CATALYTIC HYDRO-LIQUEFACTION OF LIGNITE COALS UNDER MILD CONDITIONS

by

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Dedication

In the memory of Oussama Elbajermi,

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In the name of ALLAH; the most merciful, and the compassionate.

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Abstract

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A low-cost thermo-chemical process for the liquefaction of lignite coals is being developed at the University of Texas at Arlington (UTA). The coal-to-liquids (CTL) project has focused of developing a liquefaction process which is made economically attractive by the combination of using a cheap coal feedstock, such as lignite, use of cheap disposable catalysts, and limiting the operating conditions to mild temperatures and pressures, at least relative to many existing CTL processes. The UTA-CTL process uses a solvent which is derived from the pyrolysis of lignite, an inexpensive iron-based catalyst and mild temperatures and pressures to hydrogenate and depolymerize the carbon structures found in lignite to produce a syn crude oil substitute. Our best process conditions give a syn-crude product in 60 % liquid yield based on maf lignite. This yield translates to ~ 4.5 bbl syn oil/MT of moisture ash free (maf) lignite. Typical yields range between 35 – 55 % and a number of reaction parameters, including reaction time, temperature, pressure, catalyst loading, solvent, and initial coal moisture and ash content have been examined for their effect on the process. The nature of the catalyst has been varied within the constraints that the ultimate catalyst be very inexpensive and essentially, disposable after use. An economic analysis of the process suggests this process would be possible at larger scales at cost of $24 to 42 per bbl, which is very attractive given the current market price of crude oil is in the range of 85-105 $/bbl.

The syn oil has been characterized by a number of tests obtained both locally and from external laboratories to evaluate its quality and value. UTA syn oil is found to have an average H/C ratio of 1.4 which is close to typical crude oil ranged between 1.5 to 1.9. The elemental and metal analysis of UTA syn oil shows in average the values of 83.0% Carbon, 10.0% Hydrogen, 1.0% Nitrogen, and low concentrations of Sulfur, Mercury and Iron. UTA syn oil was compared current liquid hydrocarbons and found to be with agreements with the current guidelines and limits as placed by the United States government. On the other hand, SARA analysis of UTA syn oil shows 18.0% wt of the contains as asphlaltenes, 17.5% wt as saturated hydrocarbons, 61.5% wt as aromatics, and 3.30% wt as resins. PNA analysis Shows 21.4% wt paraffins, 10.4% wt naphthalenes, and 68.2% aromatics. UTA sun oil average carbon number is 19 with wide distribution range between 9 to 40 C atoms. The simulated distillation of the UTA syn oil shows a recovery of 95.0% at 560 C and higher distillation

temperature for UTA syn oil over the both kerosene and diesel. Given the relatively high aromatic content, this syn oil would likely be valued at a $10.0discount relative to the benchmark premium crude oils, such as west Texas light sweet crude (WTI), which sell at the market price.

Table of Contents

List of Illustrations

List of Tables

Abbreviations

API	American Petroleum Institute
ASTM	American Standard Testing Methods
AUC	Australian Brown Coal
BCL	Brown Coal Liquefaction
BTU	British Thermal Unit
CAS	Chemical Abstracts Service
CHN	Carbon, Hydrogen, And Nitrogen
CTD	Coal Tar Distillate
CTL	Coal To Liquid
d.	Density
DARPA	Defense Advanced Research Projects Agency
DCL	Direct Coal Liquefaction
DCTD	Digested Coal Tar Distillate
DOE	Department Of Energy
EDS	Exxon Donor Solvent
EDS	Energy-Dispersive X-Ray Spectroscopy
FT	Fischer–Tropsch
GCMS	Gas Chromatography Mass Spectroscopy
H/C	Hydrogen Carbon Ratio

H-COAL	Hydrogenated Coal Process
HCTD	Hydrogenated Coal Tar Distillate
ICL	Indirect Coal Liquefaction
LAL	Low Ash Lignite
LUM	Luminant Lignite Coal
MAF	Moisture Ash Free
MT	Metric Ton
NMR	Nuclear Magnetic Renounce
NRG	Energy. Inc
O/C	Oxygen Carbon Ratio
P	Pressure
SRC-I	Solvent Refined Coal Process One
SRC-II	Solvent Refined Coal Process Two
SYN OIL	Synthetic Crude Oil
T.B.P.	True Boiling Point
T.	Temperature
TGA	Thermal Gravimetric Analysis
UTA	University Of Texas At Arlington
USD	The United States Dollar
V	Viscosity

WTI	West Texas Intermediate
WGS	Water Gas Shift Reaction
XPS	X-Ray Powder Spectroscopy
XRD	X-Ray Diffraction Analysis

Chapter 1

Introduction

Coal to Liquid Fuels: An Answer to Energy Crisis

Almost three years ago in 2008, world petroleum prices reached record highs.[1] Concerns about current and future petroleum costs for imported oil have renewed interest in finding ways to use unconventional fossil-based energy resources to replace petroleum-derived gasoline and diesel fuels. The US has vast coal reserves, however as a solid, coal is a poor substitute for oil in the production of liquid transportation fuels. Technology to convert coal to a synthetic crude oil (synoil) substitute could potentially address this problem to a significant degree. This course of action would lower prices and reduce the transfer of wealth from the United States oil consumers to foreign oil producers and could result in domestic economic gains and potential national-security benefits.[2-3]

Coal has been converted into liquid and gaseous products for well over 100 years, with late 19th century cities and towns in the US often using coal-derived ‘town gas’ to light city streets. The Bergius process was in wide scale use in Germany during WWII and produced near 70% of Germanys liquid fuels from lignite coal. [4]REF This reaction required temperatures of 400-500 C and very high pressures (3000 to 6000 psi), which made it uneconomical after the war. Current coal to liquid (CTL) technology can be divided into two distinct approaches: direct or indirect conversion.[5-6] In a direct CTL process, coal is directly converted to liquid products that can later on be refined into a variety of petrochemicals products.[7] The indirect process utilizes a two-step process in which the coal is first converted to synthesis gas or syn gas (a mixture of CO and H_2) and then converted into liquid fuel by using Fischer–Tropsch (FT) chemistry.[7] For both approaches a major challenge is to increase the hydrogen-carbon ratio. For finished hydrocarbon fuels, such as gasoline and diesel, H/C ~ 2. For petroleum crude oil, the ratio ranges from 1.3 to 1.9. and for typical Lignite coals, H/C ~ 0.8

Direct Coal Liquefaction (DCL)

DCL technology involves making a partially refined synoil from coal, by breaking down the large molecular weight coal into smaller desired molecular weight hydrocarbons.[7-8] Which is then further refined into synthetic gasoline and diesel as well as LPG hydrocarbon fuel products similar to hydrocarbon fuels derived from petroleum crude oil. With DCL technology the H/C ratio is increased by adding gaseous H_2 to a slurry of pulverized coal and recycled coal-derived liquids in the presence of suitable catalysts to produce synthetic crude oil.[9] Typical process conditions require temperatures in excess of 400 C and pressures of 2000 psi or greater. A slate of partially refined gasoline-like and diesel-like products, as well as propane and butane, are recovered from the synoil mainly by distillation.[10] Each of the products is made up of not one but many different large molecules that are recovered via distillation in different temperature ‘‘cuts’’. Hydrogen is needed in the DCL process both to make synoil and to reduce the oxygen, sulfur, and nitrogen in the coal feedstock. These elements are removed from the liquid fuel products in the forms of H_2O, H_2S, and NH_3. The oxygen is removed so that hydrocarbon fuels can be obtained. The nitrogen and sulfur compounds are removed because they would otherwise poison the cracking catalysts in the refining operations downstream of the DCL plant.

Indirect Coal Liquefaction (ICL)

ICL technology involves first gasifying coal to make synthesis gas (syn gas) by breaking down the large molecular weight coal into small molecular weight syn gas (CO and H_2).[7,11] The CO and H_2 molecules in the syn gas are then combined catalytically to produce compounds that can be used as fuels, either hydrocarbon fuels such as synthetic gasoline, synthetic diesel, or oxygenated fuels.[11] The challenge of increasing the H/C ratio is addressed by using the water-gas-shift (WGS) reaction ($CO + H_2O \rightarrow H_2 + CO_2$) and removing the CO_2 thereby produced from the system.

The label ‘‘indirect’’ refers to the intermediate step of first making syn gas. ICL technology can also provide hydrocarbon fuels that resemble crude oil-derived products. One possibility is synthetic middle distillates derived via the F-T process that can either be used directly as diesel or in blends with petroleum-derived diesel.[12] Another possibility is gasoline via the route of first making methanol from syn gas and then converting methanol into gasoline.[13] But methanol can also be used directly as a fuel, and other oxygenates (fuels containing some oxygen) such as dimethoxyether (DME) can also be provided via ICL process technology and used directly as fuels.[13]

Both direct and indirect CTL processes have their advantages and disadvantages. Direct CTL result in primary products (liquids or solids) of molecular weight greater than the fuels and chemicals desired. Catalysts may be used.[14] Secondary processing is usually required to form fuels and chemicals with desirable molecular weight, or required chemical pretreatment of the coal, manipulation of the feed source by addition of heavy fractions of petroleum oil.[15] The two processes of dissolution and oil upgrading can take place in the single reactor, producing high H/C ratio products, and a fast reaction time. The main disadvantages of DCL are high gas yields due to the thermal cracking processes, high hydrogen consumption, and generally a lower quality of oil due to high aromatic content and impurities present. On other hand, the first step in indirect CTL liquefaction processes is always gasification of coal to syngas and this is followed by additional steps in which the syngas is catalytically recombined to form hydrocarbons and /or oxygenates. This two-step process is energetically expensive and often requires high capital investment costs. The advantage is that the hydrocarbon product is generally of very high quality and can command a premium price. When comparing DCL technology with ICL technology, DCL generally has a lower capital cost for a comparably sized plant. DCL produces 50

% more liquid product per ton of coal, 50% less plant generated CO_2, and requires less water consumption. Thus when given the choice, DCL is usually more energy and cost efficient then ICL technology.

Chemistry and Mechanisms of Coal Liquefaction:

Liquefaction is the generic term for converting coal to distillate products to be used as fuels and chemicals. In this work, we will use this term exclusively to refer to direct liquefaction processes, unless specifically stated otherwise. In order to understand the chemical transformation that is required for a CTL process, it is important to understand the general structure and properties of both the coal feedstock and the desired synoil, which is a petroleum or crude oil substitute. A high quality conventional crude oils is characterized by a H/C ratio of 1.4- 2.0, low sulfur and nitrogen content, low metal impurities, and medium to high API values..[16-17] Thus, the viability of synoil as refining feedstock is determined by placing its value in the liquid-fuel sector where the synoil competes with the other indigenous and foreign crudes. For a synoil to compete with the conventional crude oils, the liquefaction process must transform the coal, inherently low in hydrogen (i.e. H/C ratio for lignite ~0.8), to a liquid product with comparable metrics to conventional crude. It is clear that the central issue in DCL processes revolves around increasing the H/C ratio.[17-18]

Coal Deposit and Usage in the United States

Coal is a versatile fossil fuel that has long been used for a variety of domestic and industrial purposes.[19] It currently provides around 25% of the world's total primary energy, although this share is subject to some possible variation with different policy developments, it is expected to provide a similar share in future years. [20]

The availability of coal resources has been a major contributor to the economic growth of many countries, either directly through their own resources or indirectly through access to the international coal trade. In the late 19th and early 20th centuries, coal was mainly used as a transport fuel or as a source of heat and power for industrial and domestic applications.[21] In the middle of the 20th century the use of coal decreased in some areas because of low oil prices, and the large scale switch to diesel and gasoline powered vehicles for transportation. The oil supply crisis of the 1970s partially reversed this trend with an increase in coal consumption to electric power generation. Another consequence of the oil supply crisis was a significant increase in coal liquefaction research and development, although much of this work was subsequently put on hold when oil prices stabilized.[22-23]

The United States has major reserves of all ranks of coal: lignite, subbituminous, bituminous, and anthracite; their geographical occurrence is shown in Figure 2.[24] As of January 1, 2008, the demonstrated reserve base

(DRB) was estimated at 489 billion short tons (a short ton is a unit of weight equal to 2,000 pounds). [22-23,25] Although 90 percent of the United States coal reserves are concentrated in 10 states, coal is mined in 27 states and can be found in even more.[25] Montana has the most coal, 25 percent of demonstrated reserves. Wyoming, third among states with the most coal, is first in coal output, accounting for 18 percent of annual production. The United States uses just over a billion short tons of coal each year.[24,26-27]

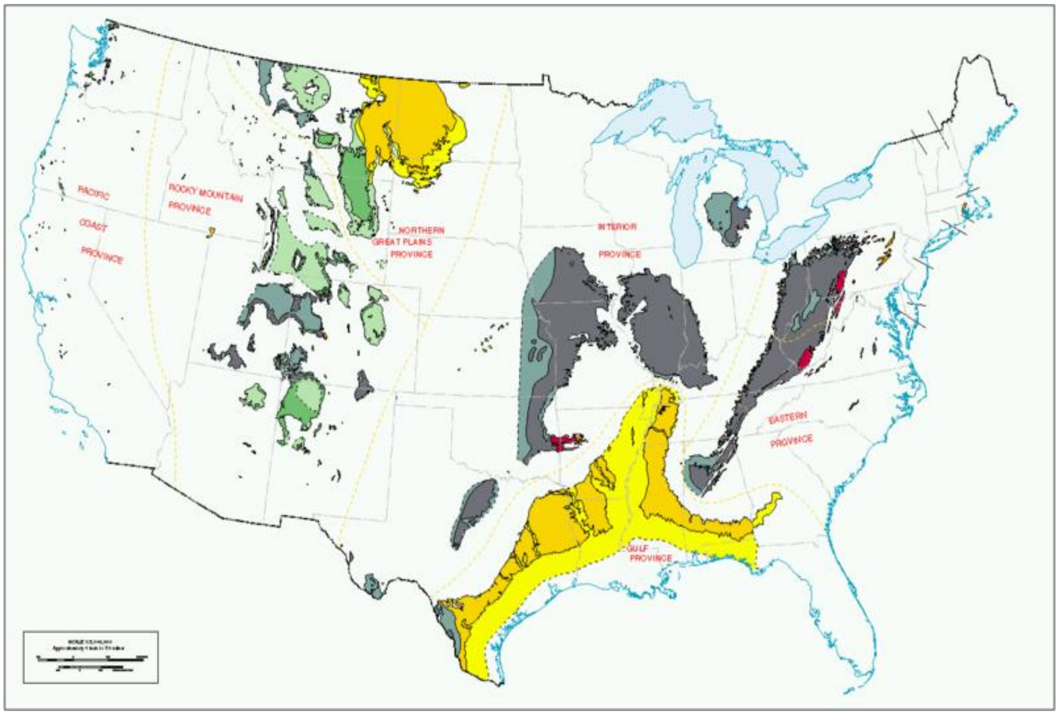


Figure 1. Deposits of lignite in United States. Yellow: lignite coal deposits, green: subbituminous coal deposits, dark grey: bituminous coal deposits, and red: anthracite coal deposits.[24]

Coal: Ranks and Structure

Coal is a black or brownish-black rock that is made from plants that lived and died about 100 to 400 million years ago. The public has always looked at the coal as this fossilized plant materials but no two coals are exactly alike. Heating value, ash melting temperature, sulfur and other impurities, mechanical strength, and many other chemical and physical properties must be considered when classifying coals.

The mean source for classifying coal into it rank depends on the heat content per unit mass, with lower grade coals giving approximately 8300 -10000 BTU/lb and the highest quality coals giving 15500 BTU/lb. In general, the longer the coal has been fossilizing, the greater the heat content per unit mass. Over geological time periods, the combination of pressure and heat transform the organic matter (dead plants) to first peat, then lignite, then subbituminous, bituminous, and finally anthracite coal. Figure 2 illustrates the process of forming coal form peat to anthracite.

