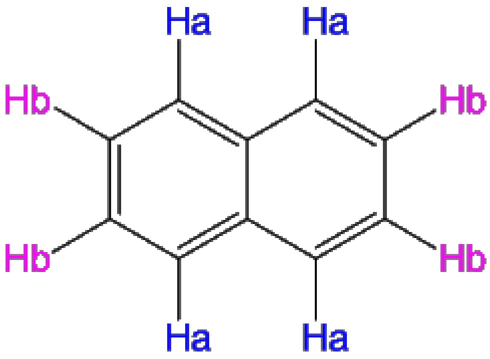


Figure 4-14: Naphthalene

These two types (Ha and Hb) of aromatic protons are present in Naphthalene. Since all these Ha protons are equivalent, we suppose to get a doublet peak corresponding to these 4 Ha protons. Similarly, for Hb protons we will get another doublet peak corresponding to these 4 Hb protons. Therefore, we expect two doublet peaks in ^1H NMR spectrum of Naphthalene. ^1H NMR spectrum for the extracted Naphthalene crystals is shown in Figure 4-15 and the result are presented in Table 4-12.

Table 4-12: Proton Types in Extracted Naphthalene

Types of proton	Proton spectra region ppm	Percentages/%
Aromatic Proton 1	7.85-7.89	50.60
Aromatic Proton 2	7.48-7.52	49.40

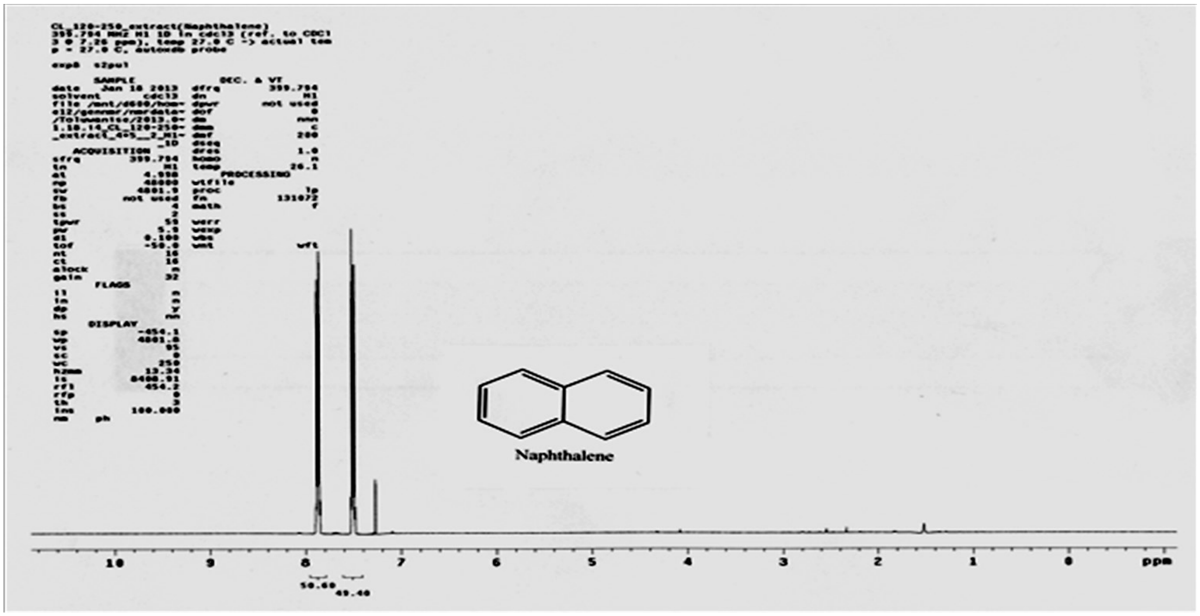


Figure 4-15: ^{1}H NMR spectrum of Naphthalene

There are four different types of protons present in acenaphthene as shown in Figure **4-16**. These are: methylene protons (blue), and three different types of aromatic protons (pink, green and brown), and they are present in the ratio 2:1:1:1 respectively. Therefore, we would expect to see four peaks in the spectrum with percentages in similar ratios.

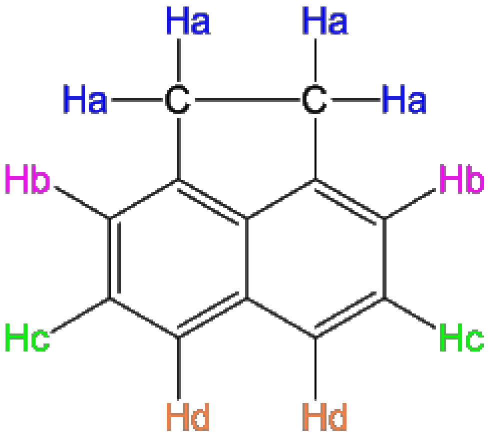
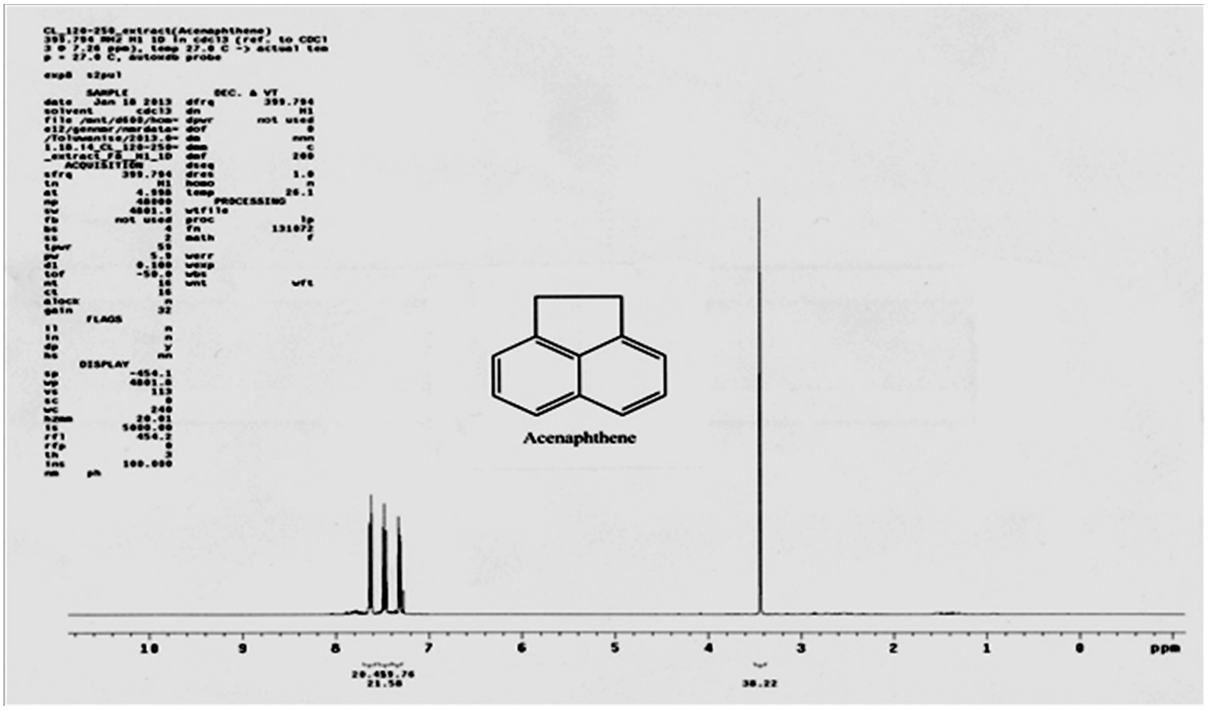


Figure 4-16: Acenaphthene

Table 4-13: Proton Types in Extracted Acenaphthene

Types of proton	Proton spectra region (ppm)	Percentages/%
Methylene Proton	3.44	38.22
Aromatic Proton 1	7.61 – 7.63	20.45
Aromatic Proton 2	7.47	21.56
Aromatic Proton 3	7.27 – 7.30	19.77



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CL_120-250_extract(Acenaphthene)
399.794 MHz H1 1D in cdcl3 (ref. to CDCl
3 @ 7.26 ppm), temp 27.0 C -> actual tem
p = 27.0 C, autoxdb probe

exp8  s2pul

     SAMPLE              DEC. & VT
date   Jan 18 2013   dfrq       399.794
solvent      cdcl3   dn              H1
file /mnt/d600/hom-  dpwr      not used
e12/genmr/nmrdata-   dof              0
/Toluwanise/2013.0-  dm             nnn
1.18.14_CL_120-250-  dmm              c
_extract_F8__H1_1D   dmf            200
   ACQUISITION       dseq
sfrq       399.794   dres           1.0
tn              H1   homo             n
at           4.998   temp          26.1
np           48000       PROCESSING
sw          4801.9   wtfile
fb        not used   proc            lp
bs               4   fn          131072
ss               2   math             f
tpwr            59
pw             5.9   werr
d1           0.100   wexp
tof          -50.0   wbs
nt              16   wnt            wft
ct              16
alock            n
gain            32
     FLAGS
il               n
in               n
dp               y
hs              nn
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sp          -454.1
wp          4801.8
vs             113
sc               0
wc             240
hzmm         20.01
is         5000.00
rfl          454.2
rfp              0
th               3
ins        100.000
nm      ph
```

Figure 4-17: ^{1}H NMR spectrum of Acenaphthene

4.9 Motor-gasoline refining from coal liquids

Motor-gasoline is refined from naphtha, which is the boiling fraction lighter than 175 °C in the coal liquid. In this investigation the naphtha fraction made up only 10 vol % of the 120-250 °C boiling fraction and it was a minor constituent of the overall liquid product from the solvent extraction of lignite (Table 4-1). This is a very small fraction when compared to other solvent extraction processes, such as the Exxon Donor Solvent process.[10] The product yield and composition is very different to that obtained from catalytic coal liquefaction, which is more hydrogen-rich.[8]

The coal-derived naphtha can potentially make a good blending component for motor-gasoline, because it is very aromatic. Mono-nuclear aromatics have high octane numbers. However, for the same reason the coal-derived naphtha by itself does not make an on-specification motor-gasoline, because it is too aromatic. Before the naphtha can be used as a blending component for motor-gasoline, there are a few conditions that have to be met though:

(a) The heteroatom content must be close to zero. In many countries motor-gasoline has a maximum sulfur content of 10-15 μg/g. The sulfur content of the 120-250 °C boiling fraction is 1100 μg/g (Table 4-2). Hydrotreating of the naphtha fraction is required. Little difficulty in this is anticipated.[11] This should also result in a decrease in the acid number (Table 4-9).

(b) The heavy paraffin content must be low. Heavy paraffins have very low octane numbers and coal tar naphtha streams with a meaningful heavy paraffin content have low octane numbers, despite their high aromatic content.[12,13] When present, hydrotreating is typically followed by catalytic naphtha reforming.[14-16] Performance tests of catalytic naphtha reforming with coal liquids indicate that a liquid yield of 89-90 vol% can be anticipated when producing reformate with research octane number of 98.[17] The present analyses indicated almost no paraffins (Table 4-6 and Figure 4-4). The solvent extraction process investigated in this study produced a more aromatic product than is typically associated with coal liquefaction. This may at least partly be ascribed to the aromatic nature of the hydrotreated coal-derived distillate, which had an aromatic carbon content of 84.5 wt% (Table 3.1).

4.10 Jet fuel refining from coal liquids

The kerosene fraction, which in this study is considered to be the 175-250 °C boiling fraction, is the feed material that can be considered for jet fuel production. The kerosene fraction made up 90 vol% of the 120-250 °C boiling fraction that was 7 vol % of the total coal liquid (Table 4-1).

Coal-derived liquids have been used in a commercial jet fuel blend in South Africa for some time[18]. This jet fuel is a semi-synthetic blend that contains at least half petroleum derived kerosene to dilute the more aromatic coal-derived kerosene.

In the United States a jet fuel (JP-900) that is based on coal-derived liquids was under development since the 1990's.[19-22] Deep hydrogenation of the kerosene was required to remove the heteroatoms and hydrogenate binuclear aromatics. Despite extensive hydrodearomatization

(HDA) some jet fuel specifications were still problematic to meet, namely, the hydrogen content and the density. This is understandable, because binuclear cycloalkanes (naphthenes) have high densities and inherently have lower H:C ratios compared to isoparaffinic kerosene on account of their cyclic structure. For example, decalin ($C_{10}H_{18}$) has a H:C ratio of 1.8 and density at 20 °C of 893 kg/m^3.[23] The acceptable density range for Jet A-1 is 775 to 840 kg/m^3. [24,25] On the positive side, the coal-derived jet fuel had better high temperature thermal stability than typical jet fuel. [21]

In France direct coal liquefaction was combined with high pressure (>12 MPa) hydrocracking of the coal liquids to produce a kerosene that met Jet A-1 density and gravimetric energy density specifications.[15] The jet fuel was more naphthenic than a typical jet fuel, with an cycloalkane content of 89 wt% and aromatic content of 3 wt%. The aromatic content was therefore below the minimum aromatic content of 8 vol% for synthetic jet fuel.[24]

The composition domain for on-specification Jet A-1 defined by Cookson, et al.[26] supported the preceding observations. It indicated that a large fraction of branched and cycloalkanes can be accommodated in jet fuel, but that jet fuel must ultimately contain a meaningful amount of aliphatics in order to meet specification. It was unfortunate that their work did not specifically differentiate between branched and cycloalkanes, even though it pointed out that it is impossible to produce on-specification jet fuel comprising exclusively of cycloalkanes.

The refining requirements for the coal liquids from solvent extraction of coal are similar to those noted in the development of the JP-900 jet fuel and other coal-derived jet fuels:

(a) The heteroatom content must be reduced. Elemental analysis (Table 4-2) indicated that the 120-250 °C boiling fraction contained 0.45 wt% N, 0.11 wt% S and 3.9 wt% O. Although the nature of these heteroatom-containing compounds was not apparent from the GC-MS analysis (Figure 4-4), infrared spectroscopy (Figure 4-3) indicated that the oxygen was mainly present in ether linkages. In addition to the removal of the heteroatoms, naphthalene and alkyl naphthalenes were present in high concentration. Jet A-1 specifications place a maximum limit on the total aromatic content (25 vol%), as well as on the naphthalene content (3 vol%), which is related to the smoke point specification.[24,25] Deep hydrodearomatization (HDA) is therefore needed to meet these specifications.

(b) In order to produce a jet fuel that conforms to the requirements for Jet A-1 or JP-8, it will also be beneficial to perform ring-opening of the binuclear cycloalkanes produced during deep HDA. Ring-opening is partly necessary to increase the overall hydrogen content of the product and partly to reduce the density. Cycloalkanes have higher densities than acyclic alkanes. Ideally one would like to combine the HDA and ring-opening, because it would facilitate HDA by removing decalin and tetralin from the hydrogenation-dehydrogenation equilibrium.[27] Although high pressure hydrocracking does an admirable job in converting coal-derived kerosene to a product that meets almost all Jet A-1 specifications,[15] more ring-hydrogenolysis and less HDA is required to meet fully synthetic Jet A-1 specifications.

Although the viability of producing blending materials for jet fuel from coal-derived liquids have been demonstrated, it is clear that the refining of coal-derived kerosene is onerous. Deep HDA is hydrogen intensive and ring-opening without dealkylation is a technical challenge. Some reports are quite upbeat about the beneficial properties of cycloalkane-rich materials for military jet fuel applications.[14] Although this is not disputed, Jet A-1 specifications are out of necessity international. It is unlikely that waivers for gravimetric energy density, aromatic content and fuel density can be obtained. There is consequently a distinct benefit in blending coal-drived kerosene with blending materials that are rich in branched alkanes, such as isoparaffinic kerosene. Whatever the blending strategy, coal-derived kerosene is only a jet fuel blending material and it will be difficult to produce an on-specification jet fuel just from coal-drived kerosene.

4.11 Diesel fuel refining from coal liquids

About two thirds of the coal liquid produced by the solvent extraction process is distillate in the 370 °C and lower boiling range (Table 4-1). The atmospheric gas oil fraction, 250-370 °C boiling range, was found to be very aromatic. The H:C ratio was in the range 0.7-0.9 (Table 4-2) and the amount of aromatic carbon increased from 83 wt% in the 250-300 °C fraction to 94 wt% in the 343-370 °C fraction (Table 4-6). Acenaphtene, phenanthracene, fluoranthene and pyrene were present in high concentration. The high content of di-, tri- and tetra-nuclear aromatics was also confirmed by HPLC analysis (Table 4-3). In fact, the aromatic content of the distillate obtained from solvent extraction of coal in this study was more aromatic than that from other solvent extraction processes.[10]

Deep hydrogenation of coal-derived liquids can produce a distillate that is suitable as diesel fuel. Heteroatom removal and HDA are both essential in order to do so. For example, various coal-derived distillates were hydrotreated over NiW/alumina and NiMo/silica-alumina catalysts at 400 °C, 1.5 MPa H_2 pressure and space velocity of 0.5-1.0 h^{-1} to yield distillates with <10 μg/g S, cetane number of around 42, density of 860 kg/m^3 and that contained less than 4 vol% aromatics.[28] Although such a diesel fuel would be acceptable in the North American market, it would not meet European EN590 diesel fuel specifications. The cetane number of 42 is too low (minimum 51 required) and the density of 860 kg/m^3 is too high (maximum 845 kg/m^3). Higher cetane numbers can be achieved by deep hydrogenation or hydrocracking,[13,15] or the addition of cetane number improvers as blending additives, but it does not reduce the density unless the cycloalkanes can be ring-opened. Hydrocracking of coal-derived distillate does not necessarily reduce the density sufficiently to meet European diesel fuel specifications. Increasing the hydrocracking severity is not always beneficial to the cetane number either.[29]

The analysis by Cookson et al.[30] of the property requirements for diesel fuel is insightful. It showed that in order to produce a diesel fuel that has a cetane number of 45 or higher and a cloud point of –4 °C or lower, the molecular compositions must fall within a very specific range: 0 to 58 vol% *n*-alkanes, 25 to 100 vol% branched and cyclic alkanes and 0 to 37 vol% aromatics. It should therefore be possible to produce a North American diesel fuel from coal liquids without resorting to blending with petroleum, as may be necessary in the case of jet fuel. Once density is added to the diesel fuel specification, as is the case for European diesel fuel, dilution with material having a lower density becomes necessary.

The challenge associated with the refining of coal distillate to diesel fuel is one of hydrogenation severity. Sullivan and Frumkin outlined the requirements very simply: it is possible to obtain a cetane number of 40 only if the aromatic content in the distillate can be reduced to 10-20 vol%.[14] For the European market, it would also be necessary to perform some ring-opening to reduce the density. Ring-opening may or may not yield a further increase in cetane number.[31] It should also be noted that cetane index calculations are poor predictors of the actual cetane number.[15]

If one compares these requirements with the properties of the distillate in this study, the calculated amount of hydrogen addition that is required is very high. Based on the ^{13}C NMR analysis (Table 4-6) about 6 wt% equivalent of the feed mass must be added as H_2 just in order to reduce the aromatic content to the level indicated by Sullivan and Frumkin;[14] even more H_2 is required if heteroatom removal is also considered. The hydrogen content of the distillate from solvent extraction of coal is low and any application that requires substantial HDA will be very costly. It may technically be possible to convert the coal distillate into a diesel fuel of acceptable quality, but considering the high H_2 requirements, it is not clear whether this is an economically attractive proposition. It may be preferable to blend coal derived distillate with petroleum distillate, or Fischer–Tropsch derived distillate, which in some aspects have the opposite challenge to meet European diesel fuel specifications.[32]

4.12 Chemicals from coal liquid refining

The aromatic content of the coal liquids that were investigated was very high. It was also reflected in the low H:C ratio of the liquids (Table 4-2). Any refining strategy that requires HDA to an appreciable extent, as was required for jet fuel and diesel fuel production, becomes costly in terms of H_2 consumption. The high content of specific aromatic compounds and the high aromatic content of the liquids in general, suggest that aromatic-based chemical production could be a better option than fuels refining.

Earlier, this type of value addition was evaluated.[33] It was found that some of the more abundant aromatic chemicals can be recovered by fractionation. However, some of the compounds, such as carbazole, which is also present in significant quantities (Figure 4-6), proved to be difficult to recover. The process design required a partial hydrogenation step to saturate close boiling aromatics and thereby facilitate the recovery and purification of carbazole.

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5 TEMPERATURE AND TIME EFFECTS ON COAL LIQUID YIELD AND QUALITY

Unlike crude oil, coal cannot be immediately refined into fuels. It has to be converted to synthetic crude. Direct liquefaction is one of the two methods employed in converting coal to synthetic crude. Synthetic crude from direct liquefaction of coal have been characterized with low H:C ratios, high nitrogen content and a high poly aromatic hydrocarbon (PAH) content. This is a reflection of the properties of coal from which the liquids are derived, since direct liquefaction of coal essentially involves breaking of weak ether linkages and hydro aromatic bridges.