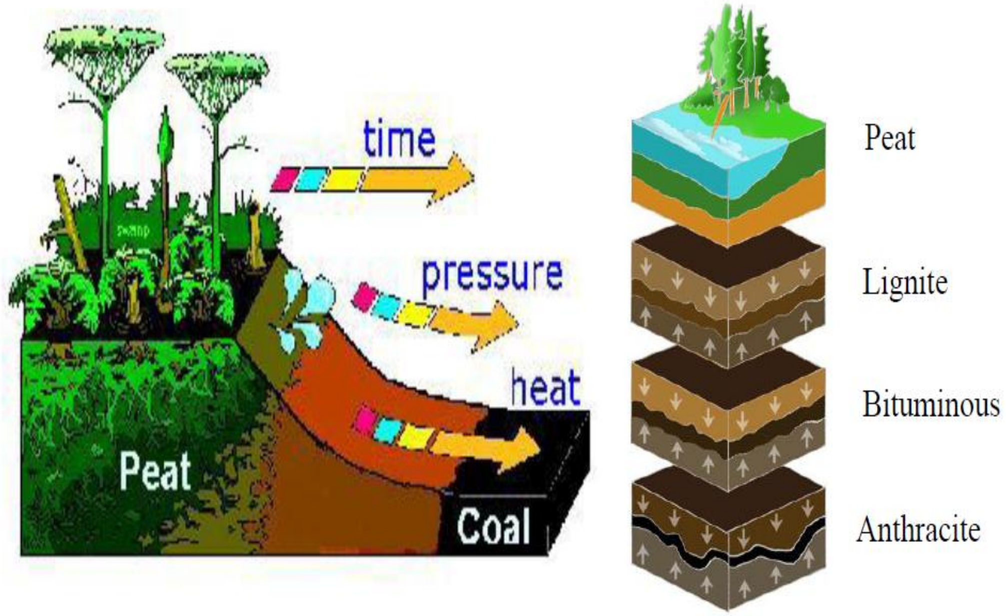


Figure 2. The process of forming coal form peat.[27]

The four main ranks or types of coal lignite, sub-bituminous, bituminous coal, and anthracite are also classified based on the amount of carbon, oxygen, and hydrogen present in the coal as well as less obvious metrics such as ash melting temperature, sulfur and other impurities, mechanical strength, and many other chemical and physical properties. Figure 3 Illustrates the fossilization process for low density, open structure, more aliphatic, and oxygenated lignite to the more aromatic, less hydrogenated sub-bituminous coal, and then onto the even more aromatic structure of high density anthracite. Pure anthracite is very near to graphite in structure and composition. The carbon content of coal supplies most of its heating value, but other factors also influence the amount of energy it contains per unit of weight. Anthracite, for example, has the highest carbon content, between 86 and 98 percent, and a heat value of nearly 15,000 BTUs-per-pound. Most frequently associated with home heating, anthracite is a very small segment of the United States 3coal market. There are 7.3 billion tons of anthracite reserves in the United States, found mostly in 11 northeastern counties in Pennsylvania. Where bituminous is the most plentiful form of coal in the United States, bituminous coal is used primarily to generate electricity and make coke for the steel industry. The fastest growing market for coal, though still a small one, is supplying heat for industrial processes. Bituminous coal has a carbon content ranging from 45 to 86 percent carbon and a heat value of 10,500 to 15,500 BTUs-per-pound. In addition, coal ranking below bituminous is sub bituminous coal with 35-45 percent carbon content and a heat value between 8,300 and 13,000 BTUs-per-pound. Although its heat value is lower, this coal generally has a lower sulfur content than other types, which makes it attractive for use because it is cleaner burning. Finally, lignite is a geologically young coal, which has the lowest carbon content, 25-35 percent, and a heat value ranging between 4,000 and 8,300 BTUs-per-pound. Sometimes called brown coal, it is mainly used for electric power generation.

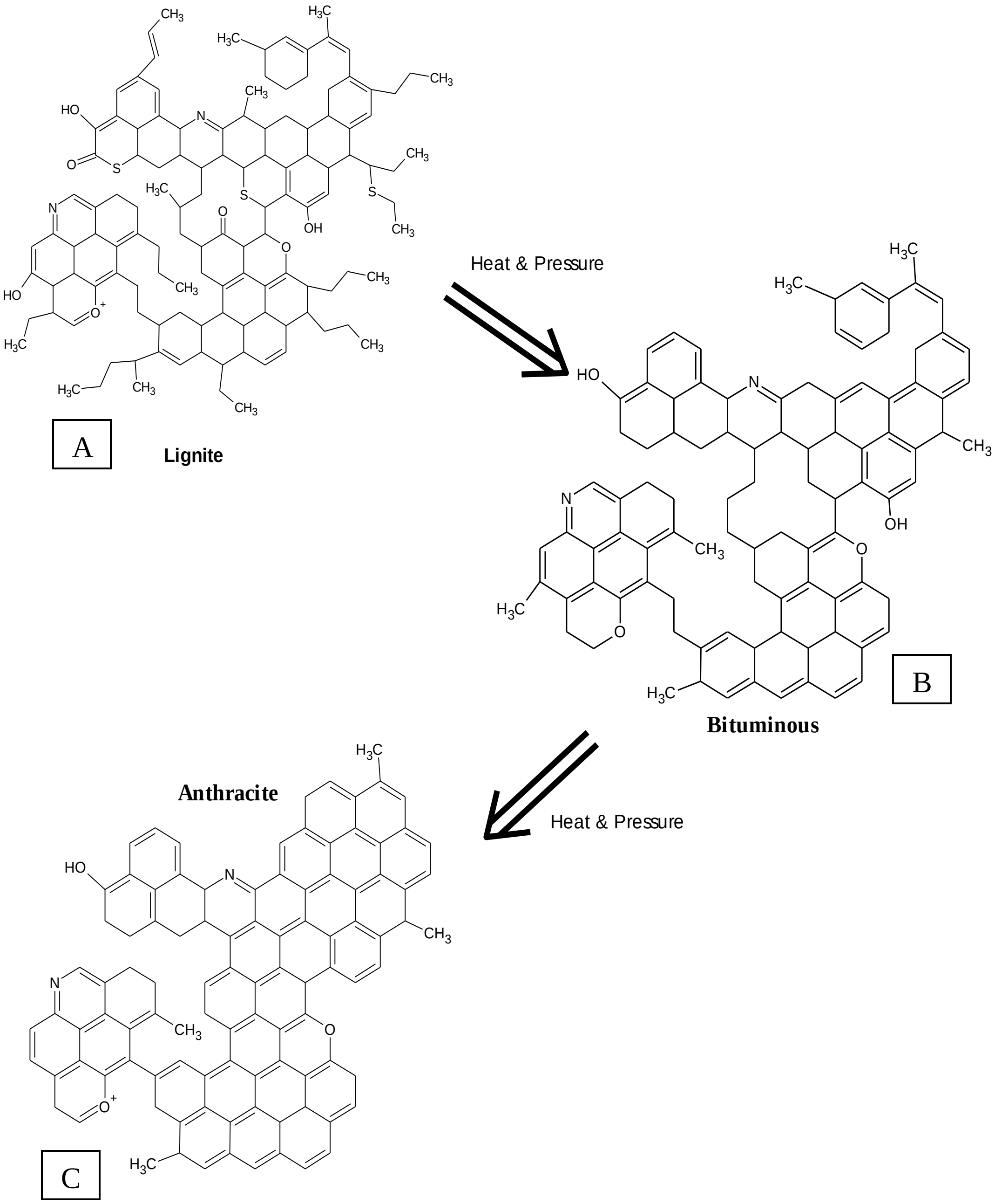


Figure 3. Process of transformation of low density, open structure, aliphatic, and oxygenated lignite coal to higher aromatic, and dense anthracite coal: A Liginte coal, B Bituminous coal, and C Anthracite coal.

Coal is a highly cross-linked amorphous copolymer with aliphatic weak links between stable aromatic cluster units. The degree of carbon aromaticity ranges from 60% (lignite) to 80% (bituminous), depending on coal rank. Hydrogen is found bound to aromatic carbons, in aliphatic side chains and bridges, and as part of the nitrogen, oxygen, and sulfur functional groups contained in the coal and is generally more abundant in lower ranked coals (see Figure 4).[28] It is also found as retained moisture in the coal. . Oxygen is mainly contained in a phenolic (-OH) form, with some ethers, carboxyl, and carbonyl groups. Sulfur functionality is similar to oxygen, as thiols (-SH), ethers, or thiophenes. Nitrogen appears mainly as pyrrole and pyridines. Removal of heteroatoms, such as O, N, and S, is essential for producing better quality synoil and improve hydrogen efficiency. It is hypothesized that during coal pyrolysis, rupture of heteroatom-carbon bonds occurs at a rapid rate, causing production of gaseous products such as hydrogen sulfide, water, and ammonia. The large polymeric matrix of aromatic structures found in coal is commonly called the coal macromolecule.[29-30] This macromolecular network consists of clusters of aromatic carbons that are linked to other aromatic structures by bridges. Bridges between the aromatic clusters are formed from a wide variety of structures. Most bridges are thought to be aliphatic in nature, but may also include other atoms such as oxygen and sulfur.[31-33] Those bridges that contain oxygen as ethers are thought to have relatively weak bond strengths.[34-35] Other bridges are made up of aliphatic functional groups only. Some bridges consist of a single bond between aromatic clusters; this is known as a bi-aryl linkage. Due to the large variety of functional groups that make up the bridge structures of coal, bridges have a large distribution of bond strengths.[36] This distribution of bond strengths becomes important during the liquefaction process as the weakest bonds are broken first. There are other attachments to the aromatic clusters that do not form bridges. These attachments are referred to as side chains and are thought to consist mainly of aliphatic and carbonyl functional groups.

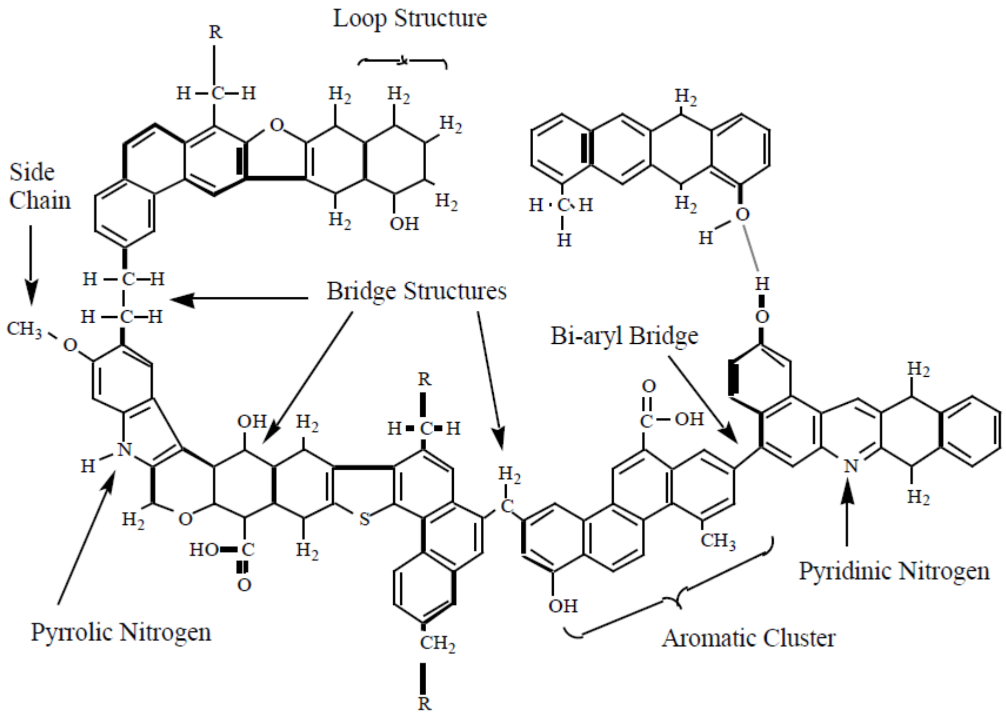


Figure 4 Schematic representation of generic structural groups and connecting bridges in coal.[28]

Coal liquefaction involves breaking down the vast complex structure of coal into desirable molecular weight hydrocarbons. Based on the structure of coal lattice, three reaction categories are targeted in coal liquefaction: depolymerization, hydrogenation, and heteroatom removal, in which they relate to each other.[37-43] When coal is heated, rupture of a sufficient number of the chemical bonds linking clusters together is required to free these clusters and at the same time form free radicals. The extent of radical formation via thermal rupture of relatively weak chemical bonds increases with increasing temperature. The production of a significant yield of liquid product requires stabilization of these fragments to inhibit polymerization to form a solid mass. The presence of hydrogen inhibits the polymerization of coal fragments reacting with the free radicals to form CH bonds. The continued bond rupture further reduces viscosity by reducing the mean molecular size of the product; however, it usually also results in the production of more gases therefore an optimum temperature must be determined.

Coal Proximate Analysis

Coal has been described variously, depending on the context, from ‘‘nature’s dump’’ to ‘‘nature’s storehouse.[44] Because of the various conditions under which it is formed, coal is generally very heterogeneous being composed of the carbonaceous material, inorganic components (contaminants), and water. The carbonaceous material can be further categorized into volatile carbon and fixed carbon based on the ability of this carbon to be lost upon pyrolysis. A proximate analysis of any coal is a common and useful initial characterization of coal quality and composition and typically reports coal composition as percentages of moisture, ash, volatiles, and fixed carbon below we consider each of these components in the context of coal analysis.

Moisture

Moisture is generally characterized as the water which is removable by gentle heating (temperatures around 100 to 120 C) of the coal under a nitrogen atmosphere. Higher temperatures may release additional water as coal depolymerization releases oxygen-containing functional groups from the coal but this is not H_2O prior to this reaction. Percent moisture is an important metric as it can greatly alter the coal heating value and therefore value. For heating applications, obviously less is better and higher ranked coals are generally also low in moisture. Water also can affect the depolymerization chemistry. Artok et al.[45] investigated the effect of water in de-carboxylation of coal during depolymerization of Turkich Göynük lignite. The coal sample was subjected to moderate-severity heat treatment with or without added water, under N_2 or H_2 atmospheres at 285−330 °C. In their investigation, the samples processed in H_2−H_2O combination seemed to be more dissociated or decomposed than those processed in N_2─H_2O or under H_2 without water. Gas analyses and spectroscopy of samples clearly indicated that the presence of water enhanced the de-carboxylation reactions and that oxygen rejection from the coal was mainly due to CO_2 formation. Water also enhanced the cleavage of aryl─ether bonds.

Volatile Matter and Fix Carbon

Coal consists of two organic components, volatile material and fixed carbon. Volatiles are a mixture of short and long chain hydrocarbons, aromatic hydrocarbons, and gasified heteroatom structures (thiols, ammonia, water some sulfur). The fixed carbon content of the coal is the carbon that remains after volatile materials are driven off – generally remaining even after pyrolysis at 500 C or greater. The volatiles and fix carbon represent are an important estimate of the amount of carbon in the coal and the amount of raw coal that can be converted to liquid or gas products. It should be understood that coal is a raw martial with a deficiency in hydrogen content relative to crude oil. [22,46-47] Liquefaction yields are in turn significantly affected by atomic H/C ratio, which also involves the effect of coal rank. Redlich et al.[48] have correlated the liquefaction yield and the H/C ratio. For Australian coal with atomic H/C ratios range is between 0.6 to 1.2, the liquefaction yield increased from 10 wt% maf to almost 60 wt % maf with increasing H/C ratio. Other studies have correlated the type of hydrogen and the chemical structure of the coal with the liquefaction yield, which was not the focus of this study.[48-51] Nevertheless, the coal H/C atomic ratio and hydrogen distribution into aliphatic and aromatic structure could be of special interest in an assessment of coal liquefaction reactivity.

Ash Content

Ash content of coal is a measurement of the non-combustible residue left after coal is burnt. It is mainly inorganic material and it represents the bulk mineral content after carbon, oxygen, sulfur and water have been driven off during combustion. Several research papers reported the role of the inorganic minerals as heterogeneous hydrogenation catalysts that aid in the liquefaction process. Sert et al.[52] investigated the effect of the mineral content and temperature on gas, liquid, and residue yields.. According to the results, the removal of the minerals causes a decrease in the conversion for all lignite samples and an increase in the carbon content of solid residue.[52] the main product in gaseous state is CO_2. In their findings temperature plays a key role, with increasing temperature lowering liquid yields and increasing affecting the product distribution when compared to the effect of the minerals in lignite. In our studies, ash content has been found to impact the CTL process.

Lignite Coals as Feedstock for Coal Liquefaction

Lignite is considered a geologically young coal, just slightly more energy rich per unit mass than peat. The lower energy content is largely related to the higher oxygen content relative to higher grade coals and its inherent tendency to retain more moisture. Because it is still ‘young’, the coal is considerably more hydrogen rich in the form of having more saturated carbon centers. These qualities which make lignite a poor heating fuel are actually favorable for the conversion of lignite into a synoil product. The higher degree of saturation means that less hydrogenation is needed to produce hydrocarbons, and the open porous, hydrophilic nature of the lignite means that it is less compacted and more easily de-polymerized than bituminous or sub-bituminous coals. We reasoned that with this feedstock we may be able to develop a CTL process that is less chemically severe and therefore more economical than existing methods, most of which focus on the conversion of higher-grade coals.

Existing Liquefaction Technology

All direct methods for converting coal to liquid fuels invoke to two key processes: depolymerization to break the coal extended structure down into smaller molecular sizes, and hydrogenation to add hydrogen to the unsaturated portions of the structure and to remove heteroatoms such as oxygen, nitrogen, and sulfur, ideally as H_2O, NH_3, and H_2S. Typical crude oil and natural gas have molar H/C ratios of 1.4-1.9 and 4.0, respectively, while premium products like jet, diesel, and gasoline, have an H/C value around 2.0. However, coal is hydrogen-deprived material, which means it has a low H/C ratio; anthracite in particular has extremely low hydrogen-to-carbon ratios (H/C ~ ???), whereas lignite have values closer to 0.8. The addition of hydrogen to coal, along with the depolymerization, results in its transformation to a liquid with a hydrogen-to-carbon ratio close to 1.3-1.5, typically.