Results from coal liquid characterization shows that coal liquids have high aromatic and fairly high polyaromatic content. A study of the molecular composition of different on-specification fuels (Jet and Diesel fuel) reveals that refining of coal-derived liquids (CDLs) must result in increasing the H/C ratio, and decreasing the aromatic content. To produce on-specification transportation fuel from CDL, the aromatic content has to be reduced to 37% for diesel fuel and 21% for jet fuel[1,2] A high PAH concentration is also not desired in an aromatic gasoline blend. Hydrogenation, therefore, becomes necessary if these liquids are to be transformed into transportation fuels. However, the severity of hydrogenation required to reduce increase H/C content and reduce aromatic content significantly increases as the degree of condensation in PAHs increase. Hydrogenation of a PAH becomes increasingly difficult beyond the first aromatic ring[3]. This has a negative impact on the economics of refining CDLs. Refining of coal-derived liquids, thus, becomes much easier when direct liquefaction of coal results in liquids with a low poly aromatic condensation.

As the reaction temperature increases beyond 350^{o}C, weak ether and aliphatic bridges are ruptured, forming free radicals[4]. These free radicals are very unstable and under suitable hydrogenation conditions, become stabilized to form smaller molecules. At even higher temperatures, rate of bond dissociation increases, and free radicals of smaller molecular size are expected to be formed. This should lead to increase in light products in the presence of sufficient hydrogenation conditions. It's been reported that mineral content of coal exhibit some catalytic properties[5]. On this premise, it is expected that coal-derived liquids produced should contain a higher content of light components as the severity of liquefaction is increased.

This research was carried out to study the influence of liquefaction conditions such as temperature and time on the aromatic class distribution of CDLs from a thermal digestion of a Canadian lignite. A lignite coal was chosen because coal-derived liquids have an increasing content of low molecular weight compounds as the rank of the parent coal decreases. This is reported to related to the lower ring-cluster sizes in the lower rank coals[4]. High Performance Liquid Chromatography (HPLC), which has been widely employed in the qualitative and quantitative study of petroleum[6,7] and coal liquids[8,9]**,** is employed in the study of coal liquids.

All experiments were performed at initial Hydrogen pressures of 4MPa. The reactor temperature versus time profile for a liquefaction run at 450°C and residence time of 30 minutes is shown in Figure 5-1. The liquefaction can be divided into approximately 120 minutes of heating up to the desired temperature, 30 minutes of residence time, and an additional 53 minutes of cooling, a total of about 213 minutes.

Figure 5-1: Temperature –Time Profile for Liquefaction at 450°C and for 30 minutes

5.1 Effects of Temperature and Residence time on Conversion

Coal conversion for all the runs are presented in Table 5-1**.** Conversion was determined using the formula:

$$\mathrm{C} = \frac{[\mathrm{M}_{\text{feed coal}} - (\mathrm{M}_{\text{feed coal}} * \text{Moisture}) - (\mathrm{M}_{\text{feed coal}} * \text{Ash})] - [\mathrm{M}_{\text{coal res}} - (\mathrm{M}_{\text{coal res}} * \text{Ash}_{\text{res}})]}{\mathrm{M}_{\text{feed coal}} - (\mathrm{M}_{\text{feed coal}} * \text{Moisture}) - (\mathrm{M}_{\text{feed coal}} * \text{Ash})} * 100\%$$

Where:

C: percentage conversion

$\mathrm{M}_{\text{feed coal}}$: is the mass of feed coal

Moisture: fraction of moisture in feed coal

Ash: is the fraction of ash in feed coal

$\mathrm{M}_{\text{coal res}}$: is the mass of the coal residue

Ash_{res}: is the fraction of ash in the coal residue.

Table 5-1: Coal Conversion on DAF (Dry Ash Free) Coal

Experiment Number #	Gas Atmosphere	Hold Time mins	T (°C)	Feed Coal (g)	Coal Residue (g)	Ash in Coal Residue (wt%)	Coal Conversion (wt ~~%~~)
1	H_2	0	350	50.01	43.61	16.41	9.1
2	H_2	0	350	50.15	43.09	16.71	10.52
3	H_2	0	383	50.03	27.24	26.28	49.92
4	H_2	0	400	50.01	23.17	30.61	59.91
5	H_2	0	415	50.09	13.76	52.1	83.56
6	H_2	0	415	49.98	15.18	47.56	80.14
7	H_2	0	415	50.11	16.01	44.88	78.01
8	H_2	0	415	50.04	15.79	45.67	78.61
9	H_2	0	450	50.02	11.14	63.39	89.83
10	H_2	15	350	50.12	40.71	19.42	16.18
11	H_2	15	400	49.95	21.09	33.74	65.18
12	H_2	15	450	50.32	10.71	65.87	90.89
13	H_2	30	350	50.04	33.88	21.08	33.31
14	H_2	30	450	50.09	10.16	70.45	92.51
15	N_2	30	350	50.02	34.68	20.76	31.46

Moisture and ash content of feed coal are 5.2 and 14.6 wt% respectively as shown in Table 3-2. An example calculation of coal conversion for experiment number 6 is shown below:

$$\mathrm{C} = \frac{[49.98 - (49.98 * 0.052) - (49.98 * 0.146)] - [15.18 - (15.18 * 0.4756)]}{49.98 - (49.98 * 0.052) - (49.98 * 0.146)} * 100\%$$

$$\mathrm{C} = \frac{40.08 - 7.96}{40.08} * 100\%$$

$$\mathrm{C} = \frac{32.12}{40.08} * 100\% = 80.14\%$$

5.1.1 Effect of temperature on conversion

Weak ether and aliphatic bridges are ruptured as the reaction temperature approaches 350 °C, thus forming free radicals. Other bonds get dissociated as the temperature increases beyond 350 °C[10] . This leads to higher carbon conversion. As the liquefaction temperature was increased from 350 to 450°C at a residence time of 0 minutes, an expected increase in conversion was observed (Table 5-2). At a residence time of 15 (Table 5-3) and 30 (Table 5-4) minutes similar increase in conversion was observed at temperature increased from 350, 400 to 450°C, and from 350 to 450°C respectively.

Table 5-2: Effect of Temperature on Conversion at Residence time of 0 minutes

Experiment Number	Gas	Hold Time	T	Feed Coal	Coal Residue	Ash in Coal Residue	Coal Conversion
#	Atmosphere	mins	(°C)	(g)	(g)	(wt%)	(wt ~~%~~)
1	H_2	0	350	50.01	43.61	16.41	9.1
2	H_2	0	350	50.15	43.09	16.71	10.52
3	H_2	0	383	50.03	27.24	26.28	49.92
4	H_2	0	400	50.01	23.17	30.61	59.91
5	H_2	0	415	50.09	13.76	52.1	83.56
6	H_2	0	415	49.98	15.18	47.56	80.15
7	H_2	0	415	50.11	16.01	44.88	78.01
8	H_2	0	415	50.04	15.79	45.67	78.61
9	H_2	0	450	50.02	11.14	63.39	89.83

Table 5-3: Effect of Temperature on Conversion at Residence time of 15 minutes

Experiment Number	Gas	Hold Time	T	Feed Coal	Coal Residue	Ash in Coal	Coal Conversion
#	Atmosphere	mins	(°C)	(g)	(g)	Residue (wt%)	(wt %)
10	H_2	15	350	50.12	40.71	19.42	16.18
11	H_2	15	400	49.95	21.09	33.74	65.18
12	H_2	15	450	50.32	10.71	65.87	90.89

Table 5-4: Effect of Temperature on Conversion at Residence time of 30 minutes

Experiment Number	Gas	Hold Time	T	Feed Coal	Coal Residue	Ash in Coal	Coal Conversion
#	Atmosphere	mins	(°C)	(g)	(g)	Residue (wt%)	(wt %)
13	H_2	30	350	50.04	33.88	21.08	33.31
14	H_2	30	450	50.09	10.16	70.45	92.51
15	N_2	30	350	50.02	34.68	20.76	31.46

5.1.2 Effect of residence time on conversion

Conversion of coal during liquefaction was observed at 350 and 450°C as the residence time was increased from 0 minutes to 15 minutes and then to 30 minutes, as a shown in Table 5-5 and Table 5-6 respectively. At 350°C, there was a 55.6% increase in conversion as the residence time increased from 0 to 15 minutes and a 106% increase in conversion as the residence time was increased from 15 minutes to 30 minutes. However, at 450°C, an increase in conversion of 1.2% and 1.8% was observed as the residence time increased from 0 to 15 minutes and from 15 to 30 minutes respectively. This indicates that most of the conversion occurred during the desired heating time.

Table 5-5: Effect of Time on Conversion at Temperature of 350°C

Experiment Number #	Gas Atmosphere	Hold Time mins	T (°C)	Feed Coal (g)	Coal Residue (g)	Ash in Coal Residue (wt%)	Coal Conversion (wt %)
1	H_2	0	350	50.01	43.61	16.41	9.1
2	H_2	0	350	50.15	43.09	16.71	10.52
10	H_2	15	350	50.12	40.71	19.42	16.18
13	H_2	30	350	50.04	33.88	21.08	33.31
15	N_2	30	350	50.02	34.68	20.76	31.46

Table 5-6: Effect of Time on Conversion at Temperature of 450°C

Experiment Number #	Gas Atmosphere	Hold Time mins	T (°C)	Feed Coal (g)	Coal Residue (g)	Ash in Coal Residue (wt%)	Coal Conversion (wt %)
9	H_2	0	450	50.02	11.14	63.39	89.83
12	H_2	15	450	50.32	10.71	65.87	90.89
14	H_2	30	450	50.09	10.16	70.45	92.51

5.1.3 Liquid yield versus conversion

A high carbon conversion is not necessarily desirable for transportation fuel production. A high liquid yield is more desired. Due to limitations associated with the experimental set-up, liquid yield determination was successful with only three set of experiments. These are shown in Table 5-7. There were two methods through which material balance closure could be accomplished.

Firstly, yield was determined through direct measurement of reactor and its content before and after the experiment. Measurement of the reactor and its' content at the completion of the experiment has to be done as quickly as possible after the reactor is removed from the autoclave, to prevent cooling. When the reactor cools down, removal of the liquid products becomes more difficult. Measurement of the reactor and its contents required a measuring balance with the capacity to measure weights of over 8 kg. Access to such measuring balance was limited to three experimental runs. Liquid products which got stuck on the reactor impeller could not be measured and this is a source of error in the material balance.