Many CTL liquefaction processes have been developed over the decades since the original Begius process, each has its advantages and disadvantages. In this section, we will discuss of the pros and cons of the major direct coal liquefaction processes, including some of the research results on catalytic direct coal liquefaction. Table 1 lists CTL processes which have been tested at large scale and the conditions in which they operate. Most of those processes use a one or two stage reactor, temperatures and pressures in excess of 400 C and 2000 psi, respectively, and either hydrogen or a hydrogen donating solvent.. While some processes do not use a catalysts, most use a Fe-based catalyst and some using more expensive Ni, Co, and Mo-based catalysts. It should be noted that as the severity of the conditions increases, the capital costs of the associated equipment also increases, often exponentially. Table 1 represents the current processes of coal to liquid technology shown the condition and the yield of each process as it has been reported in the literatures. The operating parameters for the UTA process are included to illustrate just how significantly we have improved on existing technology while still yielding a similar amount of syn-crude per ton of moisture and ash free coal.

Table 1 Current processes of coal to liquid technology shown the condition and the yield of each process as it has been reported in the literatures.[6,53-56]

Process	# of Reactors	1st Reactor Temp.	1st Reactor Pressure(psig)	Reactor residence time (min)	Catalyst	Yield %
SRC-I	1	450	1000	45-60	none	60
SRC-II	1	445-465	2700	30-70	Fe-S Catalyst	55
H-Coal	1	425-455	3000	40	Co-Mo, Ni-Mo	50
EDS	1	425-500	2000-3000	30-45	Tetralin Solvent	50-60
Kohloel	1	400	4500	45-60	Fe-S Catalyst	74
BCL-Nedol	2	450	2500	30-45	Iron catalyst	65
CMSL	2	400	2500	30-60	Fe, Mo, Ni and Co	60-65
Shenhua	2	455	2800	45-60	FeOOH nanocatalyst	57
UTA	1 or 2	320	1000	30	BXFs Catalyst	50

In virtually every direct CTL process, crushed coal is slurried with a solvent and heated under high pressure to cause depolymerization and hydrogenation of the coal structures. Hydrogen is either added directly as a gas or is ‘donated’ by the solvent or some other component. For example, the EDS process uses tetralin, preheated and pumped into a pressure vessel under pressure of 2,000–5,000 psi and temperature range in between 300-700° C in the presence of hydrogen gas with or without a catalyst for some 30 to 150 min time duration[5,57] Under these conditions thermal ruptures of chemical bonds occur helping to depolymerize the 3-D network structure found in coal.[5] In addition to acting as a carrier medium, the solvent disperses molecular fragments and stabilizes free radicals by hydrogen transfer.[58] This process may be enhanced in the presence of a catalyst so that the coal-derived chemicals remain low in molecular mass.[59-60] If free radical stabilization is impeded, the coal-derived chemical components may recombine into high mass products leading to the formation of non-distillable liquids and solids.[58] For example, in 1970’s Chevron invented the SRC-I and II method of coal liquefaction. In SRC-I process coal is first slurried in a recycle solvent, then preheated, and finally reacted in a bubble column-type reactor at 450°C in the presence of gaseous hydrogen. Because of the high reactivity of the coals tested, primarily eastern United States high-and-medium volatile bituminous coals, no catalysts were added and the reaction was carried out at pressures as low as 1000 psig. The mean residence time in the reactor was reported to be on the order of 30 min. SRC-I achieved maf yields of approximately 60%. On the other hand, SRC-II process was developed to minimize the production of solids from the SRC-I process. The principal variations were incorporation of a recycle loop for the heavy ends of the primary liquefaction process and imposition of more-severe conditions during hydrogenation. It was quickly realized that minerals that were concentrated in this recycle stream served as heterogeneous hydrogenation catalysts that aid in the production of distillate. In particular, pyrrhotites, Fe_xS_y, were identified as being especially important. Pyrite was subsequently added for cases where the inherent pyrite content of the coal was low. SRC-II achieved maf yields of approximately 45%. In another example, in 1980's Exxon Mobil introduce the Exxon Donor Solvent Process (EDS) of coal liquefaction. Coal in EDS is chemically reacted and dissolved in a recycle solvent (Tetralin) that is hydrogenated between passes to the liquefaction reactor. The primary liquefaction part of the reaction system operated at temperatures of 425 – 480° C and pressures of 1450–2030 psi, using mean residence times in the range of 15 min to 2 h, depending on coal reactivity and process configuration. Operation at these conditions required significant advances in hardware, such as the design of a slurry let-down valve, required to reduce the pressure of the let-down slurry (15% solids) from 2030 psi to 145 psi at 450C. H-coal EDS achieved maf yields of approximately 50-60%. Finally, in 1970's Headwaters Inc introduce the H-Coal process, single stage catalytic liquefaction process. The process consists of coal-refine oil slurry preparation followed by catalytic hydrogenation/hydrocracking at 450C and 2200 psi in the well-mixed bed reactor. The heart of this process is the reactor, where coal, catalyst, solvent, and hydrogen are all present in the same vessel. The reactor is maintained in a well-mixed state by internal agitation using a slurry recirculation pump, coupled with the action of the gas bubbling through the fluid. H-coal achieved maf yields of approximately 50%.

Extraction Solvent, Hydrogen Donor Solvent and Solvent/Coal Ratio

Direct coal liquefaction proceeds primarily through a sequence of bond breaking and hydrogen transfer reactions involving coal and a donor solvent.[14,59,61-62] The presence of a donor solvent is considered essential for direct coal liquefaction.[63] The choice of solvent depends on the presence of mobile carbon-hydrogen bonds. Curran et al.[64] suggested that in the case of coal liquefaction the transfer of hydrogen from a hydrogen-donor solvent takes place by a free-radical mechanism. Free radicals formed during the depolymerizations stage seek stabilization and in the presence of a hydrogen-donor solvent, are hydrogenated.[45] Wilson et al.[65] showed that the major role of hydrogen in uncatalyzed liquefaction is reaction with the products of alkyl fission and hydrogenolysis reactions and not with hydrogenating aromatic rings. McMillan[66] et al. have postulated that a radical hydrogen transfer process along with donor solvent capping of thermally produced radicals from the coal as possible processes involved with the hydro-aromatic donor solvents in coal liquefaction. Thus, the main advantages of hydrogen-donor solvents over gaseous hydrogen in the liquefaction process stem from the much lower operating pressures that can be employed, and the enhanced effectiveness in stabilizing the primary thermal decomposition products. Thus, preventing charring and increasing the yield of upgraded liquid fuels.

The solvent/coal ratio is important for the free radical stabilization, dissolving the catalysts, and the extraction of the dissolved material from the inside of the coal particle to the bulk solution.[67] In lignite liquefaction, it is critical to achieve a certain value of solvent/coal ratio because the rate of recombination of the radicals fragments, after the thermal decomposition of coal structures, occurs rapidly[68].

Catalyst for Coal Liquefaction.

The advances in the understanding of the use of catalysts and improvements in catalyst formulations have allowed for significant advances in direct coal liquefaction. The limitation of the thermal process in direct coal liquefaction was the production of large quantities of gaseous products; the introduction of improved catalytic processes has led to a reduction in the amount of the light products and to an increase in the desired liquid products. For example, in SRC-II it was quickly realized that minerals such as pyrrhotites (Fe_xS_y) served as heterogeneous hydrogenation catalysts that aid in the production of distillate. In particular, iron sulfides produced by the reduction of iron pyrite (FeS_2), were identified as being especially important.

Iron based catalysts are the most conventional catalytic material for coal liquefaction. Iron-sulfur and iron-oxide in various forms have been successfully employed for direct hydrogenation during coal liquefaction on a commercial scale.[40,69-70] They are preferred because of their simplicity and economic reasons, although coal liquefaction can proceed even in the absence of the catalyst. The iron catalyst was also utilized with a hydrogen-donor solvent to enhance the liquefaction of coal. Liquefaction catalysts can be added to coal as a fine powder, supported over Al_2O_3, SiO_2 and TiO_2 or as dispersed catalyst. Watanabe et al.[71] investigated the hydro-liquefaction of Japanese Miike subbituminous and Taiheiyo lignite coals using various iron complexes as catalysts in tetralin at 375-445 °C. All of the iron complexes catalysts show increases in the reactivity toward hydro-liquefaction of the sub-bituminous and lignite coals, iron pentacarbonyl ($Fe(CO)_5$) showed the highest catalytic activity and increasing coal conversion by about 10% at 425 °C under an initial hydrogen pressure of 750 psig. Amounts of hydrogen transferred to coal increased from 1.4-2.3 wt% of maf coal in the absence of the catalyst to 2.5-4.2 wt% of maf coal in the presence of $Fe(CO)_5$ at 425 °C. Watanabe assigned the reactivity of the iron complexes, $Fe(CO)_5$, to decomposition to a finely dispersed metallic iron at an elevated temperature. Thus, under the coal liquefaction conditions, $Fe(CO)_5$ appears to penetrate the pores of the coal particles and decompose to metallic iron around 300ºC.

Direct Coal Liquefaction Products

There are three main products obtained from coal liquefaction, solid residue, liquid oil, and gaseous product. The solid and liquid products of direct coal liquefaction are defined by their solubility in specific solvents from lighter hexane soluble fractions to heavier tetrahydrofuran (THF) liquid fractions. The direct coal liquefaction liquid product can be used for the production of gasoline and diesel fuel with additional processing for jet fuel, utility fuel oil, and other fuel blends. The solid, or residue, products can be used in different applications, such as being utilized to produce hydrogen via gasification or process heat in a boiler. It has also been suggested that it may be possible to market direct coal liquefaction residues as a coke for metal production (i.e.aluminum and vanadium).[72]

Liquid products obtained from coal liquefaction are produced from the cleaving and hydrogen capping of the initial coal's structure; therefore, some of the initial coal components are found in the liquid products. Most of the liquids produced in direct coal liquefaction are highly naphthenic and aromatic. Many of the inorganics in the liquids are likely organically bound.[73] The THF-soluble products of direct coal liquefaction may only have an H/C atomic ratio of 1.1-1.4 and contain a higher concentration of nitrogen, oxygen, sulfur, inorganic species, and aromatic compounds when compared to petroleum products. These liquids would still have to enter refining processes and upgrading to form more marketable transportation liquid fuels.[6] After distillation, these liquids contain higher yields of naphtha, kerosene and heavy fuel oils and lower yields of gas oils when compared to natural crude oil yields.

Mechanism of Coal Liquefaction

The mechanisms of coal liquefaction have been already been established and most scientists agree are radical based mechanisms.[37-43,74-82] Understanding of the chemistry of coal liquefaction is essential if the processes for mobilizing the carbon matter in coal to liquid fuel are to be optimized. Curran et al.[64] studied the mechanism of hydrogen-transfer reaction in coal and coal extract. In his study, the conversion of the coal molecules to soluble products was correlated to the amount of hydrogen consumed in the process.[64] His proposed radical based mechanism focuses on the cleavage of carbon-carbon bonds in the coal molecules.[38] In this mechanism, the radicals produced in the initial reaction, $R_{1,}$ react with other coal molecules or with hydrogen atom donor-solvent molecules, to form other radicals. Several recombination reactions terminate these radicals. Reaction 1.1-1.6 is a representation of a generic reactions sequence.

$$R'\text{-}CH_2\text{-}CH_2\text{-}R'' \xrightarrow{\text{H\& P}} R'CH_2^{*} + R''CH_2^{*} \qquad \text{Eq. 1}$$

$$R\text{-}CH_2^{*} + H_2 \longrightarrow R\text{-}CH_3 + H^{*} \qquad \text{Eq. 2}$$

$$R'\text{-}CH_2\text{-}CH_2\text{-}R'' + H^{*} \longrightarrow R'\text{-}CH_3 + R''CH_2^{*} \qquad \text{Eq. 3}$$

$$\begin{aligned} R'\text{-}CH_2\text{-}CH_2\text{-}R'' + R'''CH_2^{*} \longrightarrow\ & R'''CH_3 + R'CH{=}CH_2 \qquad \text{Eq. 4} \\ & + R''CH_2^{*} \end{aligned}$$

$$R'\text{-}CH_2^{*} + R''CH2^{*} \longrightarrow R'\text{-}CH_2\text{-}CH_2\text{-}R'' \qquad \text{Eq. 5}$$

$$R'\text{-}CH_2^{*} + H^{*} \longrightarrow R'\text{-}CH_3 \qquad \text{Eq. 6}$$

note:. $R \neq R' \neq R' \neq R'''$

He concluded that presence of aromatic and hydro-aromatic molecules found in coal stabilize radicals derived from these structures. Moreover, methyl and hydroxyl groups increase the free radical reactivity of the molecules to which they are substituted.[64] Shi et al.[38] considered the process of coal hydrogenation reaction to be a three steps process. In the first step, the smaller molecules associated with coal structure units are released, some as some gases and water.. In this step, some of the weaker bonds in the coal structure are ruptured to form free radicals which react with hydrogen atoms from donor solvent and/or H_2. In the second step, conditions are more vigorous and chain reactions occur quickly. The covalent bonds of coal structure units are attacked by radicals to form some asphlaltenes. In the third step, asphlaltenes are hydrogenated from more liquids and some gases. In coal liquefaction, the second step of coal hydrogenation reaction should be controlled to avoid integration of radicals, and the third step of coal hydrogenation should be accelerated to increase the coal conversion and the oil yield. In many respects, liquefaction is closely related to pyrolysis and they share a similar mechanism.

Chapter 2

The UTA-CTL Process

Introduction

This chapter will describe the development of direct coal liquefaction (DCL) technology by the CREST team at UTA which uses inexpensive, lignite coal as the feedstock. The UTA CTL process has been successful with liquefaction yields up to 60% of the theoretical value and a synoil product is similar in characteristics to medium to heavy sweet crude. The biggest differences being the relatively high oxygen content (~5%) and aromatic content (~60%) of the synoil product relativel to crude oil. While DCL had been previously explored in the US with higher grade coals, Texas lignite had not been previously examined.[83-85] None of these previous DCL technologies are currently in large scale use, due to the high costs associated with processing the coal at pressures that exceed 2000 psi and the quality of the resulting synoil is often not enough to merit the cost. At one time, there were four major coal liquefaction pilot plants that were operating in the U.S., however, all of them experienced problems with high capital and production costs. A commercial plant based on the UTA CTL process may be more economical because the operating conditions are less harsh than those previously reported, and the related capital costs will be significantly lower.

UTA CTL Process Rational

The UTA process described herein uses lignite coal for the coal liquefaction process, which is the cheapest and lowest quality coal mined. There is an estimated total deposit of 43 billion tons in the United States.[86] Figure 5 shows the deposits of lignite in United States, the largest lignite deposits are in the northern Great Plains, under parts of North Dakota, South Dakota, and Montana. Large deposits of lignite are also found in the southern region of the Gulf Coastal Plain including Texas and Louisiana. Both of these states have actively mined and used this lignite for electric power generation since the 1980s..

The price of lignite coal in the United States market as of 2010 was ranged between USD $ 50 and 55 per metric ton, because of its low energy density, high ash and moisture content. Lignite is inefficient to transport and is not traded extensively on the world market compared with higher grade coal. Lignite coal produces an average of 13 million BTU per ton and has higher emissions of nitrous and sulphurous oxides (NO_X and SO_X) when compared to higher rank coal, which is why it is used almost exclusively in the production of electricity. However, the use of lignite for generation of electricity is not the best use of this coal because of its low heat value.

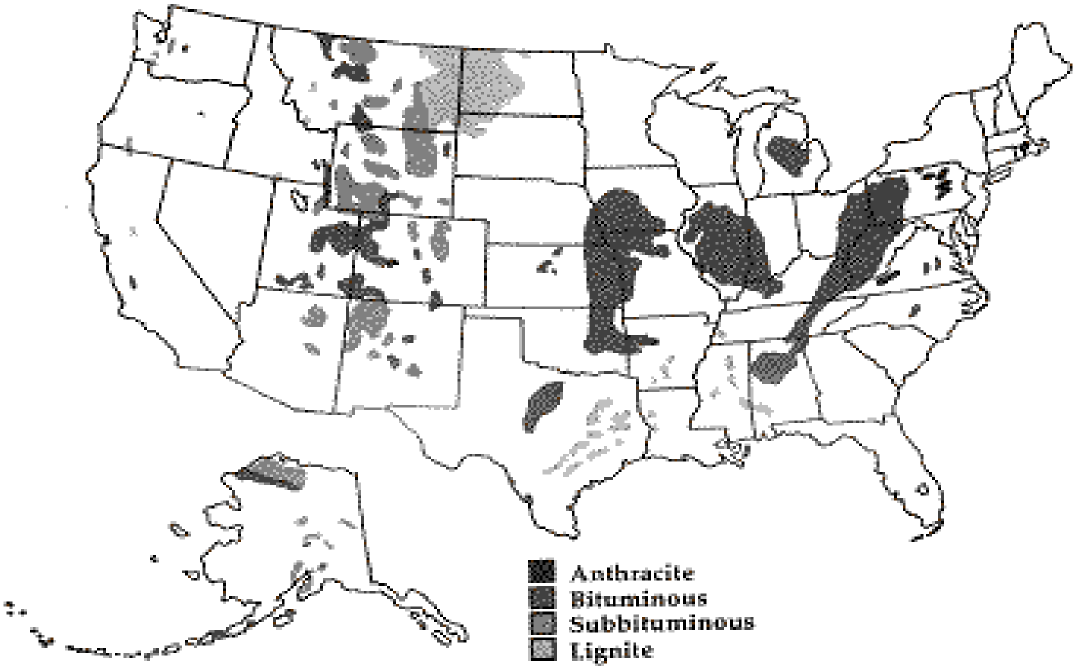


Figure 5 Deposits of lignite in The United States based on rank and geographic areas. Coal fields of the United States. Coal rank not distinguished in Alaska.[87]

Conversion of lignite to snyoil may be a better use for this resource since it already has a relatively high hydrogen content (useful hydrogen - already bonded to carbon) and it has a open and reactive structure. We examined and optimized a low pressure method for the conversion of lignite to synoil to determine if yields and oil quality could be obtained to make this process more economically favorable. As with most DCL processes, a solvent was required and we chose to use the synoil product as the solvent (as is frequently done) to minimize cost and because such solvents have been shown to be quite good at dissolving the depolymerize coal (like dissolves like). Because in a DCL process more oil is produced than is used as a solvent, a portion of the product can be siphoned off while the majority is recycled to produce the next batch of synoil. With continuous operation the solvent is constantly being made, recycled, and removed to achieve a steady state composition. Figure 6 is a simple scheme block diagram showing the major operations in the DCL process. Typically the solvent is rehydrogenated with H_2 in a separate step over a transition metal catalyst. In our process, we eventually settled on adding H2 directly to the liquefaction reaction so as to aid with the liquefaction and to rehydrogenate the solvent in one step. This simplication helped reduce the time and complexity of the process which helps reduce the cost of production.

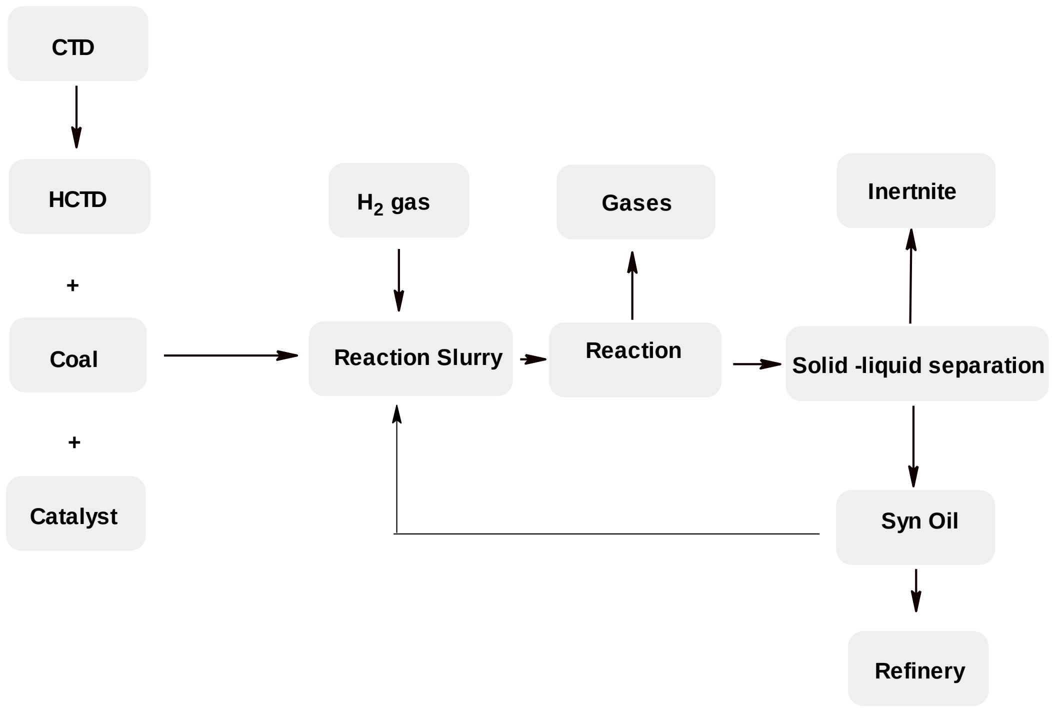


Figure 6 Schematic of the UTA process and the hydrogen donating solvent recycling though the process.

Addition of molecular hydrogen to the carbon skeleton of coal requires a catalyst to assist with the Iron based catalysts are the most common catalytic material for coal liquefaction.[69,88-91] Iron-sulfur and iron-oxide in varies forms have been successfully employed for direct hydrogenation during coal liquefaction on an industrial scale.[69,89,92] The preference for iron based catalysts is related to economic and chemical reasons. Iron is an inexpensive highly abundant element. In addition iron complex catalysts report reactivity toward hydro-liquefaction of lignite coals. For that reasons an iron catalyst was utilized in the liquefaction of coal with a hydrogen-donor solvent. This liquefaction catalyst can be added to coal as a fine powder, supported over Al_2O_3 or as dispersed catalyst.[93-95]

Most of direct CTL processes use harsh operating conditions of high temperature and pressure and/or multi-stages reactors.[19] In some cases they use relatively expensive catalysts or hydrogen donating solvent.[96-97] It is these conditions that increase the capital costs of the equipment which decreases the economic efficiency of the process.[98] As noted in chapter one, most of the direct CTL processes, use slurry of crushed coal and are heated under high pressure to depolymerize and hydrogenate of the coal structure. Hydrogen can be added directly as a gas or is donated by the solvent or some other component. The typical minimum operating pressures and temperatures in those processes are typically 2000 psi and 400° C. In this thesis, we examined the ability to run the DCL process at pressures of 1000 psig or less, while varying time, temperature, solvent, and catalyst. In a few reactions, pressures of up to 1500 psi were examined simply to see if product yields would significantly increase. In all cases, yields were insensitive to this relatively minor increase in pressure and 1000 psi served as the upper limit for most parametric testing. This simple improvement, a 50% reduction in maximum operating pressure, could represent a major advance in improving the economics of this technology.

Chapter 3

The UTA Process Optimization

Introduction

The objective of this research was to evaluate the parameters affecting liquefaction of lignite coal at modest operating pressures (~ 1000 psi). Parameters examined included solvent, pressure, reaction temperature, and effect of different coal combinations, reaction time, and initial hydrogen pressure were evaluated in terms of the oil product obtained as THF soluble materials and conversion of the solid coal to gases and liquids. The most challenging factor we faced in this process was that coal samples vary in ash, moisture, fixed carbon, and volatile matter. This makes duplication of the experimental results difficult and requires a careful consideration of the input/output data to draw specific conclusions. For example, based on the proximate analysis of various coal samples studied though out the course of this research, it was clear that lignite coals differ widely is moisture, ash, volatile and fixed carbon composition. Even coal samples from the same mine have variation in the proximate analysis. Nonetheless, we were able to demonstrate that lignite was very susceptible to digestion under the conditions we developed, and it can used as feed stock for a coal liquefaction plant with a conversion yield of 80% and oil product yield of 60%.

The question now is what are the optimum conditions to achieve the highest conversion yield? To answer this question, two things need to be focused on 1) the reaction feeds and 2) the reaction conditions. Several studies have been conducted evaluating the various parameters and feeds on coal conversion.[37,59,67-68,99-108] Studies reporting high yield coal conversion typically required temperature range between 360°C to 425°C and pressure above 2000 psig. Pinto et.al.[100] studied the effects of the temperature, pressure, reaction time, and catalyst loading on liquefaction with sub-butimous coal. Pinto's research shows a correlation between synoil yield and the reaction temperature, catalyst loading, pressure and time. High conversions were obtained at 400 °C but with higher temperatures no change in the yield was noted. In addition, an increase of the reaction time to 45 min shows no effects in the yield. They reasoned that to the completion of the reaction at the first 15 min. The catalyst loading and pressure also had their effects in the oil yield and total conversion. 100% conversions were obtained at 3200 psi pressure. Those studies should set a starting point for what is needed to be done in regard of finding the optimum conditions to achieve high quantity and quality synoil.

Experimental Section

Chemicals and Materials

Reagent grade Al_2O_3 (Particle size?? other details…pores size 0.53mL, CAS# 1344-28-1), THF (CAS# 109-99-9), $Fe(NO_3)_3{\cdot}9H_2O$ (CAS# 7782-61-8), and Na_2SO_4(CAS# 7757-82-6 were purchased from VWR Chemical Company's. Diesel and Jet-A fuel samples were obtained from local sources. Coal samples were provided from several sources, but predominantly from local active lignite mines operated or leased by Luminant or NRG power companies. Powder River Basin (PRB) sub-bituminous coal was obtained from an active mine in Wyoming. Australian lignite was provided by Greenpower Energy LTD, West Perth, Western Australia.

Instrumentation

Two Parr pressure reactors were used during the course of these experiments. A small scale reactor (model numbers 4848) had a reactor volume of 450 mL and was made of type 316 Stainless Steel. This reactor was equipped with a pressure gauge, thermocouple, high torque magnetic derive stirring impeller, safety rapture disk tuned to 2000 psi maximum pressure, confined and contained flat PTFE Gaskets for Temperatures to 350 °C . The large scale reactor had a 2 gallon in reaction volume (model numbers 4848) and was made of type 316 Stainless steel. The large scale reactor was equipped with a pressure gauge and temperature controller, thermocouple, high torque magnetic derived stirring impeller and controller, safety rapture disk tuned to 2000 psi maximum pressure, confined and contained flat PTFE Gaskets for temperatures to 350 °C.

Syntheses

Coal tar distillate (CTD)

CTD was prepared by heating crushed coal in a three neck round bottom flask reactor to 410°C in the presence of inert gas atmosphere. Effluent gases were cooled and the liquid products collected in condensing column at temperature of 5 °C. The CTD and water were collected and then separated first by simple decanting. Further separation was obtained by heating the oil to 200 °C before it centrifuged, the water layer was removed by vacuum suction.

Hydrogenated oil coal tar distillate (HCTD)

In a typical run, CTD was reduced to HCTD using the following procedure. CTD (100 g) and BXF1(6.0 g)) were placed in the 450 mL Parr Reactor, the reactor sealed, mechanical stirring begun, and pressurized to 400 psig with hydrogen gas. The hydrogen feed was closed (static feed) and the closed reactor was heated at a rate of 15 °C/min to 360 °C and then held at this temperature for 2 h.. During this period, the reactor pressure increased to a maximum value of 800 psig at 360 °C. After cooling, the vessel was vented, opened, and the mixture was diluted with THF and decanted from the autoclave at 75C, dried over Na_2SO_4 and filtered by vacuum filtration using a coffee filter.

Coal Liquefaction Experiments (DCTD)

In a typical run, synoil or digested coal tar distillate (DCTD) was produced using the following procedure. A mixture of lignite coal (25.0 g, sometimes pretreated or dried, sometimes not), HCTD (50.0 g), and fresh catalyst (3.00 g, i.e. BXF1) were added together in the autoclave. The vessel was sealed, mechanical stirring begun, and pressurized to 300 psig with H_2 (static) and then heated at a rate of 15 °C/min to the desired temperature (i.e. 320 °C). The reaction was kept at the final temperature for a period (i.e. 30 min) after which it was cooled either by turning off the oven or by removal from the oven (for faster cooling). During the reaction period, the pressure was monitored and usually increased to somewhere between 700 and 1000 psig. In some reactions, the pressure was made up to 1000 psig once the set point temperature was reached.

Workup: After cooling, the vessel is depressurized (in some case theses gasses were trapped for further analysis) and the mixture slurry was removed from the autoclave.

The oil was extracted by two different methods:

1. The first method (THF method) involves diluting the slurry with THF and filtering by vacuum filtration. The filter cake was washed with THF and. The whole THF extract was dried over $MgSO_4$ and filtered again. The THF was then removed from the filtrate using a rotary evaporator monitored by ^{1}HNMR. The liquid fraction that was soluble in THF was referred to as oil. The THF-insoluble fraction (inertnite) is further dried in the oven at 104 °C.

2. The second method involves opening and depressurizing the reactor while the slurry is still relatively hot (~ 75 C) and filtering the slurry through a 170 mesh sieve. This method does not involve a diluents but results in greater synoil losses due to retention/sticking to

the reactor walls and retention of some synoil in the filter cake. Analysis of this synoil reveals that some suspended solids are found in the synoil. This method was only used when a diluents treatment was not desirable.

Effects of Feedstock and Reaction Parameters on Lignite Coal Liquefaction

The UTA DCL process initially focused on the liquefaction of lignite coals because this feedstock is both abundant , inexpensive, and local in Texas.. As previously mentioned, the BTU content of lignite is typically quite low (i.e. 8000 BTU/mT) relative to higher-grade coals. This is due to the relatively high moisture and ash content and low fixed carbon content. Lignite also typically contains an appreciable volatile content. This is desirable for DCL applications as volatiles component typically have favorable H/C ratio. The mild conditions of the UTA DCL process make it a feasible process for the production of synoil from lignite coal.

In order to discuss the UTA DCL process we must first consider the coal characteristics, specifically in terms of the proximate analysis: moisture, ash, volatiles, and fixed carbon. While these vary considerably among coals, lignite typically contains 25-30% moisture, 10-30% ash, 20-30% volatiles, and 20-40% fixed carbon.

Coal Characterization:

Proximate analysis was performed on the coal using thermogravimetric techniques.. A representative TGA scan on lignite (NRG2) is shown in figure 3. In brief, the scan shows two heating curves, 1) heating rate at 10°C/min to 800°C under a nitrogen atmosphere, and 2) heating rate at 10°C/min to 800°C in air. Analysis of these two curves can quickly give the moisture, volatile matter, fixed carbon, and ash content on a percent basis. Ash content measured by TGA is in close agreement with that determined by ASTM methods.[109] When coal samples are brought to 150°C under nitrogen and held for 10 min or to constant mass, the weight loss is a measure of the moisture content.

Figure 7 and Table 2show the proximate and ultimate (CHN) analysis for lignite and sub-bituminous coal samples. Proximate analyses were obtained by TGA and ultimate analyses by CHN analyses.. Ultimate analysis is typically a complete elemental analysis of the coal. This was not frequently practiced; however, CHN and sometimes S were obtained in all coal samples.

The theoretical yield was based on maf coal; subtracting the amounts of moisture and ash from the initial weight of coal correspond to the theoretical yield. This is likely an overestimate, as the maf lignite undoubtedly contains an appreciable amount of C-O species, of which the oxygen will mostly be lost as water. Regardless, this is an easy and straightforward measurement of potential oil yield and was used as proximate analytical data was readily available. In certain cases, where a full ultimate analysis was obtained, further refinement of this yield is possible. Importantly, this method of calculating theoretical yield will always overestimate the yield, meaning that further corrections will only improve our yield data.

The oil yield percent was the THF soluble fraction divided over the theoretical yield as it defined by eq 1. Where the conversion present was defined by the maf lignite mass lost as eq 2 illustrates.

$$\text{Oil Yield } (\%) = \frac{\text{THF} - \text{soluble fraction (g)}}{\text{Theoretical yield(maf)}} \text{ X } 100\% \qquad \text{Eq. 1}$$

$$\text{Percent Conversion } (\%) = \frac{\text{mass of lignite(maf)} - \text{mass of inertnite(maf)}}{\text{mass of lignite(maf)}} \text{ X } 100\% \quad \text{Eq. 2}$$

The theoretical yield represents the sum of the masses of fixed carbons and volatiles present on the coal sample. Oil yield gives the amount of lignite converted to liquid oil product. The percent conversion gives the total amount of lignite converted to gas and liquid products.