The second method involved measuring the liquid products after the washing solvent (THF) had been completely recovered by the rotary evaporator. However, a complete THF recovery could not be accomplished. Some THF got vaporised while the reactor and its impeller were washed at 100°C, although, the vaporization of other components of coal liquid was not confirmed. Some THF vapor also escaped during the solvent recovery. As a result, the amount of unrecovered THF from the coal liquid could not be determined, which inhibits a material balance closure.

Table 5-7: Liquid Yield

Exp	Gas	Hold Time	T	Feed Coal	Solvent (g)	Coal Residue	Coal Conversion	Mass of Reactor[a] and Products	Total Liquid Produced	Liquid Yield (%)	Gas produced[b]
#		mins	(°C)	(g)		(g)	(wt %)	(g)	Total Products - Residue		excluding H_2(g)
1	H_2	0	350	50.01	105	43.61	9.1	-	-	-	-
2	H_2	0	350	50.15	105	43.09	10.52	-	-	-	-
3	H_2	0	383	50.03	105	27.24	49.92	-	-	-	-
4	H_2	0	400	50.01	105	23.17	59.91	-	-	-	-
5	H_2	0	415	50.09	105	13.76	83.56	-	-	-	-
6	H_2	0	415	49.98	105	15.18	80.15	-	-	-	-
7	H_2	0	415	50.11	105	16.01	78.01	-	-	-	-
8	H_2	0	415	50.04	105	15.79	78.61	-	-	-	-
9	H_2	0	450	50.02	105	11.14	89.83	-	-	-	-
10	H_2	15	350	50.12	105	40.71	16.18	-	-	-	-
11	H_2	15	400	49.95	105	21.09	65.18	6868.4	127.0	45.6	6.9
12	H_2	15	450	50.32	105	10.71	90.89	6858.9	127.9	45.6	16.7
13	H_2	30	350	50.04	105	33.88	33.31	-	-	-	-
14	H_2	30	450	50.09	105	10.16	92.51	6856.0	125.5	41.7	19.4
15	N_2	30	350	50.02	105	34.68	31.46	-	-	-	-

[a] Mass of empty reactor = 6720.3 g

[b] Mass of gas produced = feed coal + solvent – coal liquid – coal residue

As shown above, a high carbon conversion does not always imply a high liquid yield. Liquid yield at 450°C and residence time of 30 minutes was markedly lower than at 400°C and 15 minutes though there was a higher conversion recorded. An increase in gas production accounts for this. From a standpoint of liquid production, it is undesirable to perform liquefaction at 450°C and for 30 minutes. However, liquid yield at 450°C and 15 minutes equals that at 400°C and 15 minutes. With a higher conversion recorded, there must have been a higher production of gaseous product at 450°C than at 400°C. Since the interest is in liquids, it is therefore more economically to operate at 400°C.

However, this research is focused more on the quality of liquid products than on the quantity. As such, the quality of liquids produced was assessed by different analytical techniques.

5.2 Effects of Temperature and Residence Time on Coal Liquid Quality

5.2.1 Appearance of coal liquid at 10 wt% concentration

Figure 5-2 shows the appearance of a 10 w % concentration of coal liquids at 350, 400, 415, 450 °C and at a residence time of 0 minutes.

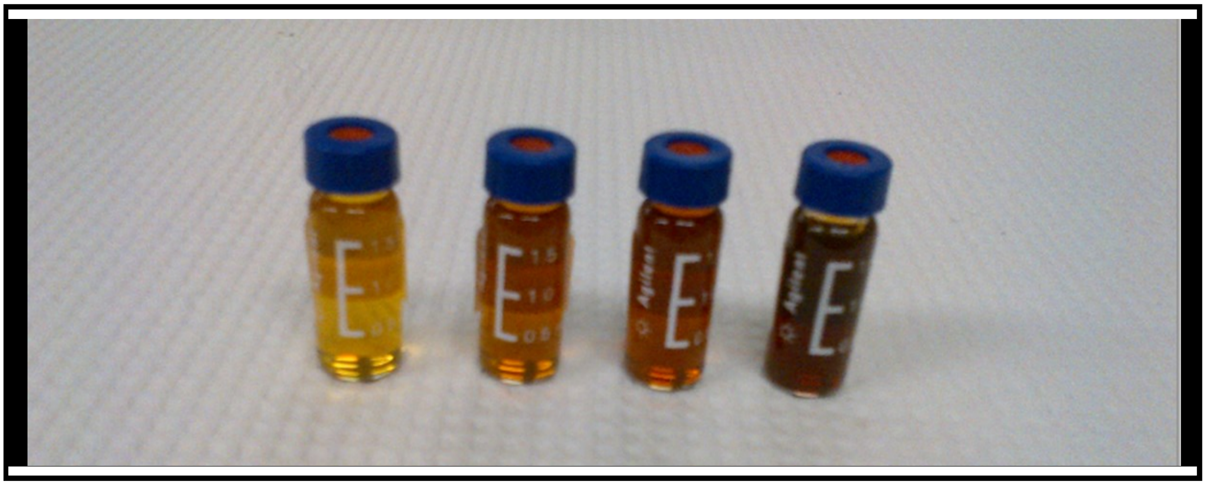

Figure 5-2: From left to right: Coal Liquids derived at temperatures of 350, 400, 415, 450 °C and at residence time of 0 minutes

The dark coloration of the liquids obtained at higher temperatures indicates that they are heavier than those obtained at lower temperatures. This is in contrast to expected results. It's been reported that mineral content of coal exhibit some catalytic properties[5]. On this premise, it is expected that coal-derived liquids produced should contain a higher content of light components as the severity of liquefaction is increased. This observation was further investigated by determining the micro carbon residue (MCR) content by thermogravimetric anaylysis (TGA).

5.2.2 MCR Content

Coal liquids with high content of small sized molecules is expected to have a lower MCR content than coal liquids with lower contents of small molecular compounds. Determination of MCR content can therefore provide an indication on how lighter or heavier coal liquids become when liquefaction temperature and residence time are changed. MCR data are presented in table XXX. Results documented in Table 5-9 show that the micro carbon residue (MCR) content of the coal liquids (containing about 10wt% THF) increased from 1.6 wt% at 350 °C to 6.74 wt% at 415 °C when the hold time was 0 minutes. No significant increase in MCR was observed as the reaction temperature was increased to 450 °C, when the hold time was 0 minutes.

Table 5-8: MCR for Coal Liquids (containing about 10 wt% THF)

Exp Number/ #	Temperature/ °C	Hold time/ minutes	Gas Atmosphere	MCR Wt%
1	350	0	H_2	-
2	350	0	H_2	1.58
3	383	0	H_2	-
4	400	0	H_2	4.55
5	415	0	H_2	-
6	415	0	H_2	6.73
7	415	0	H_2	-
8	415	0	H_2	-
9	450	0	H_2	6.70
10	350	15	H_2	-
11	400	15	H_2	6.33
12	450	15	H_2	8.44
13	350	30	H_2	-
14	450	30	H_2	-
15	350	30	N_2	-

-not analysed

Table 5-9: Effect of Temperature on MCR of Coal Liquids at Residence time of 0 minutes

Exp Number/ #	Temperature/ °C	Hold time/ minutes	Gas Atmosphere	MCR Wt%
2	350	0	H_2	1.58
4	400	0	H_2	4.55
6	415	0	H_2	6.73
9	450	0	H_2	6.70

When the residence time was increased from 0 minutes to 15 minutes (Table 5-10), there was an observed increase in the MCR content from 4.55 wt% to 6.33 wt% at 400 °C and from 6.7 wt% to 8.44 wt% at 450 °C. MCR content further increased to 17.9 wt% when the hold time was increased to 30 minutes at 450 °C.

Table 5-10: Effect of Residence Time on MCR of Coal Liquids

Exp Number/ #	Temperature/ °C	Hold time/ minutes	Gas Atmosphere	MCR Wt%
4	400	0	H_2	4.55
11	400	15	H_2	6.33
9	450	0	H_2	6.70
12	450	15	H_2	8.44

These results indicate that there is an increase in concentration of heavier molecules in the liquids as the reaction temperature and residence time was increased. To establish this observation, semi-quantitative analysis of coal-derived liquids was carried out with the HPLC.

5.2.3 Composition of Aromatic Hydrocarbons

The HPLC was employed in the analysis of the aromatic hydrocarbon fraction of coal liquids. The polar content was not analysed. The different compound classes were first identified, and then quantified.

5.2.3.1 Qualitative HPLC

Identification of compounds in coal liquid derived at 450°C and 0 minutes is shown in Figure 5-3.

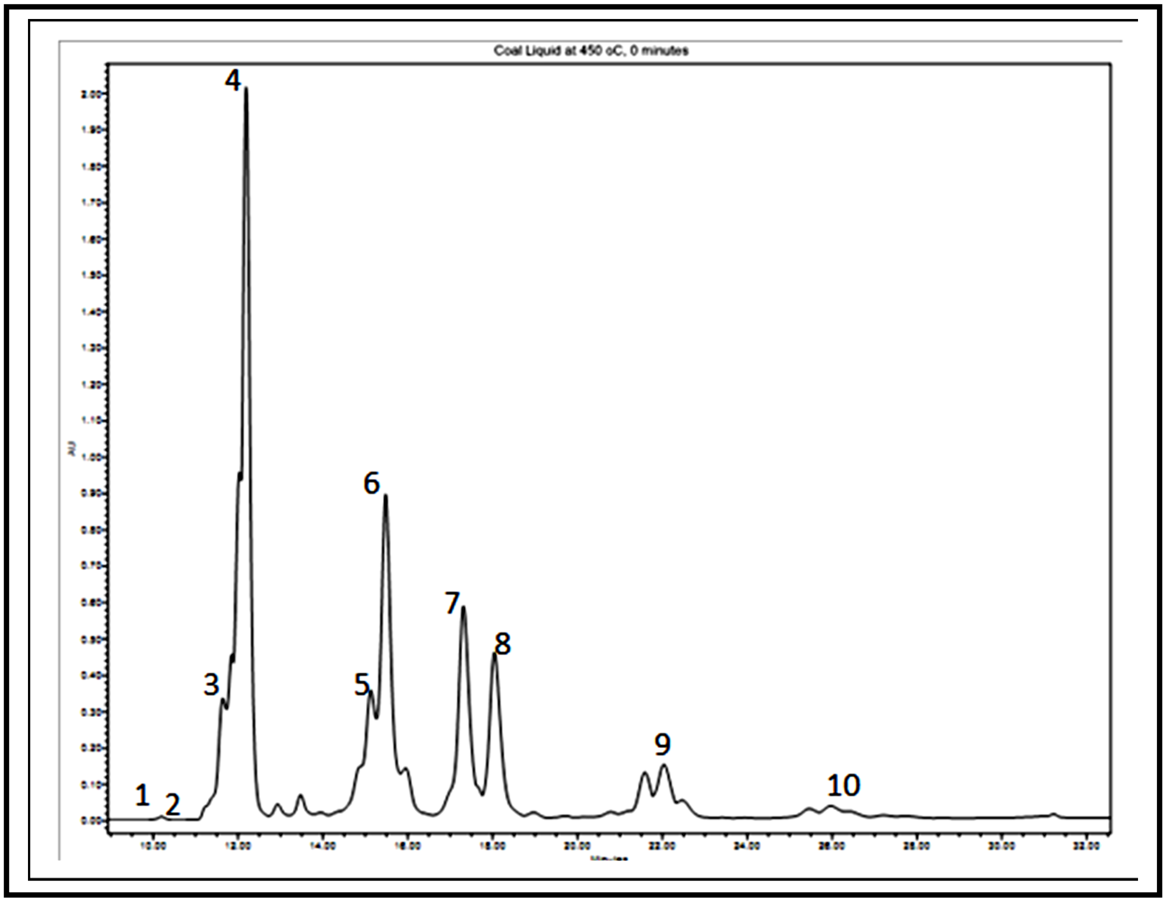

Figure 5-3: Maxiplot of coal-derived liquid at of 450 °C and 0 minutes
1 =1,3,5-Trimethylbenzene 2 = o-xylene, Toluene, 3 = methylnaphthalene, 4= naphthalene, 5 = Anthracene, 6 = Phenanthrene, 7 = Pyrene, 8 = Fluoranthene, 9 = Chrysene, 10 = Benzo[a]pyrene

Compounds that were identified in all coal liquids include: toluene, methylnaphthalene, naphthalene, anthracene, phenanthrene, pyrene, fluoranthene, chrysene and benzo[a]pyrene. Compounds that were not identified were assigned to compound classes using their retention times.