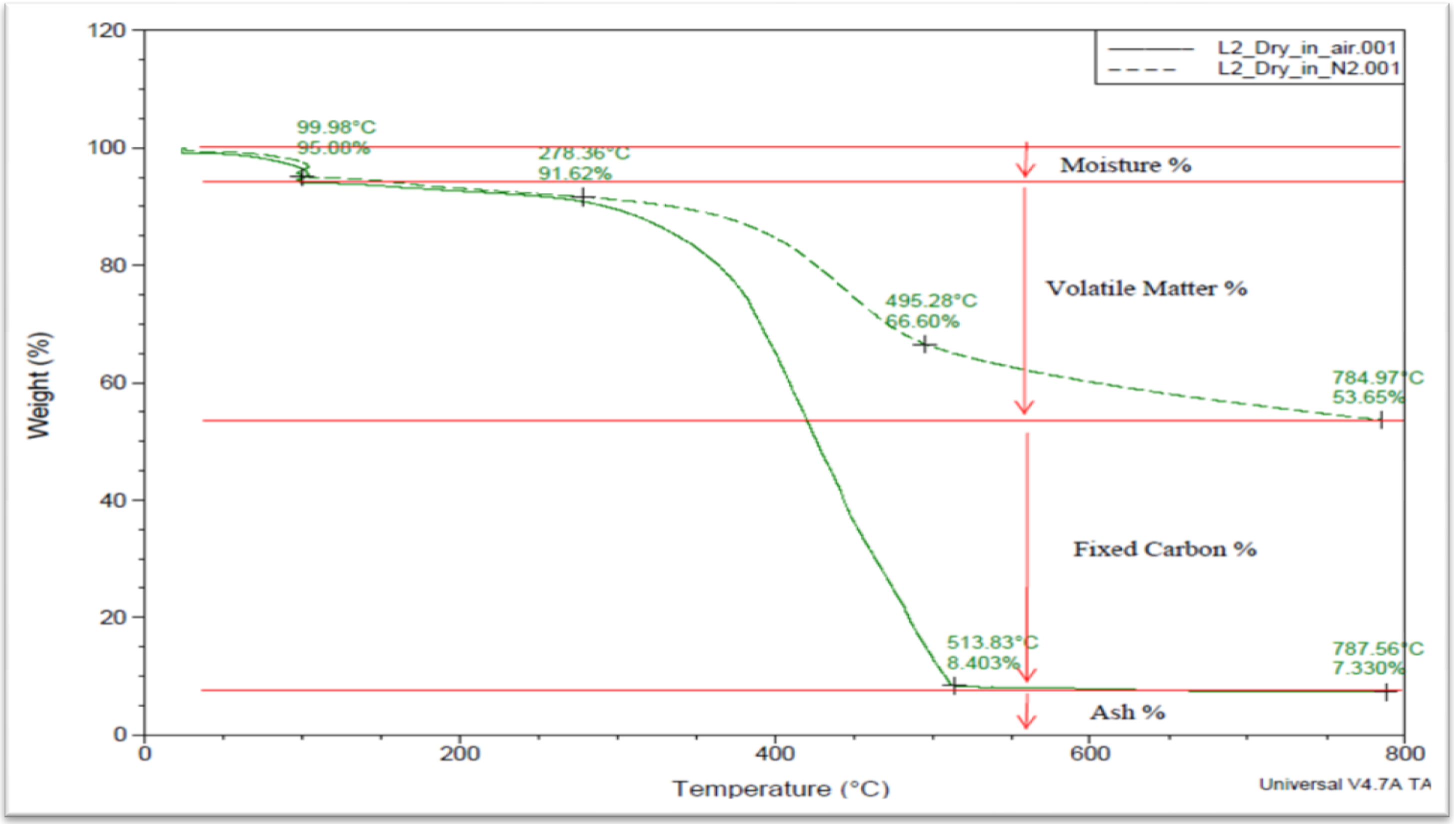


Figure 7 The Proximate analysis of a sample of lignite (NRG2) as determined by the TGA. Two runs are required, one under an N2 atmosphere (solid line) and the second under an air atmosphere (dotted line). The % moisture, ash volatiles, and fixed carbon are determined as shown.

Table 2 The proximate andCHN analyses of the coal used in this dissertation. Proximate analyses were obtained by the TA Q50 TGA at flow rate of 10 mL min^{-1} at heating rate of 10 °C min^{-1} from 250C to 1000° C. The CHN analyses was obtained by Perkin Elmer CHNS Analyzer.

Coal	Fixed carbon %	Ash %	Volatile matter %	Moisture %	Carbon %	Hydrogen %	Nitrogen %
Jewett	23	15	31	31	42.51	3.58	1.02
LAL (form Jewett)	40	9	28	23	51.71	3.56	0.99
Benton	20	7	39	34	63.66	6.62	0.73
Bauxite	21	16	25	38	47.35	4.64	0.71
Malvern	18	26	25	32	45.35	4.25	0.66
NRG	34	11	31	24	42.08	3.23	0.80
LUM	42	8.5	18.5	32	61.12	4.70	1.38
LUM1	32	18	22	28	52.25	4.93	1.03
LUM2	32	9	29	30	64.60	5.20	1.23

Table2 — Continued

LUM3	42	20	7	32	59.73	4.75	1.17
NRG2	34	13	23	30	54.56	4.23	0.93
AUC	21	1	18	60	63.05	4.99	0.56
Kasse1	30	13	26	30	43.67	4.31	0.87
WVU	41	13	36	10	56.88	4.09	1.06
SUB1	53	7	30	9	66.72	4.57	1.53
LUM4	29	15	26	30	45.17	4.28	0.88
LUM4 P1	42	16	30	12	52.25	4.98	0.95
LUM4 P2	24	22	34	20	49.62	4.58	1.02
PRB	n.d	n.d	n.d	n.d	65.11	5.23	0.92
AUCH	51	2	47	0.0	65.19	5.12	0.90
AUCD	51	2	47	0.0	63.80	4.72	0.52

n.d : not determined

Parametric Studies

The liquefaction process was partially optimized though a series of parametric studies examining parameters such as solvent, solvent/coal ratio, coal quality, temperature, partial pressure of H_2, partial pressure of water, catalyst composition and loading, stirring rate, reaction time, and reaction cycle. The crude data from all these studies were collected in a master table which recorded the various experimental parameter and recorded synoil yield and quality as assayed by CHN analysis. This master table which lists each experimental run chronologically is a (Table 1) is shown in Appendix G. Select data from individual runs was extracted from this table in the sections that follow. These runs were related in that, ideally, a single variable was altered systematically. However, it should be noted that over time, we would consume all of a particular lignite stock and could not always replace it with an equivalent lignite, thus absolute comparisons are not always possible. to the extent we were comfortable in making 'cross-coal' comparisons we have done so, usually by normalizing the data by always running at least one digestion under a standard set of conditions (1000 psi H2, 320 C, 3 g BXF1 cat, 30 min residence time, with mechanical stirring).

Effects of Catalyst and Catalyst Loading.

Iron-oxide catalysts have been frequently employed as coal liquefactions catalysts. BXF1 is a proprietary iron-based catalyst which was employed for the majority of the DCL studies in this thesis. One of the first parameters examined was the effect of catalyst loading on the liquefaction and conversion yields. As shown in Figure 8, reactions involving 0 to 16 mass percent catalyst were performed on 25 g samples of NRG lignite in 50 g HCTD at 320 C and 1000 psi H_2 for 30 min. Yields increased with catalyst loading up to 12 mass % after which no further increases were observed. The THF-soluble or liquid yield peaked at 45 % with a corresponding 80 % conversion overall. Higher loadings do not further improve the yield and are avoided so as to minimize catalyst. The initial drop in conversion yield upon addition of BXF1 was counterbalanced by an increase in liquid yield, indicating that the presence of the catalyst inhibited gasification and favors liquefaction.

Ibrahim et al,[110] tested nine Fe oxide-based catalysts for their hydrocracking abilities of Blind Canyon lignite coal, and found that, above 350°C, the catalyst loaded samples yield a higher free radicals density ratio comber to none a catalytic process in all nine catalysts. He correlates the high free radical dentistry ratio to hydrocracking abilities of the catalyst, which correlates to the liquefaction of coal. In addition, Watanabe et al,[71] studied the hydroliquefaction of Japanese Miike lignite coal using various iron complexes as catalysts in tetralin at 375-445 °C. In his study $Fe(CO)_5$ showed the highest catalytic activity, increasing coal conversion by about 10% at 425 °C under an initial hydrogen pressure of 750 psi. Amount of hydrogen transfer to the coal increased from 1.4-2.3 wt% of maf coal in the absence of the catalyst to 2.5-4.2 % of maf coal in the presence of $Fe(CO)_5$ at 425°C. Watanabe observed that the presence of iron compounds increases not only the conversion % but also increases the yield of liquid product, which is consistent with our data. Our observations of the catalyst loading indicate that the catalyst is essential for increasing the yield of synoil presumably by enhanced hydro cracking and formation of free radicals at this relatively low temperature (320 C).

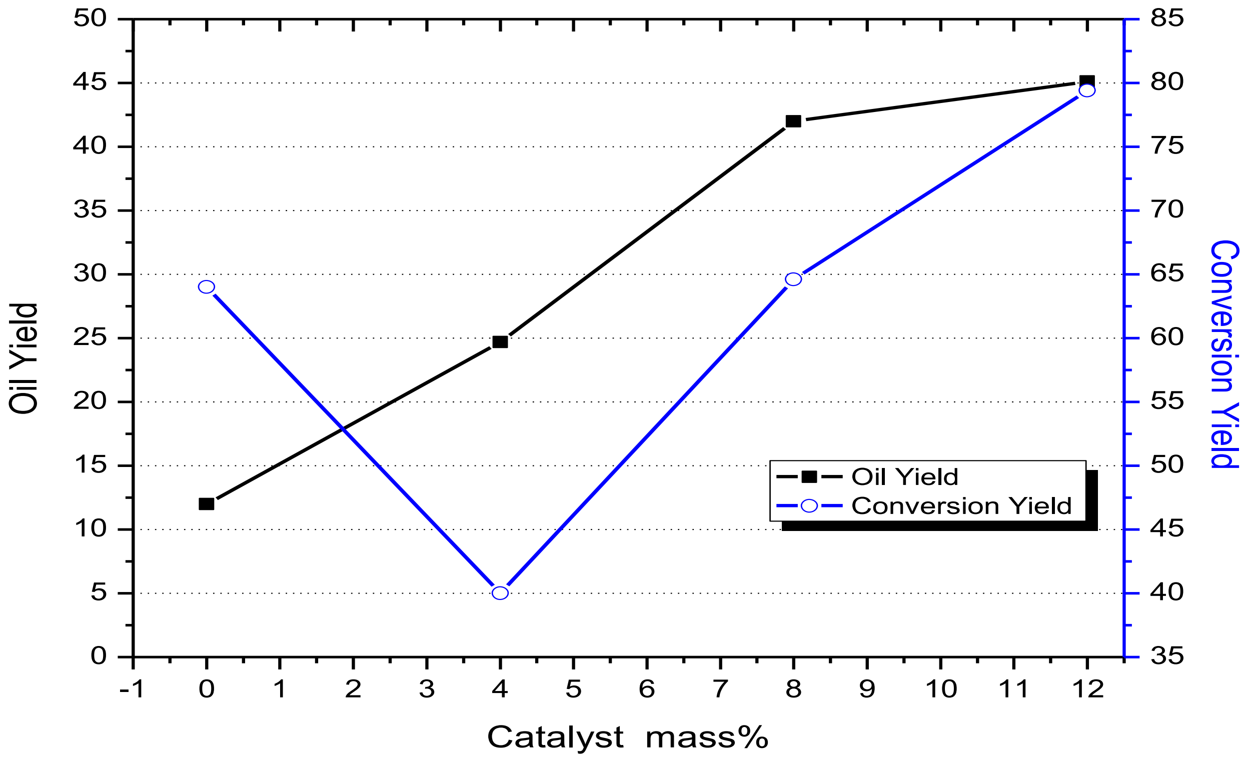


Figure 8 Effects of catalyst loading on coal liquefaction under normal conditions. Conditions: 1000 psig H_2 pressure, 320°C, 30min resident time, stirring speed 150 rpm, 12% w/w of BXF1catalyst, and 2:1 solvent/coal ratio.

Table 3 Effect of catalyst and catalyst loading on coal liquefaction under normal conditions. Conditions: 1000 psig H_2 pressure, 320°C, 30min resident time, stirring speed 150 rpm, 12% w/w of BXF1 catalyst, and solvent/coal ratio of 2:1.

Ref #	**Coal**	**Catalyst**	**Amountof Catalyst**	**OilYield**	**CHN% analysis solvent**			**Inertnite (g)**
	(g)		**(g)**	**(g)**	**C%**	**H%**	**N%**	**Conversion %**
00	25.0 LAL	None	0.0 g	2.0 12%	a. 83.0 b. 83.2	8.9 9.0	0.9 1.9	6.1 64%
40	25.0 NRG	BXF1	1.0 g	4.0 25%	a. 84.9 b. 85.2	10.4 10.0	1.3 2.7	12.0 40 %
45	25.0 NRG	BXF1	2.0 g	6.8 42%	a. 81.2 b. 85.2	9.0 10.2	0.5 4.6	7.0 65%
34	25.0 NRG	BXF1	3.0 g	7.3 45%	a. 84.9 b. 84.8	10.3 8.7	2.0 5.6	5.6 79%

Effects of Reaction Temperature

Temperature is a critical operating parameter with most liquefaction processes requiring temperatures on the order of 400 C. Initial studies indicated that even lower temperatures were desired in our DCL process. As shown in

Table 4 and Figure 9, the liquefaction yields were the best at 320 C and actually dropped as temperature was further increased to a maximum of 420 C. Conversion yields, on the other hand, increased with increasing temperature indicating that higher temperatures favor gasification over liquefaction. It should be noted that the liquefaction and conversion yields for this particular lignite (LUM4) were, in general, significantly lower than that seen for many other lignites. For example, liquid yields were 20%, 15%, and 10% at reaction temperatures of 320 ˚C, 360 ˚C and 420 ˚C respectively. The proximate analysis of LUM4 revealed it was a relatively high ask coal with 15 % ash and 30 % moisture (or 21 % ash on a dry basis). As will be shown later, ash content can have a significant impact on the liquefaction yields. Nonetheless, the trend in the temperature dependence data is revealing and 320 C was picked as the optimum operating temperature as a compromise between too little heat (where the reactions will presumably be slow) and higher temperatures (where the yield suffers). Oil quality was monitored by taking the CHN analyses of the solvent/synoil before and after each run. This data indicated a constant H/C ratio of 1.4 as the operating temperature increased.

Temperature is one of the key parameters in lignite coal liquefaction. At high temperatures numerous radicals are formed due to bond cleavage reactions. The concentration of free radicals is a function of the weak bonds in the coal structure.[108,111] The outcome of these free radicals depends largely upon the nature of surrounding solvent molecules. In general, low temperatures are not suitable for liquefaction (<300 °C) due to low radical formation rate, while higher temperatures (<450 °C) may also not be suitable since decomposition of the solvent becomes considerable. This indicates the choice of suitable temperature is very important in coal liquefaction. Font et. al. studied the influence of temperature on the co-processing of two types of Spanish lignite. They showed that temperature has a great influence on the conversion and quality of coal. The optimum temperature for coal conversion was between 400 °C and 420 °C. Hu et al.[112] studied the temperature effect in direct liquefaction of Shenhua bituminous coal with an iron catalyst at the heating-up stage for the direct coal liquefaction. Lower temperature is favored for the reaction of coal to pre-asphaltene and asphaltene, while higher temperature is more appropriate for the reaction of pre-asphaltene and asphaltene to oil and gas.[112] Thus, the process temperature at which coal liquefaction occurs can affect the overall conversion and the product yields for each fraction. For untreated high-sulfur coals, reaction temperatures of 400 °C and below tend to favor the formation of increased pre-asphaltene and asphaltene yields. Direct coal liquefaction above 400 °C favors the formation of oil products.[39]

Table 4 Effect of temperature on coal liquefaction under normal conditions. Conditions: 1000 psig H_2 pressure, 30 min resident time, stirring speed 150 rpm, 12% w/w of BXF1 catalyst, and solvent/coal ratio 2:1.