Figure 5-4 to Figure 5-7 shows the HPLC chromatograms of coal liquids obtained at temperatures of 350, 400, 415, 450°C and at the same residence time of 0 minute.

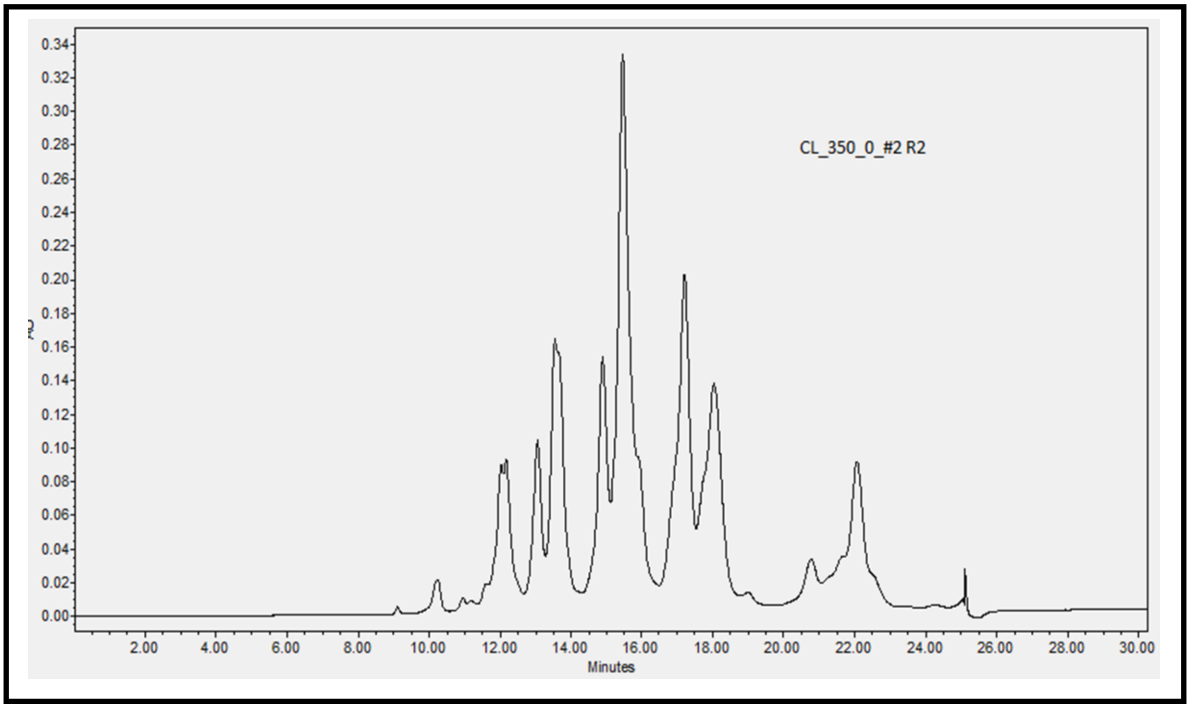

Figure 5-4: HPLC Chromatogram at wavelength of 254nm of Coal Liquid derived at temperature of 350 °C and at residence time of 0 minutes

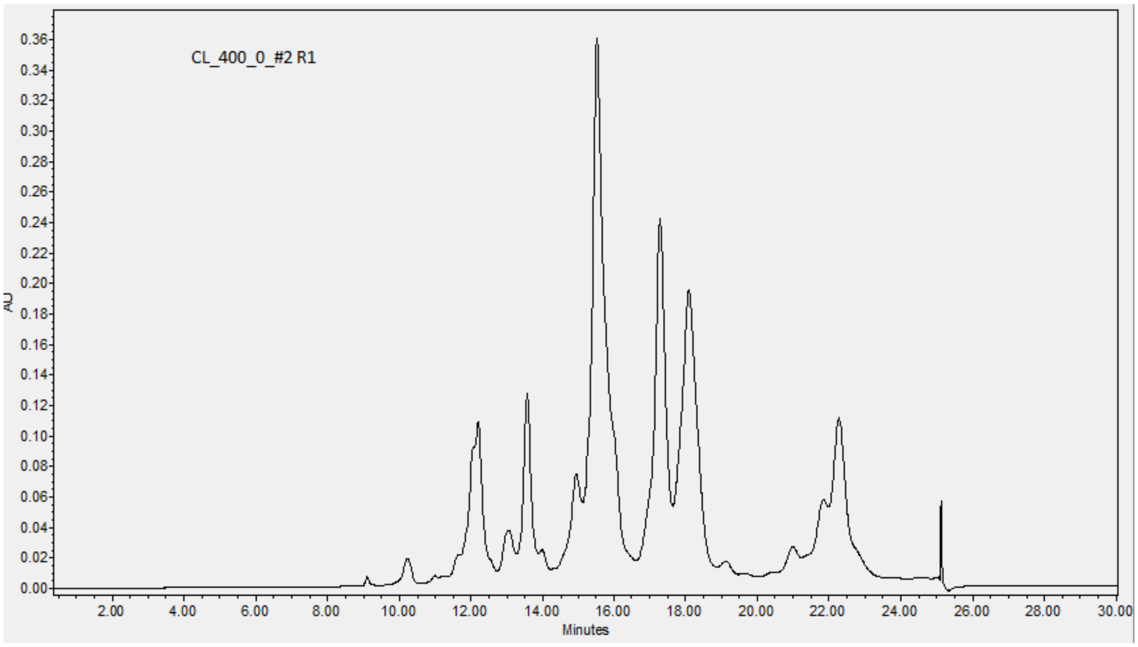

Figure 5-5: HPLC Chromatogram at wavelength of 254nm of Coal Liquid derived at temperature of 400 °C and at residence time of 0 minutes

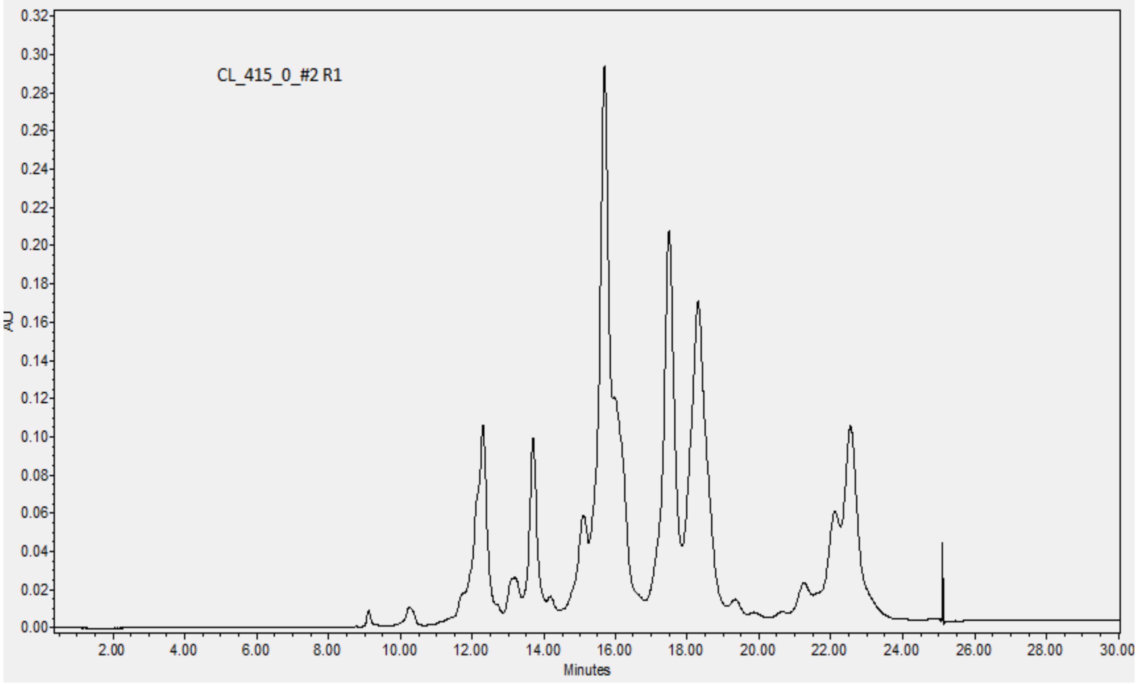

Figure 5-6: HPLC Chromatogram at wavelength of 254nm of Coal Liquid derived at temperature of 415 °C and at residence time of 0 minutes

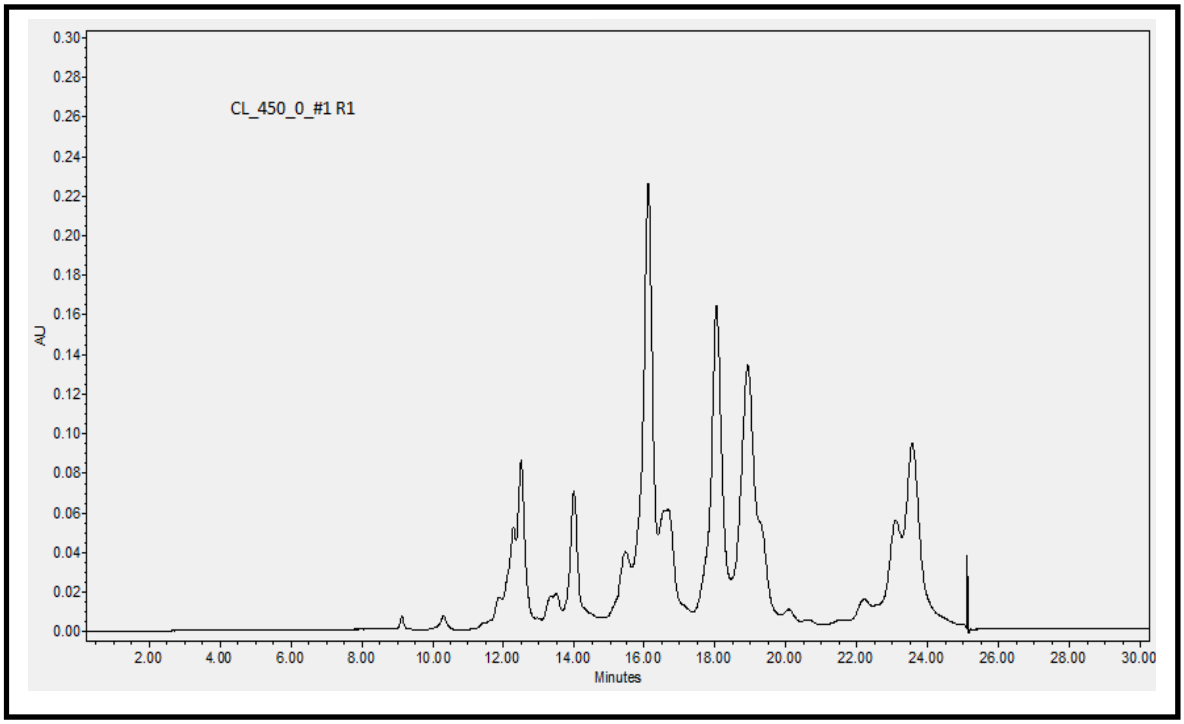

Figure 5-7: HPLC Chromatogram at wavelength of 254nm of Coal Liquid derived at temperature of 450 °C and at residence time of 0 minutes

By taking a careful look at the chromatograms, the following observations were made:

1. The peak that eluted at 10.5 minutes continually decreased as the liquefaction temperature increased
2. The two tall peaks that eluted between 13 and 14 minutes at 350°C were replaced with a group of three peaks at 400 and 415°C and which were reduced to two small peaks at 450°C
3. The peak that eluted at about 15 minutes reduced in height as temperature increased from 350 to 450°C
4. At 450°C, there is a new peak that eluted at 17 minutes which was absent in other chromatograms and
5. There was a gradual development of the peak at 22 minutes as the temperature increased.

These observations all drive at an increase in heavier components as liquefaction temperature increased.

To assert this observation, semi-quantitative HPLC analysis was performed. The total aromatic carbon content of some of the coal liquids was determined by ^{13}C NMR, as presented in Table 5-11.

Table 5-11: Aromatic Carbon Content of Coal liquids

Exp Number	Temperature/ °C	Hold time/ minutes	Gas Atmosphere	Aromatic Carbon[a] wt%
1	350	0	H_2	-
2	350	0	H_2	-
3	383	0	H_2	-
4	400	0	H_2	-
5	415	0	H_2	-
6	415	0	H_2	-
7	415	0	H_2	-
8	415	0	H_2	-
9	450	0	H_2	-
10	350	15	H_2	78.5
11	400	15	H_2	84.7
12	450	15	H_2	88.2
13	350	30	H_2	79.3
14	450	30	H_2	88.7
15	350	30	N_2	82.4

-not analysed; [a] from ^{13}C NMR

5.2.3.2 *Effect of liquefaction temperature on composition of aromatic hydrocarbons at a residence time of 0 minutes*

Table 5-12 shows the composition by weight of aromatic hydrocarbons at different temperatures and at the same residence time of 0 minute. This is also represented in Figure 5-8. There is an observed decrease in the mono-aromatic content as the liquefaction temperature increased from 350 to 450°C, with a rapid decrease occurring between 350 and 383°C. A less pronounced decrease is observed in the di-aromatic content. There was very little variation on the content of higher PAH, However, the PAH content of coal liquids at 350°C is lower than those at higher temperatures. This is also in contrast to the expected result. The rapid change in aromatic hydrocarbon composition of coal liquid as the liquefaction temperature is increased above 350°C indicates the onset of chemical reactions (bond dissociation). There are two regimes in coal liquefaction, namely: the low temperature and the high temperature regimes. The low temperature regimes include all temperatures below 350°C, while the high temperature regime includes all temperatures above 350°C.[11] This is consistent with the results.

There is also a gradual decrease in the total aromatic hydrocarbon content. This could because more aromatic hydrocarbons are converted to gaseous products at higher temperatures. The rather unusual dip in the observed at 415°C is as a result of a higher percentage of unrecovered THF in the liquid.

Table 5-12: Effect of liquefaction temperature on composition of aromatic compounds at a residence time of 0 minutes

Exp #	Gas Atmoshphere	Hold Time mins	T °C	Mono (wt %)	Di (wt %)	Tri (wt %)	Tetra (wt %)	Penta (wt %)	Hexa (wt %)	Total (wt %)
1	H_2	0	350	-	-	-	-	-	-	-
2	H_2	0	350	24.45	13.32	5.78	8.19	1.28	0.08	53.1
3	H_2	0	383	16.83	10.45	6.73	11.12	1.71	0.17	47
4	H_2	0	400	14.93	9.5	6.82	12.973	2	0.2	46.2
6	H_2	0	415	11.5	8.64	6.16	11.51	1.8	0.17	39.8
9	H_2	0	450	12	10.26	7.66	13.21	2.13	0.16	45.4

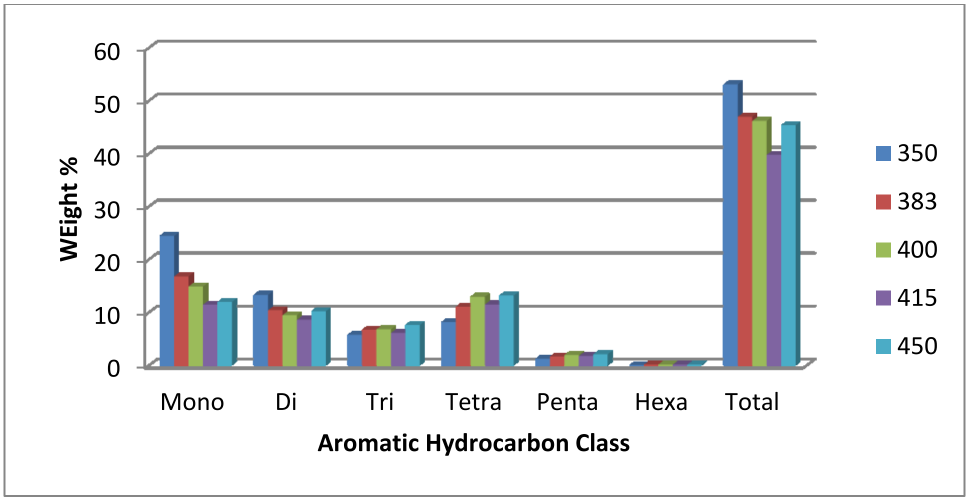

Figure 5-8: Effect of liquefaction temperature on composition of aromatic compounds at a residence time of 0 minutes

5.2.3.3 Effect of liquefaction temperature on composition of aromatic compounds at a residence time of 15 minutes

Composition of aromatic hydrocarbons of liquids obtained at a residence time of 15 minutes showed a similar trend, as shown in Table 5-13. A 50 weight percent decrease was also observed in the mono-aromatic content as liquefaction temperature increased from 350 to 400 and 450°C. The total aromatic content also decreased from 350 to 450°C. This indicates that the liquids obtained at 350°C both has higher percentage of light product as well as lower content of heteroatom containing compounds than liquids obtained at 400 and 450°C.

Table 5-13: Effect of liquefaction temperature on composition of aromatic compounds at a residence time of 15 minutes

Exp	Gas Atmoshphere	Hold Time	T	Mono	Di	Tri	Tetra	Penta	Hexa	Total	C_{ar}[a]
#		mins	°C	(wt %)	(wt %)	(wt %)	(wt %)	(wt %)	(wt %)	(wt %)	Wt%
10	H_2	15	350	25.6	12.78	6.68	12	1.75	0.25	59.1	78.5
11	H_2	15	400	12.84	5.86	4.28	7.58	1.15	0.13	31.8	84.7
12	H_2	15	450	12.94	13.91	8.51	14.22	2.33	0.17	52.1	88.2

[a] Aromatic Carbon from ^{13}C NMR

5.2.3.4 Effect of liquefaction temperature on composition of aromatic compounds at a residence time of 30 minutes

Table 5-14 shows the composition of coal liquids obtained at 350 and 450°C and at residence time of 30 minutes. Similarly, there was about 50 weight percent decrease in the mono-aromatic content as the liquefaction temperature from 350 to 450°C. A less pronounced decrease was observed in other aromatic hydrocarbon classes. There was also a decrease in the total aromatic hydrocarbon.

Table 5-14: Effect of liquefaction temperature on composition of aromatic compounds at a residence time of 30 minutes

Exp	Gas Atmoshphere	Hold Time	T	Mono	Di	Tri	Tetra	Penta	Hexa	Total	C_{ar}[a]
#			°C	(wt %)	(wt %)	(wt %)	(wt %)	(wt %)	(wt %)	(wt %)	Wt%
13	H_2	30	350	25.47	11.04	6.72	12.6	1.89	0.3	58	79.3
14	H_2	30	450	14.805	14.29	8.34	13.88	2.25	0.17	53.7	88.7

[a] Aromatic Carbon from ^{13}C NMR

These observations are consistent at residence times of 0, 15, and 30 minutes.