Run #	**Coal (g)**	**Temperature**	**Catalyst**	**OilYield (g)**	**CHN% analysis**		**Inertnite (g) Conversion %**
					C%	**H%**	
127	25.0	320°C	BXF1	4.1	a. 80.0	9.0	18
	LUM4			20%	b. 81.9	8.9	30%
129	25.0	360°C	BXF1	2.9	a. 79.9	9.5	17
	LUM4			15%	b. 81.9	8.9	35%
130	25.0	420°C	BXF1	1.9	a. 76.3	8.3	15
	LUM4			10%	b. 81.9	8.9	45%

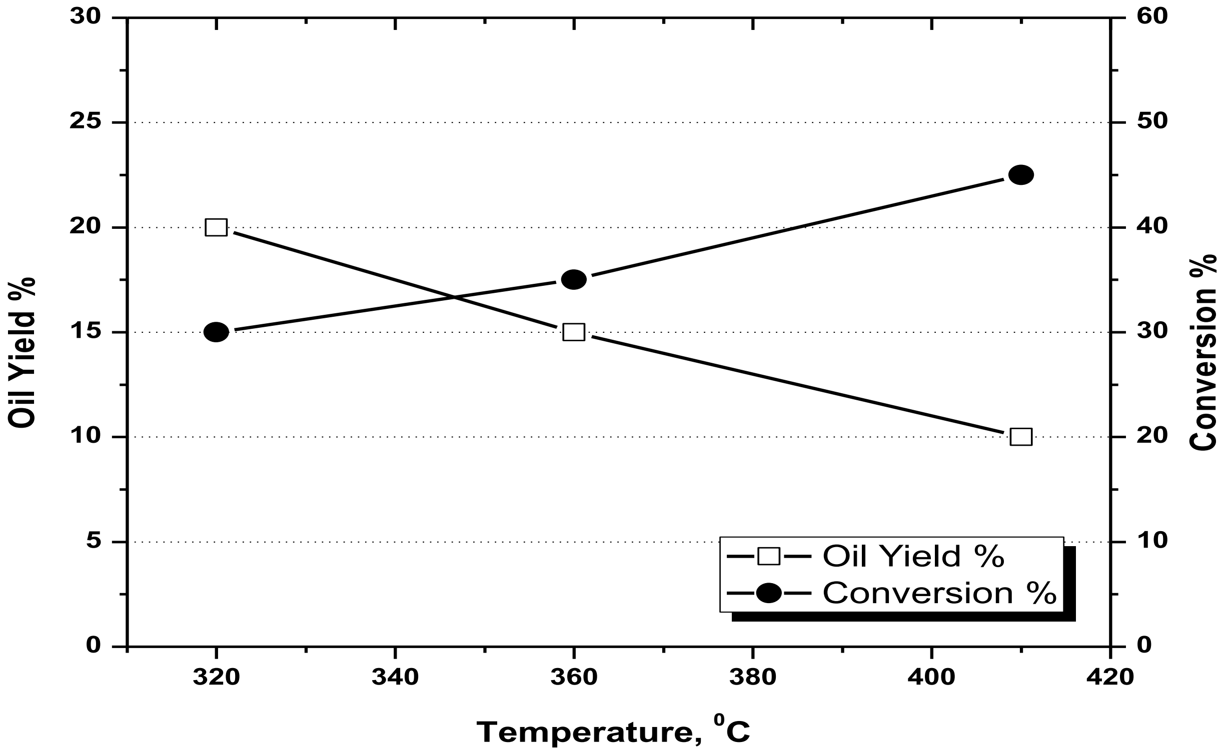


Figure 9 Effects of temperature on coal liquefaction under normal conditions. Conditions: 1000 psig H_2 pressure, 30 min resident time, stirring speed 150 rpm, 12% w/w of BXF1 catalyst, and solvent/coal ratio 2:1.

Effect of Partial Pressure of Hydrogen

In order to evaluate the effect of hydrogen partial pressure on coal liquefaction yield, we performed a set of three experiments at hydrogen partial pressures of 700 psig, 1000 psig and 1400 psig with the other reactions conditions set at 320°C, 30 min residence time, stirring speed of 150 rpm, 12 % w/w of BXF1 catalyst, and solvent/coal ratio of 2:1. The data are shown graphically in Figure 10. As can be seen, the highest synoil yield was 20% which was obtained at 1000 psig H_2. Reaction run at higher and lower pressures gave lower liquid yields but conversion yields were observed to increase as a function of H_2 partial pressure. Oil quality, as monitored by CHN analysis was consistent at a H/C ratio of 1.4 regardless of the hydrogen partial pressure. Cugini et al. [93] studied coal liquefaction, noted that in the presence MoS_2 catalyst, tetralin, at 425 °C, 1000 rpm at 400 psi that coal could be converted as successfully as at 1000 psi without catalyst.[107] The significance of his study is that he reported an increase in the gaseous products with increasing hydrogen pressure.

Hydrogen partial pressure is thought to affect the liquefaction reaction by lowering the recombination of cleaved bond and favoring addition of hydrogen.[67,107] The radicals formed by the coal and the donor solvent activate molecular hydrogen.[38,102] Shi et al. [38] summarized the role of hydrogen in coal liquefaction by two ways. First, some weaker bonds of the coal structure units are ruptured to form free radicals. These radicals are stabilized by hydrogen atoms from donor solvent and/or H_2. Second, radical chain reactions attack the covalent bonds in coal structure units to form asphaltenes and these asphaltenes are hydrogenated to form more liquids and some gases.

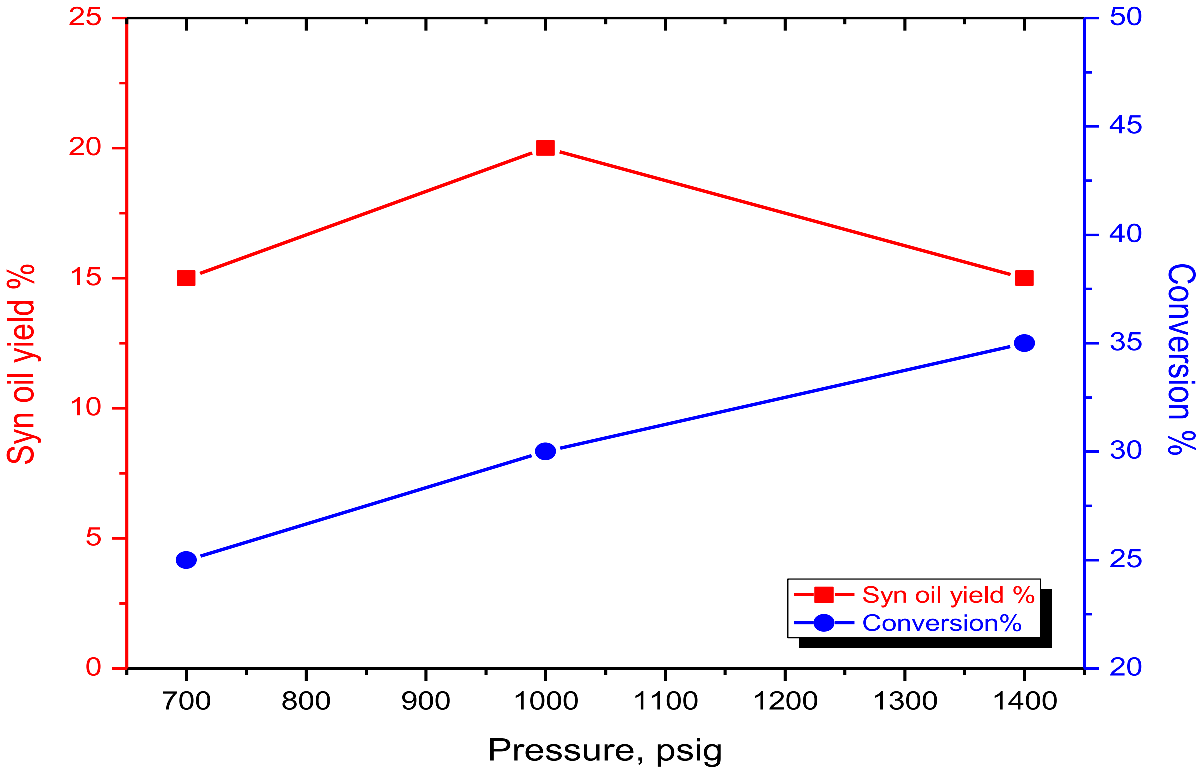


Figure 10 Effects of pressure on coal liquefaction under normal conditions. Conditions: Temperature 320 °C, 30 min resident time, stirring speed 150 rpm, 12% w/w of BXF1 catalyst, and solvent/coal ratio 2:1

The use of syngas (CO and H_2) as a reducing agents was also examined. A liquefaction run on LAL coal was performed under normal operating conditions (1000 psig, 320 ˚C, 30 min resident time, stirring speed 150 rpm, 12 % w/w of BXF1 catalyst, and solvent/coal ratio of 2:1) except that syngas ($2H_2$:CO) was used in place of hydrogen. As shown in Table 5 (Run 29), replacing the hydrogen atmosphere with a syn gas atmosphere resulted in a drop in liquefaction yield from 38% to 11% and in the conversion yield from 84% to 15%. From this, it is clear that the presence of CO has a significant negative impact of the liquefaction process and should be avoided. We assume that the CO poisons the catalyst in that its effect is so dramatic..

Liquefaction runs done on LAL coal in the absence of any external reducing agent (i.e. hydrogen gas) resulted in a synoil yield drop from 38% to 14 %, with a significant drop in oil quality. The LAL in these runs contained 23% moisture by mass. LAL samples dried to 4% moisture (Run 14) were subjected to similar liquefaction conditions in the absence of H_2 and in this case resulted in a synoil yield drop from 38% (with 23 % moisture LAL) to 23% with the dryer LAL(with5% moisture LAL). If we deliberately added additional water, i.e. 23 % moisture in LAL plus another 4% H_2O added externally, the yields also suffered, albeit less dramatically, with a drop to 30 synoil yield. n the absence of hydrogen oil yield in 5% moisture coal was observed to be 23%. Coal conversion shows a decrease in yield from 84% to 72% and 74% in the absence and presence of hydrogen gas at 5% moisture content, respectively. These results of the liquefactions of coal to THF soluble products and coal conversion percent are shown in **Error! Not a valid bookmark self-reference.**. The results show the coal conversion and the oil yield is affected by the type of reductant. Absence of H_2 cause a reduction in the oil yield without a considerably change in the conversion percent, while both oil yield and coal conversion suffers a sharp drop in values as the reactor was filled with 1000 psig synthetic gas. Using this as a base, higher conversion of coal to THF soluble products was observed with addition of molecular hydrogen then with syn gas. The presence of hydrogen as reagent favors the coal liquefaction, while the absence of hydrogen has higher effect on the oil yield than the coal conversion. This signifies the importance of hydrogen gas presence to obtain high liquid yield.

Table 5 Effects of reaction reductant on coal liquefaction under normal conditions. Conditions: 1000 psig H_2 pressure at the reaction temperature, temperature 320 °C, 30 min resident time, stirring speed 150 rpm, 12% w/w of BXF1 catalyst, and solvent/coal ratio 2:1.

Run #	Coal (g)	Catalyst	OilYield (g) (%)	CHN% analysis			Inertnite(g) Conv. %	Conditions
				C%	H%	N%		
10	25.0 LAL	BXF1	6.5 38%	a. 83.5 b. 83.8	9.8 10.2	0.5 0.5	5.1 86%	23% moisture
12	25.0 LAL	BXF1	2.4 14%	a. 83.9 b. 84.0	10.5 10.3	0.5 0.6	5.5g 84%	23% Moisture,w\o H_2
14	25.0 LAL	BXF1	3.9 23%	a. 72.6 b. 83.7	9.1 10.3	0.4 0.5	7.2 72%	1 ml of H_2O w\o H_2
15	25.0 LAL	BXF1	5.1 30%	a. 80.5 b. 82.5	9.6 10.1	0.5 0.5	7.0 74%	1 ml of H_2O, w\ H_2
29	25.0 LAL	BXF1	2.0 11%	a. 85.9 b. 84.6	10.1 10.5	4.2 2.1	17.0 15%	CO and H_2 atomsphere

Effects of Vehicle Solvent and Reaction Cycle

The UTA process uses HCTD as the ‘primer’ solvent for the CTL process. As we are restricted to batch process conditions in the laboratory, the product oil of liquefaction run, hereafter referred to as DCTC , is still predominantly composed of the initial HCTD as typical liquefaction yields increase the solvent mass by 16% or less. A true liquefaction process will use recycled DCTD for subsequent runs. Thus the questions as to how the DCTD changes upon recycling and how those changes affect the coal liquefaction yield are an important issue. Furthermore, the question as to the need to use a coal-derived solvent arose as the process to make CTD and HCTD is time-consuming. Are other oils suitable substitutes for the priming operation?

To answer this, a series of liquefaction runs using AUC coal were performed using four different types of solvent: HCTD from lignite, West Texas intermediate crude oil (WTI), and used motor oil (ExxonMobil, 5W30). The synoil yields and conversion yields are presented in Table 6 Effect of solvent type on coal liquefaction under normal conditions. Conditions: 1000 psig H2 pressure, temperature 320°C, 30 min resident time, stirring speed 150 rpm, 12% w/w of BXF1 catalyst, and solvent/coal ratio 2:1. Synoil yields were Of these three solvents, only HCTD gave any synoil yield (31%) indicating that the solvent plays a more significant role than simply to bring reactants into contact with each other. HCTD derived from sub-bituminous PRB coal ($HCTD_{sub}$) was less effective that HCTD derived from lignite ($HCTD_{lig}$), with yields climbing from 14 % for PRB feedstock with $HCTD_{sub}$ to 71% synoil yield for PRB in $HCTD_{lig}$. This dramatic increase shows that there are important components for the liquefaction process found in lignite derived solvents that are not prevalent in other oil solvents. We speculate that there are Tetralin like compounds prevalent of $HCTD_{lig}$ and that these components aid with the liquefaction process. This yield of 71% was the highest we ever observed in a single batch run and was significant as the coal used was PRB sub-bituminous coal. This is a higher grade coal and is available in large quantity on a low ash basis. Unfortunately, the DCL process is not self-sustaining if we use a sub-bituminous feedstock and a lignite derived HCTD. Because of this we returned to examining lignite feedstock's for the process.

Table 6 Effect of solvent type on coal liquefaction under normal conditions. Conditions: 1000 psig H_2 pressure, temperature 320°C, 30 min resident time, stirring speed 150 rpm, 12% w/w of BXF1 catalyst, and solvent/coal ratio 2:1.

Ref #	**Coal (g)**	**Solvent source**	**OilYield (g)**	**CHN% analysis**	**Inertnite (g) Conversion %**
115	25.0 AUC	Lignite	7.4 31%	a. 83.3 10.0 0.5 b. 84.4 10.1 0.6	11 54%
125	25.0 AUC	WTI	0.0 0.0%	a. 85.6 11.5 0.4 b. 83.5 11.5 0.2	15 38%
126	25.0 AUC	Motor Oil (Exxon Mobil, 5W30)	0.0 0.0%	a. 81.1 8.4 0.3 b. 81.9 8.9 0.3	20 17%
146	25.0 PRB	PRB	2.2 14%	a. 80.7 9.6 0.2 b. 78.5 8.8 0.3	14 26%
147	25.0 PRB	Lignite	14.6 72%	a. 82.0 59.7 0.4 b. 83.2 9.3 0.4	10 52%

In Table7 and Figure 11 the data from four sequential liquefactions runs using AUC lignite are collected. In these runs, the synoil product from the previous run was used as the solvent in the subsequent run, and therefore the solvent was recycled a total of 3 times, the first run used HCTD as a the initial solvent. As can be seen in Figure 11, the synoil yield dropped from 31% in cycle 1 to 21% in cycle 4. Conversion yields also dropped, at least initially, but only by a small factor.

There was also an apparent decrease in synoil quality as the carbon content gradually fell from 83% prior to cycle 1 to 75% after cycle 4. Also associated with the cycle number was an increase in specific gravity, shown in Figure 12,While the drop in liquefaction yields and oil quality were worry some, it was also realized that the THF work-up process was probably responsible, in part, for the data. Because the THF work-up involved extensive extractions and filtrations in air, oxidation of the synoil is unavoidable under these conditions. Similarly, the removal of the THF by rotary evaporation undoubtedly removes some of the lighter fractions of the synoil product, resulting in a heavier synoil than if it was obtained directly. Finally, it was also considered that a build-up of asphaltenes in the synoil product may explain some of the data. Asphaltenes can have dramatic effects on the synoil viscosity and are such that a small increase in asphaltenes can lead to large changes in synoil physical properties. Subsequent attempts to recycle the solvent without a THF work up were not successful as simple hot filtration resulted in significant synoil losses and suspended solids were observed to build-up in the synoil that was collected.

Table 7 Effect of solvent recycling on coal liquefaction under normal conditions. Conditions: 1000 psig H_2 pressure, temperature 320°C, 30 min resident time, stirring speed 150 rpm, 12% w/w of BXF1 catalyst, and solvent/coal ratio 2:1.