5.2.3.5 Effect of residence time on composition of aromatic compounds at temperatures of 350 and 450°C

At both 350 and 450°C, there was little change in the composition of aromatic hydrocarbon classes as the residence time increased from 0 to 15 to 30 minutes, as shown in Table 5-15 and Table 5-16. Mono-aromatic content remained approximately the same at 350°C and residence time 0, 15 and 30 minutes, whilst the di-aromatic content saw a gradual decrease. The tetra-aromatic content increased by 46.5 weight percent from a residence time of 0 to 15 minutes. The magnitude of the increase reduced to 5 weight percent as the residence time increased further to 30 minutes. The rather large increase in the tetra-aromatic content accounts for 63.5 weight percent increase in the total aromatics from 0 minutes to 15 minutes. There is almost no increase in total aromatics as the residence time increased from 15 minutes to 30 minutes.

Table 5-15: Effect of liquefaction residence time on composition of aromatic compounds temperature of 350 °C

Exp \#	Gas Atmoshphere	Hold Time	T °C	Mono (wt %)	Di (wt %)	Tri (wt %)	Tetra (wt %)	Penta (wt %)	Hexa (wt %)	Total (wt %)	C_{ar} Wt%
2	H_2	0	350	24.45	13.32	5.78	8.19	1.28	0.08	53.1	-
10	H_2	15	350	25.6	12.78	6.68	12	1.75	0.25	59.1	78.5
13	H_2	30	350	25.47	11.04	6.72	12.6	1.89	0.3	58	79.2

Table 5-16: Effect of liquefaction residence time on composition of aromatic compounds temperature of 450 °C

Exp \#	Gas Atmoshphere	Hold Time	T °C	Mono (wt %)	Di (wt %)	Tri (wt %)	Tetra (wt %)	Penta (wt %)	Hexa (wt %)	Total (wt %)	C_{ar} Wt%
9	H_2	0	450	12	10.26	7.66	13.21	2.13	0.16	45.4	-
12	H_2	15	450	12.94	13.91	8.51	14.22	2.33	0.17	52.1	88.2
14	H_2	30	450	14.805	14.29	8.34	13.88	2.25	0.17	53.7	87.6

At 450°C, there is a surprising increase in mono and di-aromatic content as the residence increased from 0 minutes to 15 minutes and from 15 minutes to 30 minutes. No trend was observed in other aromatic hydrocarbon class. The total aromatics increased by 16 weight percent at the residence time increased from 0 to 15 minutes and by only 3 weight percent as the residence time increased from 15 minutes to 30 minutes.

5.2.3.6 Effects of gas atmosphere on composition of aromatic hydrocarbons

It was anticipated that coal liquids produced at higher liquefaction temperatures would have higher content of light products given that more bond cleavages occur. This is, however, on a condition that most free radicals generated are hydrogenated to produce stable products. Results obtained thus far indicate that there was little or no hydrogenation of free radicals. This was investigated further by conducting liquefaction under nitrogen atmosphere. The results are presented in Table 5-17.

Table 5-17: Effect of gas atmosphere on composition of aromatic compounds temperature of 350 °C

Exp #	Gas Atmoshphere	Hold Time	T °C	Mono (wt %)	Di (wt %)	Tri (wt %)	Tetra (wt %)	Penta (wt %)	Hexa (wt %)	Total (wt %)	C_{ar} Wt%
13	H_2	30	350	25.47	11.04	6.72	12.6	1.89	0.3	58	79.2
15	N_2	30	350	27.51	10.24	7.4	14.34	2.03	0.2	61.73	82.4

There is little disparity seen in the composition of coal liquid obtained under hydrogen atmosphere compared to that obtained under nitrogen atmosphere. The mono-aromatic content as well as the total aromatic content is slightly higher under nitrogen atmosphere than under hydrogen atmosphere. Coal liquid obtained under nitrogen contained more aromatic carbon than coal liquid obtained under hydrogen atmosphere.

H/C ratio of coal liquid derived under hydrogen is slightly higher than those derived under nitrogen (Table 5-18). There is also observed a higher N/C ratio in coal liquid obtained under nitrogen than that obtained under hydrogen. It can be argued that not much bond dissociation occurs at 350°C. And as such, the gas atmosphere should have little effect on the composition of the liquid product. Liquefaction could not be performed at higher temperatures under nitrogen due to problems with the autoclave reactor. Howbeit, the results obtained at 350°C under nitrogen atmosphere suggest that little hydrogenation occurs under hydrogen atmosphere.

5.2.4 ^{13}C NMR analyses

^{13}C NMR results reveals an increase in the aromatic carbon content of coal liquids as the temperature of liquefaction increased from 350 to 400°C and from 400 to 450°C at a residence time of 15 minutes (Table 5-13). An increase in aromatic carbon content was also observed at residence time of 30 minutes (Table 5-14) when the liquefaction temperature was increased from 350 to 450°C. Coal liquids became more aromatic as the liquefaction temperature increased.

There was, however, no appreciable change in the aromaticity of coal liquids when the residence time increased from 0 minutes to 15 minutes and 30 minutes both at 350 (Table 5-15) and 450°C (Table 5-16).

5.2.5 Elemental Composition

The elemental composition of coal liquids were determined to observe the effect of temperature and residence time on the hydrogen content as well as the heteroatom content. The analysis provided information on the hydrogen and nitrogen content. Sulfur contents were generally about or below 0.1 weight percent and could not be accurately analysed because the detection limit of sulfur was 0.1 weight percent. The results are presented in Table 5-18.

Table 5-18: Elemental Composition of Coal liquids

Exp #	Gas Atmosphere	Hold Time /mins	Temperature (°C)	N (wt %)	C (wt %)	H (wt %)	H/C	N/C
1	H_2	0	350	-	-	-	-	-
2	H_2	0	350	-	-	-	-	-
3	H_2	0	383	0.75	92.12	6.5	0.85	0.007
4	H_2	0	400	-	-	-	-	-
5	H_2	0	415	-	-	-	-	-
6	H_2	0	415	-	-	-	-	-
7	H_2	0	415	-	-	-	-	-
8	H_2	0	415	-	-	-	-	-
9	H_2	0	450	-	-	-	-	-
10	H_2	15	350	0.67	92.23	6.8	0.89	0.006
11	H_2	15	400	0.81	92.21	6.46	0.84	0.008
12	H_2	15	450	0.83	90.6	5.98	0.79	0.008
13	H_2	30	350	0.64	90	6.58	0.88	0.006
14	H_2	30	450	0.82	91.58	5.91	0.77	0.008
15	N_2	30	350	0.7	90.1	6.51	0.87	0.007

-not analysed, all sulfur content were less than 0.1%

5.2.5.1 Hydrogen Content

Effect of Temperature

There is a continuous decrease in the H/C ratio of coal liquids as the temperature of liquefaction increased from 350 to 450°C. At a residence time of 15 minutes, the H/C ratio was 0.89, 0.84 and 0.79 for temperatures of 350, 400 and 450°C respectively. At a residence time of 30 minutes, H/C ratio decreased from 0.88 to 0.77 as the temperature increased from 350 to 450°C. This is consistent with the increase in aromatic carbon content observed as liquefaction temperature increased from 350 to 450°C.

Effect of Residence time

At temperatures of 350 and 450°C, the H/C ratio was about the same as the residence time increased from 15 to 30 minutes. However, there appeared to be a consistent but very slight decrease in the H/C ratios when the residence time increased from 15 to 30 minutes at both 350 and 450°C. A corresponding trend would have been expected in the aromatic carbon content. However, this is not the case.

5.2.5.2 Nitrogen content

Effect of temperature

Unlike the trend observed in the hydrogen content, nitrogen content increased as the liquefaction temperature increased from 350 through to 450°C. At a residence time of 15 minutes, N/C ratio increased from 0.006 to 0.0075 and 0.0079 when liquefaction was performed at 350, 400 and 450°C respectively. At a residence time of 30 minutes, the N/C also increased from 0,006 to 0.008 when liquefaction was performed at 350 and 450°C respectively. This corroborates the decrease in total aromatic content observed as liquefaction temperature increased.

Effect of residence time

There was no change in the nitrogen content as the residence time was increased from 15 to 30 minutes both at 350 and 450°C. The N/C remained 0.006 and 0.008 at 350 and 450°C respectively.

5.3 Effects of Liquefaction Conditions on Coal liquid Quality

The purpose of this study is to arrive at suitable conditions of liquefaction that will produce easy-to-refine liquids.

From the results, coal liquids obtained at 350°C have shown to be the easiest to refine. They have highest H/C ratios, highest mono-aromatic content (light products), and lowest N/C ratios. They require the least amount of hydrogenation and hydrodenitrogenation (HDN).

However, liquefaction at 350°C produced the lowest yield of liquid product. At 350°C, the highest conversion, which in this case will translate to highest liquid yield, occurred at residence time of 30 minutes. This is, however, still very low.

Since liquefaction at 350°C produces relatively easy-to-refine liquids, it might be a good proposition to carry out liquefaction in two stages. A thermal digestion at 350°C under an inert atmosphere can be done in the first stage to give a low yield but high quality liquid. A second stage involving high temperatures and the use of catalyst under hydrogenating conditions can then be performed to increase liquid yield. The use of catalyst under hydrogenating conditions should enhance stabilization of free radicals, and thus producing lighter products at high temperatures.

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6 CONCLUSION

6.1 Characterization of Coal Liquids

Excerpted from "Adesanwo, T.; Rahman, M.; Gupta, R.; de Klerk, A. Characterization and Refining Pathways of Straight-Run Heavy Naphtha and Distillate from the Solvent Extraction of Lignite. Energy & Fuels 2014, 28 (7), 4486-4495"

The heavy naphtha and distillate fraction from the solvent extraction of Bienfait lignite at 415 °C was characterized by various analytical techniques. The coal liquid characterization data was employed to suggest refining pathways for the different coal liquid distillation fractions in the boiling range 120-370 °C. The following specific observations were made:

(a) The coal liquids were very aromatic, with an aromatic carbon content ranging from 80 to 94 wt%.

(b) Hydrocarbons dominated the composition of the coal liquids. The major compounds in the coal liquids were acenaphtene, phenanthracene, fluoranthene and pyrene, which constituted 62 wt% of the combined coal liquid in the 120-370 °C boiling range. Alkyl aromatics were less abundant than aromatics without alkyl substituents.

(c) The coal liquids also contained heteroatom species, with dibenzofuran and carbazole being a major constituent of the 250-300 and 300-343 °C boiling fractions respectively.

(d) The nitrogen content did not monotonically increase with an increase in boiling point and the maximum nitrogen content was found in the 300-343 °C boiling fraction.