Run #	**Coal (g)**	**Catalyst**	**OilYield (g)**	**CHN% analysis**	**Inertnite(g) Conversion %**	**Density**	**Notes**
115	AUC 25.0	BXF1	7.4 31%	a. 83.3 10.0 0.5 b. 84.4 10.1 0.6	11 54%	0.81g/mL	DCTD1
116	AUC 25.0	BXF1	6.7 28%	a. 82.2 9.6 0.5 b. 83.3 10.0 0.5	12 50%	0.87g/mL	DCTD2
117	AUC 25.0	BXF1	6.0 25%	a. 79.6 8.7 0.3 b. 82.2 9.6 0.5	13 46%	0.96g/mL	DCTD3
118	AUC 25.0	BXF1	5.0 21%	a. 75.9 8.9 0.3 b. 79.6 8.7 0.3	12 48%	1.01g/mL	DCTD4

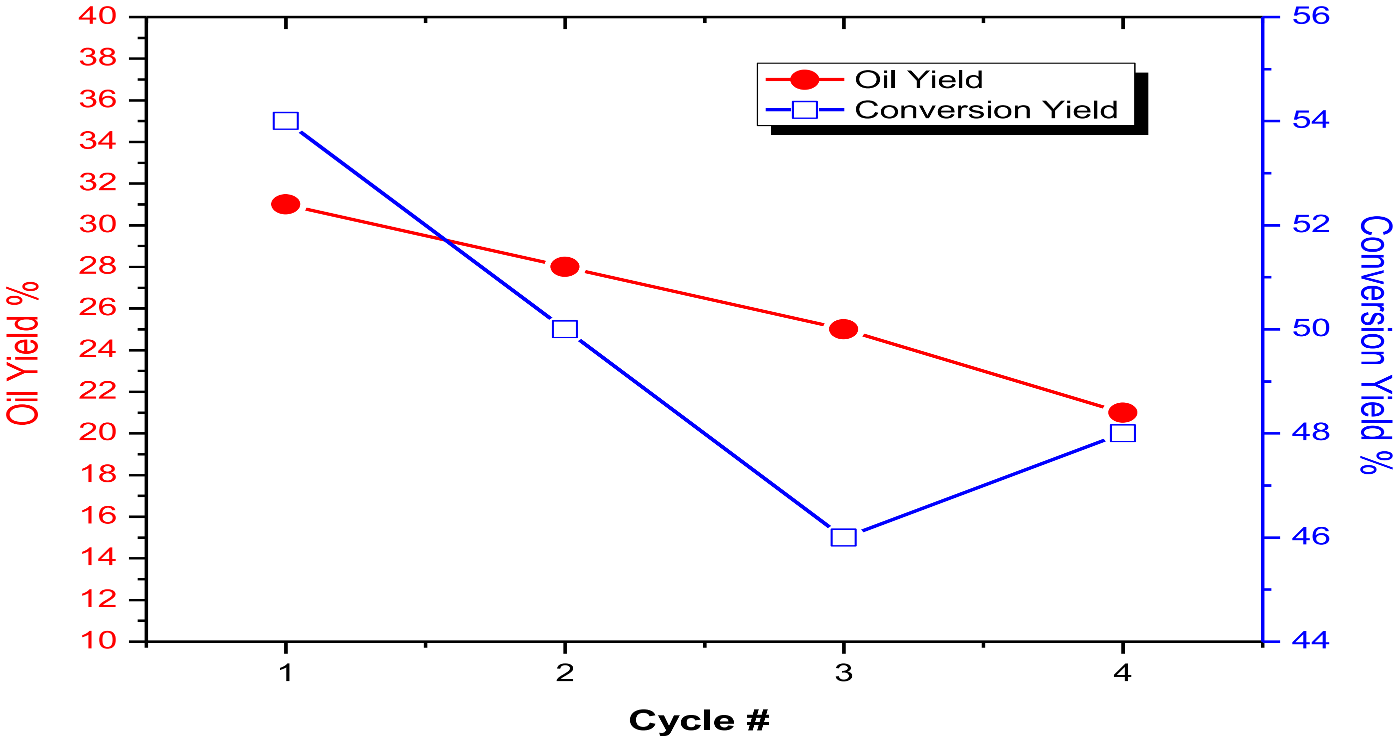


Figure 11 Effect of solvent recycling on coal liquefaction under normal conditions. Conditions: 1000 psig H_2 pressure, temperature 320°C, 30 min resident time, stirring speed 150 rpm, 12% w/w of BXF1 catalyst, and solvent/coal ratio 2:1.

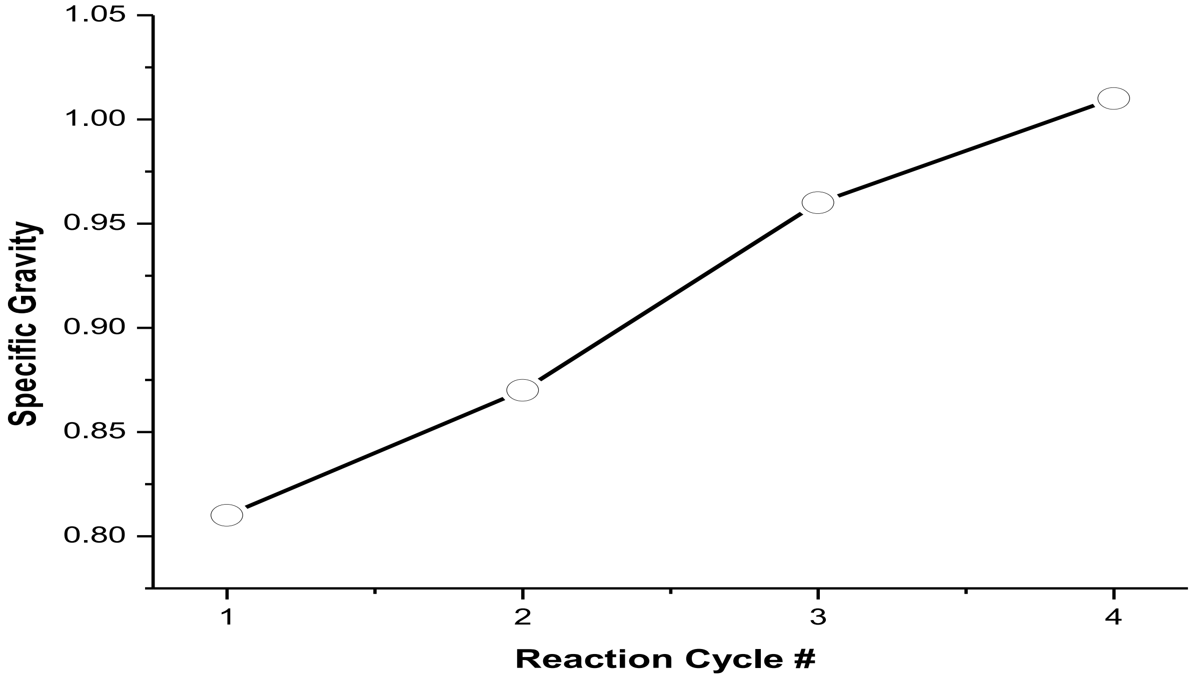


Figure 12 Effects of solvent recycling on syn oil specific gravity under normal conditions.Conditions: 1000 psig H_2 pressure, temperature 320 °C, 30 min resident time, stirring speed 150 rpm, 12% w/w of BXF1 catalyst, and solvent/coal ratio 2:1

Effect of Moisture and Ash

There are two types of moisture content in coal. Free water and water formed upon the decomposition of the coal structure. Free water is generally removed by heating the coal at temperature around 100°C for a period of time until a constant mass is achieved. The decomposition water requires temperature in excess of 200°C to remove and accounts for some of the volatile components mass.

As all lignite contains some free water, we examine the effect of free water content, on a percent basis, on the liquefaction process, specifically on the synoil yield and conversion yield.

Table 8 shows the data from five liquefaction runs with lignite containing 0.0% to 23% moisture were run under usual reactions conditions. Figure 13 shows the liquid yield and conversion yield as a function of moisture content. Apparently, some water is good for the liquefaction process with a maximum in synoil yields seen between 10 and 20 % moisture. Conversion yields are best with a little or no water (less than 5%) or a lot of water (greater than 20%) but in those cases gases are the dominant products. Gas yield is minimized between 10 and 20% moisture, where liquid yields are maximized, showing an obvious sweet spot for a DCL process. The drop of synoil yield in the dry coal to the model proposed by Artok at el, and Song et al.[113] These authors attributed large changes in the lattice structure of the coal, depending on the drying method.[60,113] They suggested that the complete removal of moisture causes a destruction of the coal lattice leading to an accumulation of coal particles and a reduction of catalyst permeability.

Table 8 Effects of moisture % on coal liquefaction under normal conditions. Conditions: 1000 psig H_2 pressure, 320 °C, 30 min resident time, stirring speed 150 rpm, 12% w/w of BXF1 catalyst, and solvent/coal ratio 2:1.

Ref #	**Coal (g)**	**Catalyst**	**OilYield (g)**	**CHN% analysis**	**Inertnite (g) Conversion %**	**Conditions**
12	17.5 LAL	BXF1	2.4 14%	a. 83.9 10.5 0.5 b. 84.0 10.3 0.6	5.5 82%	dry
15	19.0 LAL	BXF1	5.1 30 %	a. 80.5 9.6 0.5 b. 82.5 9.6 0.5	7.0 68%	5% moisture,
90	16.4 AUC	BXF1	12.1 50%	a.83.1 9.1 4.2 b.83.5 9.72 1.34	12.2 53%	10% moisture
75	25.0 AUC	BXF1	8.5 45%	a. 84.1 8.1 5.1 b. 83.8 9.7 2.7	12 54%	20% moisture
10	25.0 LAL	BXF1	6.5 38%	a. 83.5 9.8 0.5 b. 83.5 9.8 0.5	5.1 85%	23.0% moisture

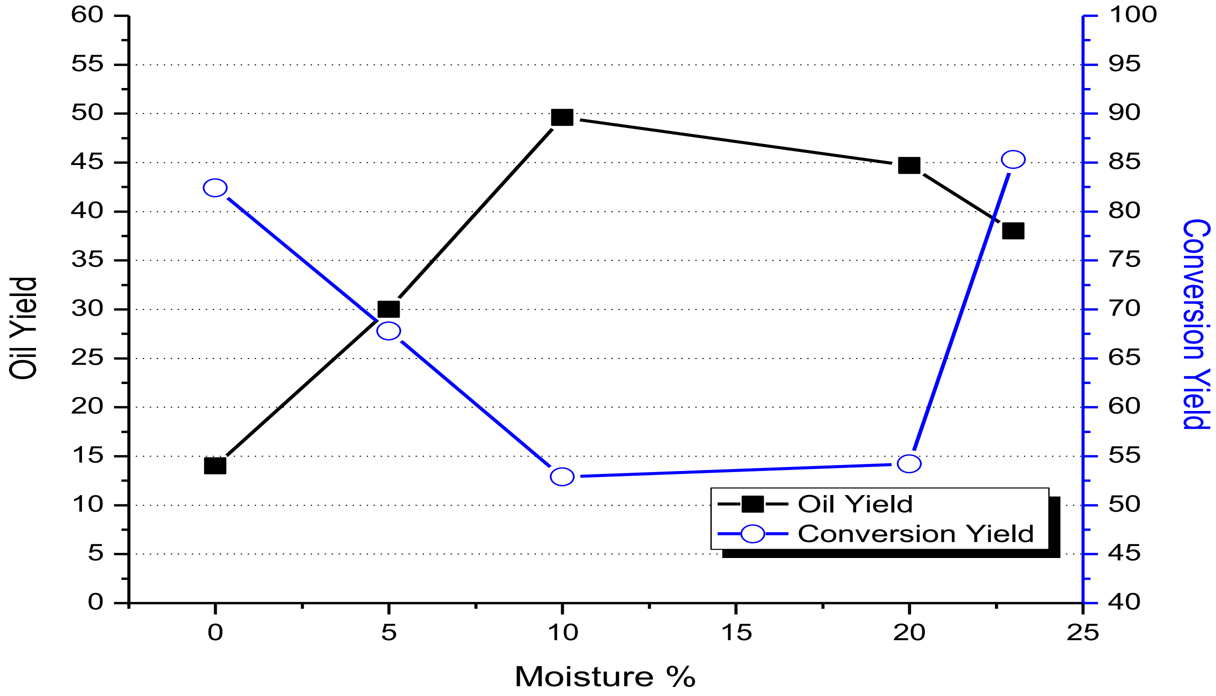


Figure 13 Effect of moisture % on coal liquefaction under normal reaction conditions. Conditions: 1000 psig H_2 pressure, 320 °C, 30 min resident time, stirring speed 150 rpm, 12 % w/w of BXF1 catalyst, and solvent/coal ratio 2:1.

Table 9 shows the oil and conversion yield obtained from those four samples. The different lignite coals show different oil and conversion yields, for example LAL lignite show oil and conversion yields of 38% and 85%, respectively. Where AUC coal shows higher oil yield of 42% and lower conversion yield of 52%. This variation in the oil and conversion yields as different type of lignite coals are used is explained by the proximate analysis of the coals, Table 10 shows the proximate analysis of the three type of coal reported in this experiment. It shows the variation in all moisture, ash, volatile and fixed carbon percentages. It is obvious, that the higher percent of fixed carbon and volatiles components the higher the oil yield, at the same time the lower the ash content the higher the conversion yield. This result was supported by the work of Mochida et al,[67] who reported a reduction in the gas, pre-asphaltene and residue yields, and significant increases on the oil yield at 450°C and reaction time of 10 min.

Table 9 Effects of coal proximate analysis on coal liquefaction under normal conditions. Conditions: 1000 psig H_2 pressure, 320°C, 30 min resident time, stirring speed 150 rpm, 12% w/w of BXF1 catalyst, and solvent/coal ratio 2:1.

Ref #	**Coal (g)**	**Catalyst**	**OilYield (g)**	**CHN% analysis**	**Inertnite Conversion %**
00	25.0 LAL	None	2.0 12%	a. 83.0 8.9 0.9 b. 83.2 9.0 1.9	6.1 64%
10	25.0 LAL	BXF1	6.5g 38%	a. 83.5 9.8 0.5 b. 83.8 10.2 0.5	5.1 85%
34	25.0 NRG	BXF1	7.3 45%	a. 84.9 10.3 2.0 b. 84.8 8.7 5.6	5.6 80%
71	25.0 AUC	BXF1	8.0 42%	a. 82.4 9.5 3.4 b. 85.6 9.8 3.9	12 52%

Table 10 Proximate analysis of LAL, NRG, and AUC lignite coal as obtained by TA Q50 TGA flow rate of 30 mL min^{-1} and the heating rate of 10 ◦C min^{-1} from 25 to 950 °C.

Coal	% Moisture	% Volatiles	% Fix carbon	% Ash
LAL	23	28	40	9
NRG	24	31	34	11
AUC	60	18	21	1

Conclusion

The UTA process for converting lignite coal into synoil is has been demonstrated in the lab and averages 40-50% yields of synoil. This synoil is of reasonable quality with carbon and hydrogen content of approximately 82 % and 10 % by mass, respectively. The UTA process uses relatively mild reaction conditions (320 C and 1000 psi), a cheap iron-based catalyst (BXF1), and a coal-derived solvent. These process conditions suggest that the UTA process is not only technically feasible but may have economic advantages over other processes which require higher temperatures and pressures. Still meaningful and important questions remain, some of which may not be addressable in a laboratory scale operations using batch reactions and laborious diluents-based work ups for synoil isolation and recovery. The three most significant ones being: 1. Can the synoil be separated from the solids at the end of the digestion in an economical fashion?, 2. How will the solvent evolve in a continuous operation facility and what will its properties be?, and 3. How will the problems associated with high ash content in the lignite be addressed and at what cost?

Chapter 4

UTA Synoil Characterization

Introduction

Liquid products from coal are significantly different from those obtained in most crude oils. Coal liquids are generally rich in polycyclic aromatics, phenols, and ethers, compared to saturates (paraffins) which are more common in high quality crude oils. Modern petroleum refining technology is so advanced that just about any quality of oil can be refined into high quality fuels and chemicals, it's simply a matter of time and cost. The lower the quality of the feedstock, the more significant of a discount relative to benchmark oil prices (i.e. $80 /bbl for West Texas Intermediate crude oil) will be demanded from the refinery. In order to fully assess the economics of the UTA DCL process, it is important to determine the composition and quality of the synoil product. There are numerous standard tests performed of crude oils to establish their value. In addition to elemental analyses of CHNS as well as numerous trace metals, specifically mercury, vanadium, nickel, lead, and iron, there are measure of quality from simulated distillations (SIMDIS), physical distillations, GC-MS, specific gravity, and viscosity. Other desirable physical analyses include synoil stability. This chapter provides some insight into the synoil quality.

In order toaddress and understand oil quality, we must first define some of the common physical properties desirable in crude oil and how they are determined.

Experimental Section

Instrumentation

^{1}H NMR spectra were recorded in $CDCl_3$ at room temperature and were obtained on a 500MHz NMR spectrometer. The chemical shifts are expressed as δ values in parts per million. Gas chromatography (GC) analysis was obtained on a GC (model SRI 8610C), the GC was equipped with Flame ionization detector (FID), two Restek Capillary columns:

1- MXT®-500, 6.0 m, 0.53 mm ID, 0.15 μm Simulated Distillation (cat.# 70104)
2- MXT®-2887, 10.0 m, 0.53 mm ID, 2.65 μm Simulated Distillation (cat.# 70199)

And two gases:

1- Gas 1: He with 5 psi, 10 mL/min (carrier gas)
2- Gas 2: H_2 with 22 psi, 25 mL/min (for the FID detector)

Thermal gravimetric analysis (TGA) was obtained on TA Q50 TGA (Pt crucibles, Pt/Pt–Rh thermocouple), equipped with a high sensitivity balance, integrated mass flow controllers with the purge gas (nitrogen or air) flow rate of 30 mL min^{-1} and the heating rate of 10 ◦C min^{-1} from 250C to 10000 C.