These observations led to the following conclusions about the refining pathways for the coal-derived liquids:

(e) The coal-derived naphtha can be refined to an aromatic motor-gasoline blending component by mild hydrotreating to remove the heteroatoms present in the naphtha. Due to the very high aromatic content of the naphtha, it was unlikely that catalytic reforming would be needed after hydrotreating.

(f) The coal-derived kerosene can be converted into a jet fuel blending component, but not an on-specification jet fuel. In order to produce a jet fuel blending component, the coal-derived kerosene will have to be severely hydrotreated. Both HDA and heteroatom removal are required. Even so, it would be unlikely that hydrogen content and density specifications would be met without significant ring-opening of the cycloalkanes produced by HDA.

(g) The coal-derived distillate is a poor feed material for diesel fuel production. To produce diesel fuel that meets a cetane number specification of 40, severe hydrotreating is required. It was calculated that about 6 wt% of the feed mass in H_2 would be required just to meet the minimum cetane number specification for the North American market. In order to produce diesel fuel for the European market even more severe hydrotreating would be required, as well as some ring-opening to reduce the density to within the specification limit. Even though it is technically possible to produce diesel fuel from the coal-derived distillate, it was considered doubtful whether this was an economically viable proposition.

(h) Aromatic-based chemical production was a better option than fuels refining for the coal-liquids characterized in this study.

6.2 Effect of Liquefaction Condition on Coal liquid quality

1. Liquid yield increased with temperature but liquid quality deteriorated with temperature increase. Liquids produced at 350 C had the highest content of light components.

2. A two stage liquefaction scheme comprising of a low temperature thermal liquefaction and a high temperature catalytic liquefaction could lead to higher yield of easy-to-refine liquids.

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APPENDIX

A.1 Trace element analysis of hydrotreated coal liquid used as solvent for coal extraction.

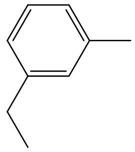
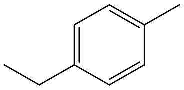
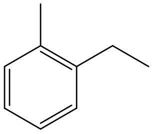
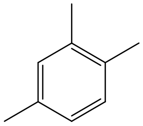
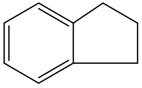
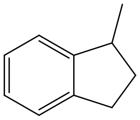
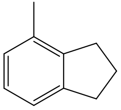
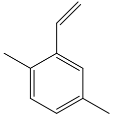
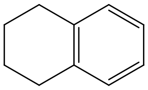
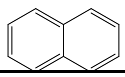
Analyte	Concentration (μg/g) [a]	
	Solvent	Detection limit (DL)
Li	<DL	0.05
Be	<DL	0.1
B	4	2
Na	1.1	0.5
Mg	4	2
Al	20.3	0.2
P	13	5
K	<DL	6
Ca	190	31
Ti	5.40	0.09
V	1.91	0.05
Cr	0.55	0.05
Fe	34.0	3.7
Mn	0.08	0.03
Co	<DL	0.03
Ni	0.15	0.06
Cu	0.05	0.03
Zn	5.60	0.08
Ga	<DL	0.01

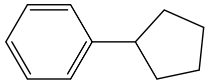
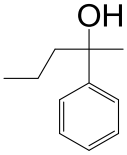
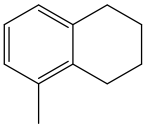
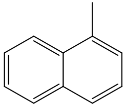
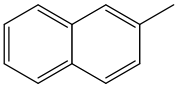
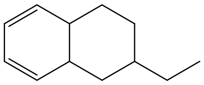
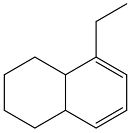
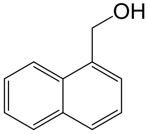
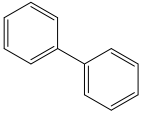
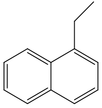
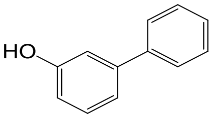
Ge	0.04	0.02
As	2.76	0.06
Se	2.2	0.2
Rb	<DL	0.04
Sr	0.27	0.03
Y	2.45	0.02
Zr	16.94	0.09
Nb	2.23	0.04
Mo	0.10	0.02
Ru	<DL	0.01
Pd	0.51	0.01
Ag	0.04	0.01
Cd	<DL	0.06
Sn	1.43	0.06
Sb	0.05	0.01
Te	<DL	0.02
Cs	<DL	0.02
Ba	0.24	0.03
La	<DL	0.03
Ce	0.12	0.03
Pr	<DL	0.004
Nd	<DL	0.03
Sm	<DL	0.04
Eu	<DL	0.03
Gd	<DL	0.03

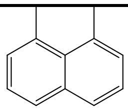
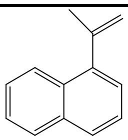
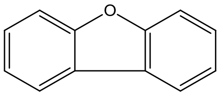
Tb	<DL	0.03
Dy	<DL	0.04
Ho	<DL	0.02
Er	<DL	0.04
Tm	<DL	0.006
Yb	<DL	0.05
Lu	<DL	0.04
Hf	0.58	0.05
Ta	3.95	0.02
W	0.52	0.08
Re	<DL	0.003
Os	<DL	0.08
Ir	<DL	0.04
Pt	0.10	0.01
Au	0.22	0.01
Tl	<DL	0.05
Pb	<DL	0.03
Th	0.04	0.01
U	<DL	0.03

[a] DL is the detection limit as indicated for the ICP-MS employed for the analysis.

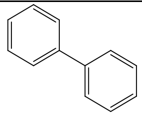
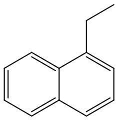
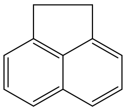
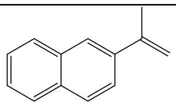
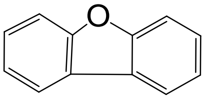
A.2: Quantification of compounds in the 120-250 °C fraction based on GC-FID peak areas

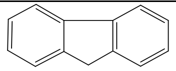
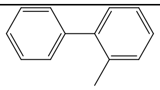
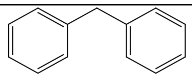
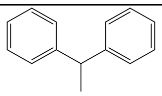
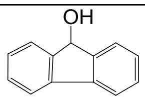
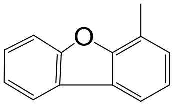
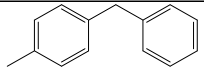
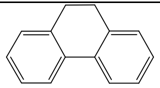
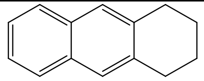
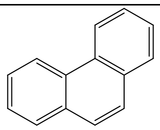
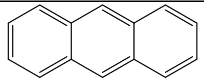
#	Structure	Retention time (min)	FID peak area of total (%)
1		11.882	0.461
2		12.012	0.227
3		12.571	0.278
4		13.138	0.205
5		14.384	9.562
6		15.665	1.326
7		16.822	0.789
8		16.995	0.895
9		17.264	2.429
10		17.752	21.887

11		18.362	0.399
12		18.488	0.619
13		19.058	0.323
14		19.568	6.497
15		19.805	4.673
16		19.903	0.309
17		20.425	0.331
18		20.723	2.877
19		20.765	2.563
20		20.972	7.050
21		22.148	0.294

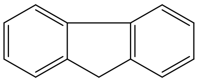
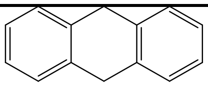
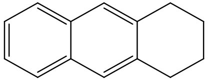
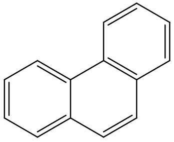
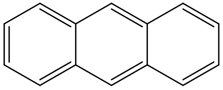
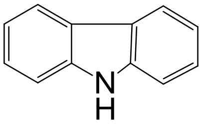
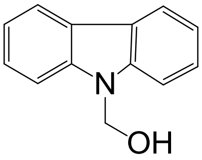
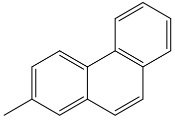
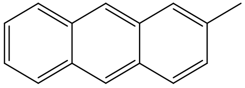
22		22.206	7.602
23		22.515	0.503
24		22.619	0.284

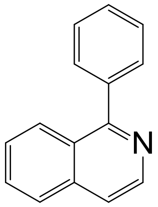
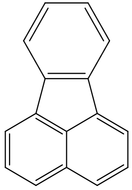
A.3: Quantification of compounds in the 250-300 °C fraction based on GC-FID peak areas

#	Structure	Retention time (min)	FID peak area of total (%)
1		20.783	0.47
2		20.987	1.16
3		22.239	47.5
4		22.532	3.97
5		22.637	5.00

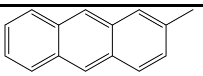
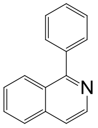
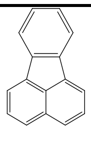
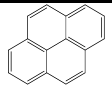
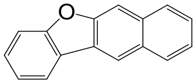
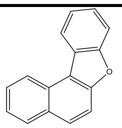
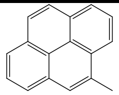
6		23.458	8.32
7		23.609	4.39
8		23.662	2.44
9		23.770	2.00
10		23.851	0.96
11		24.033	1.11
12		24.285	0.76
13		24.705	1.00
14		25.356	2.98
15		25.733	11.29
16		25.846	1.23

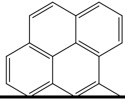
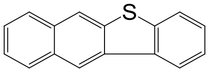
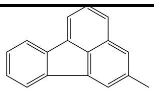
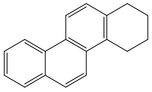
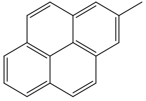
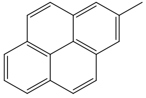
A.4: Quantification of compounds in the 300-343°C fraction based on GC-FID peak areas

#	Structure	Retention time (min)	FID peak area of total (%)
1		23.453	0.42
2		24.499	0.95
3		25.359	2.865
4		25.765	58.389
5		25.861	6.891
6		26.307	5.647
7		26.885	1.999
8		26.949	2.021
9		27.135	6.033

10		27.621	2.522
11		28.553	8.838

A.5: Quantification of compounds in the 343-370°C fraction based on GC-FID peak areas

#	Structure	Retention time (min)	FID peak area of total (%)
1		27.126	0.823
2		27.614	0.784
3		28.567	39.460
4		29.088	40.256
5		29.222	0.997
6		29.392	1.290
7		29.631	1.793

8		29.863	3.471
9		30.047	2.432
10		30.113	1.949
11		30.184	2.234
12		30.327	1.072
13		30.398	1.325