The elemental analysis (C, H, N, S) was carried out using the Perkin Elmer CHNS Analyzer from the Perkin Elmer Instrument and Software Company. During CHNS-analysis approximately 2 mg of sample is accurately weighed on a 5-digit analytical scale. The tin sample-cups are placed in an auto-sampler, the air is washed out with helium and the analysis cycle is started. Aided by the exothermal burning of tin and the dosed addition of oxygen the sample is completely burned at 925°C. Further oxidation of the sample is supported by a tube with tungsten oxide (WO_3) catalyst that provides oxygen (Eq.3).

$$C\,H\,N\,S + O \rightarrow x\,CO_2 + x\,H_2O + x\,NO_2 + x\,SO_2 \qquad \text{Eq. 3}$$

After oxidation the gasses are reduced by a very pure copper catalyst inside at 640°C as seen in Eq.4.

$$x\,NO_x + x\,SO_x \rightarrow x\,N_2 + x\,SO_2 \qquad \text{Eq. 4}$$

The gasses are reduced to CO_2, H_2O, N_2 and SO_2 and measured with thermal conductivity detection (TCD). 'CalladuisTM' software draws and integrates the chromatogram. The integrated peak height is converted to a percentage of one of the mentioned elements using acetanilide as a standard.

Results and Discussion

A typical crude oil has set physical and chemical specifications that represent its quality as a feed stock to oil refineries. Perhaps the most basic analyses is the elemental composition. As shown in Table 11, crude oils are predominantly carbon with 10 – 14 % hydrogen by mass. Trace amounts of nitrogen, sulfur, and heavy metals are all treted as impurities which must be removed or minimized. Also seen in Table 11, is the typical composition of the UTA synoil. The most significant difference in the two is the realively large oxygen content of the synoil relative to crude oil which is nearly oxygen-free. On the other hand the sulfur and nitrogen content in UTA synoil are low, which is good in terms of minimizing the effort to remove them.

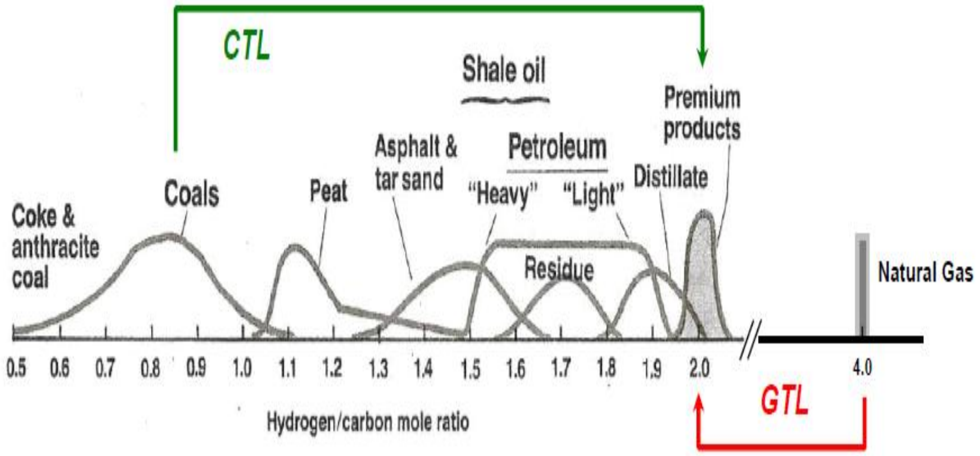


Figure 14 the H/C value of most common fossil fuel sources.

Table 11 The elemental analyses of Products of UTA syn oil.

Elements	Crude Oil	UTA Crude (average)
Carbon	83 to 87 %	81-84 %
Hydrogen	10 to 14% (H/C 1.7)	9.88 % (H/C 1.4)
Nitrogen	0.1 to 2%	0.44 %
Oxygen	0.05 to 1.5% (O/C 0.007)	5.78 % (O/C 0.052)
Sulfur	0.05 to 6.0%	0.645 %

A more detailed elemental analysis of the synoil and a typical crude are given in Table 12, along with the related data for the lignite feedstock, CTD, and HCTD used in the process.

A second qualitative test of synoil quality is to examine the product distribution by GC analyses. Chromatograms of CTD derived from lignite, HCTD derived from CTD, and digested lignite in hydrogenated coal tar distillate solvent (DCTD) are shown in Figures X to X. There are noticeable differences in the chromatograms upon going from CTD to HCTD which is expected as there is a considerable jump in carbon content (73% to 83%) in the hydrogenation process – meaning that a lot of heteroatoms (O, N, S) are removed in the hydrogenation process. On the other hand, only small changes are observed in the chromatograms of HCTD and DCTD which is to be expected as the DCTD is predominantly the starting HCTD with some portion of liquefied coal. For example, a typical reaction starts with 50 g HCTD and ends with 58 g synoil, meaning there was only a 16% increase in mass and that 86% of the product synoil is HCTD (assuming no chemical change in the HCTD which is not entirely reasonable). Thus one difficulty in these analyses is that the synoil product is not being derived under steady-state conditions under which its composition would presumably be relatively constant.

Given that the data will not be entirely representative of the ultimate synoil product, it is still revealing to examine the make-up of and physical properties if DCTD, as these will provide at least some measure of the ultimate synoil quality. The chromatograms in Figure 18 and

Figure 19 overlay the UTA data with that obtained for commercial diesel and Jet-A fuels, respectively. There is significant overlap between the synoil and diesel over wide retention time. The overlap of synoil with Jet-A is not as significant but the synoil components are generally of higher boiling point and therefore could be refined to lighter products.

Table 12 A comparison between some of the elements found UTA syn oil to typical crude oil.

Analysis	Lignite	Inertnite	HCTD	DCTD	Crude Oil
C : Carbon	46.01 %	38.59 %	84.90 %	83.07 %	83 - 87 %
H : Hydrogen	6.77 %	3.13 %	10.32 %	10.52 %	11-14 %
Fe : Iron	0.135 %	1.33 %	103 ppm	125 ppm	0.49 %
Hg : Mercury	< 2 ppm	< 2 ppm	< 2 ppm	< 2 ppm	0.004 - 2.078
N : Nitrogen	0.871 %	0.898 %	1.02%	1.16 %	0 - 1 %
Ni : Nickel	< 49 ppm	< 46 ppm	1.5 ppm	1.4 ppm	
S : Sulfur	0.848 %	1.22 %	0.395 %	0.346 %	0 - 6 %
V : Vanadium	25.4 ppm	91 ppm	< 1 ppm	< 0.9 ppm	980 ppm

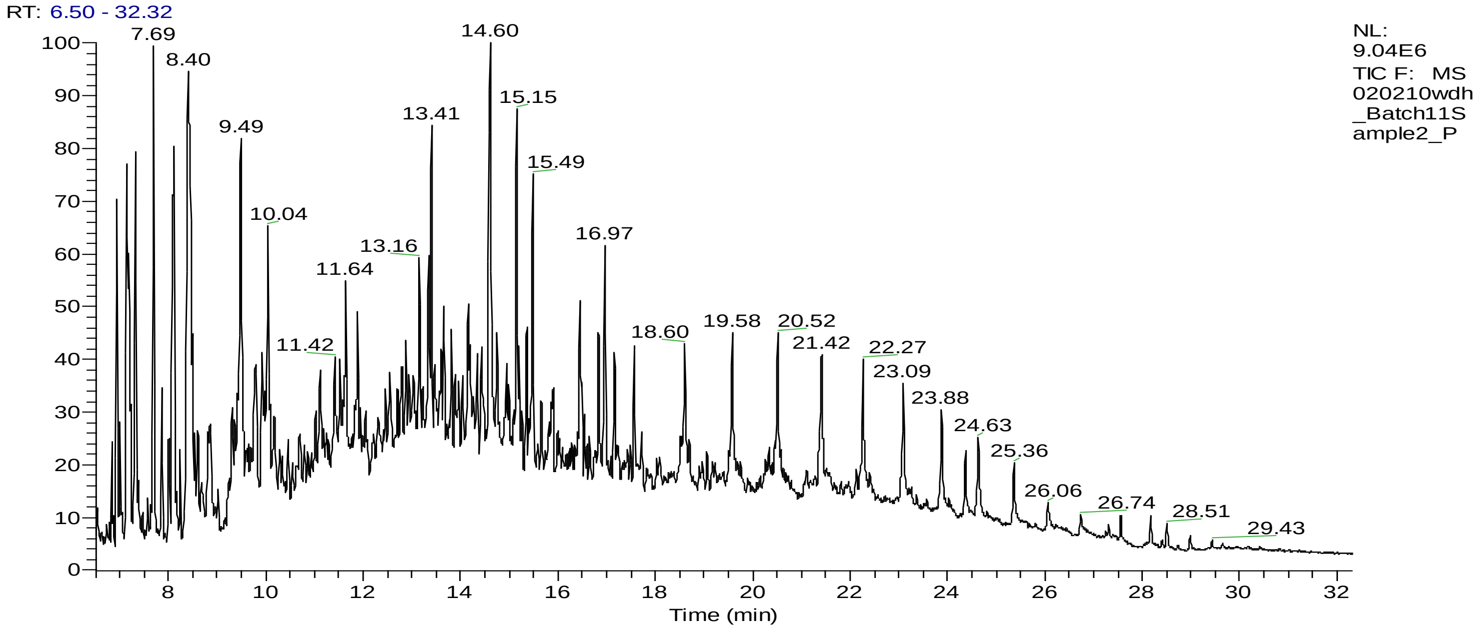


Figure 15 GC chromatogram analysis of pyrolysis coal tar distillate The GC chromatogram analysis was recorded in SRI Instruments manufacture GC (model SRI 8610C), the GC was equipped with Flame ionization detector (FID), MXT®-500, 6.0 m, 0.53 mm ID, 0.15 µm Simulated Distillation, toluene as solvent, and Carrier gas: He with 5 psi, 10 mL/min

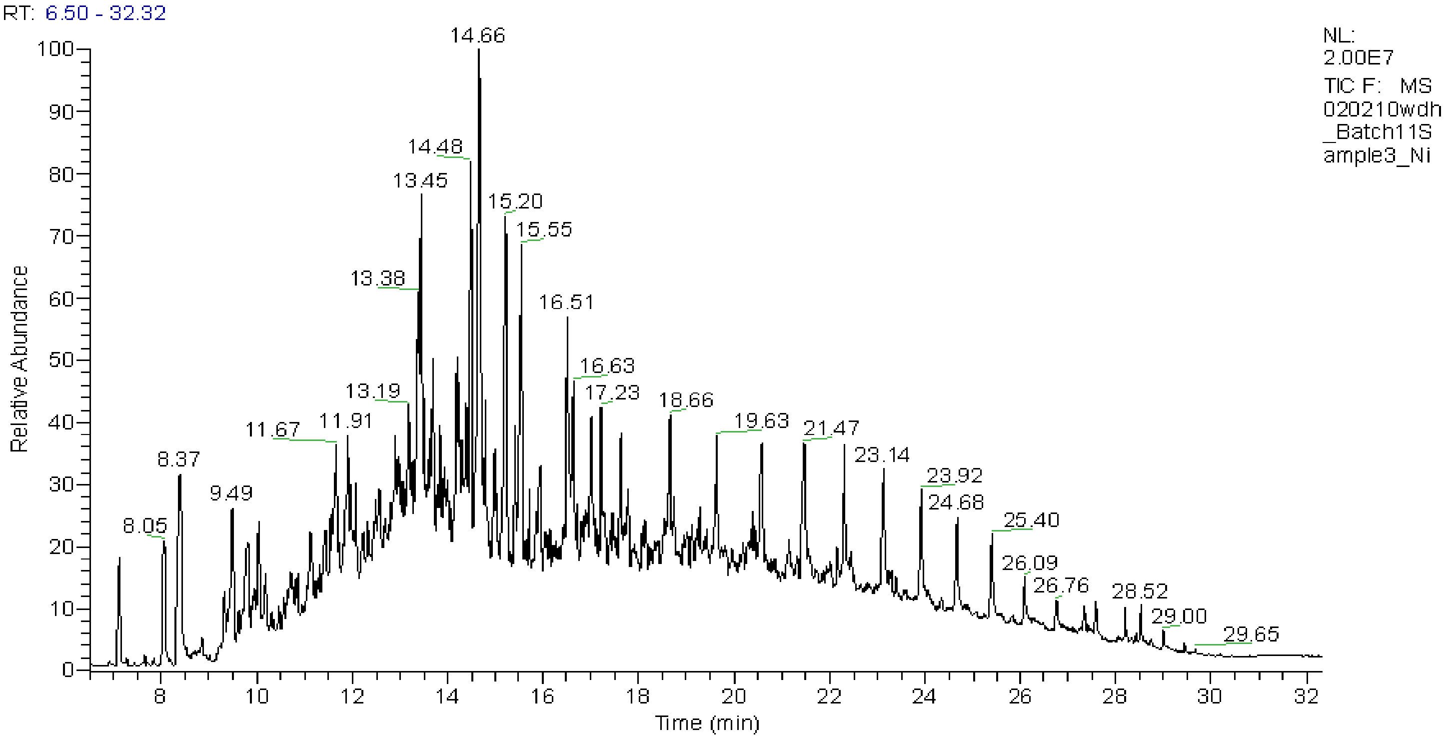


Figure 16 GC chromatogram analysis of hydrogenated coal tar distillate. The GC chromatogram analysis was recorded in SRI Instruments manufacture GC (model SRI 8610C), the GC was equipped with Flame ionization detector (FID), MXT®-500, 6.0 m, 0.53 mm ID, 0.15 µm Simulated Distillation, toluene as solvent, and Carrier gas: He with 5 psi, 10 mL/min

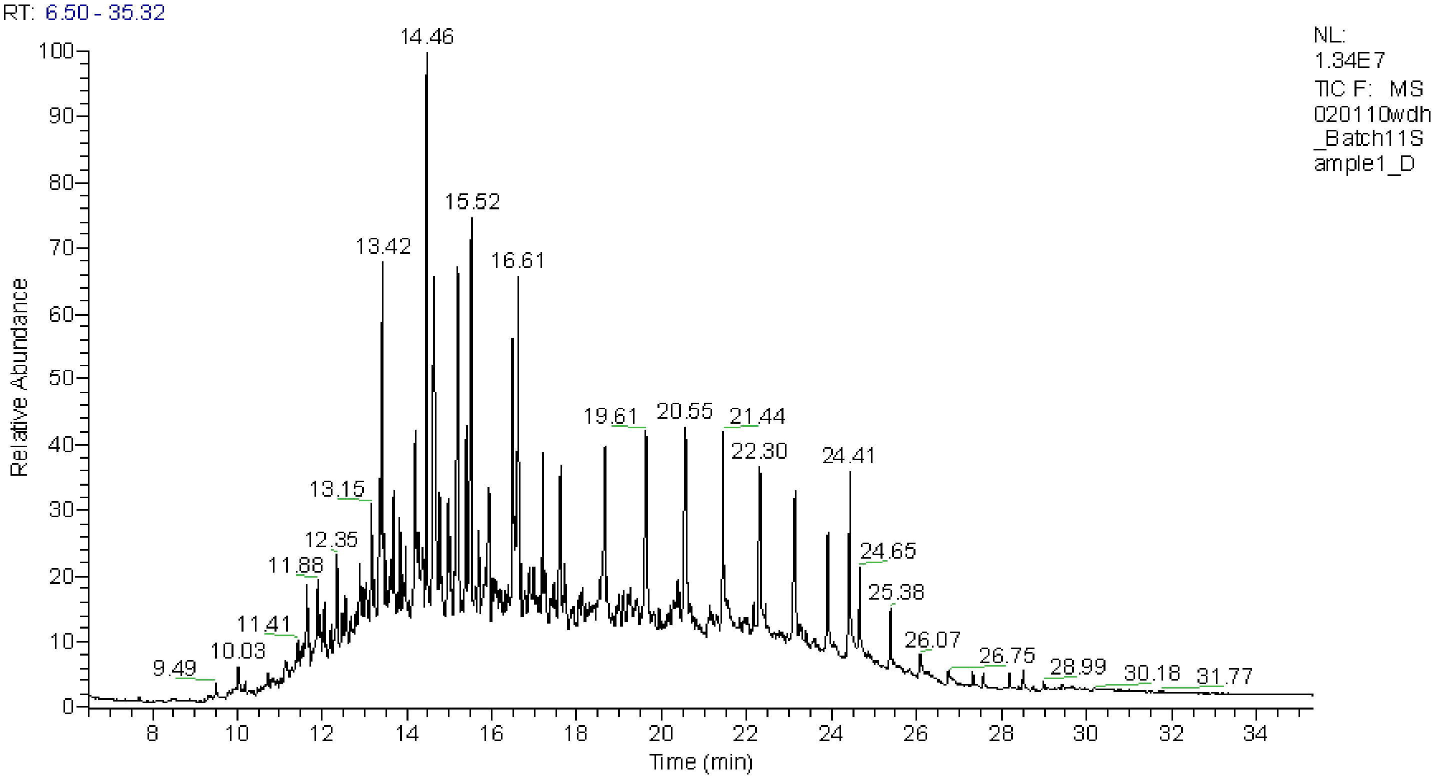


Figure 17 GC chromatogram analysis of digested coal tar distillate. The GC chromatogram analysis was recorded in SRI Instruments manufacture GC (model SRI 8610C), the GC was equipped with Flame ionization detector (FID), MXT®-500, 6.0 m, 0.53 mm ID, 0.15 µm Simulated Distillation, toluene as solvent, and Carrier gas: He with 5 psi, 10 mL/min

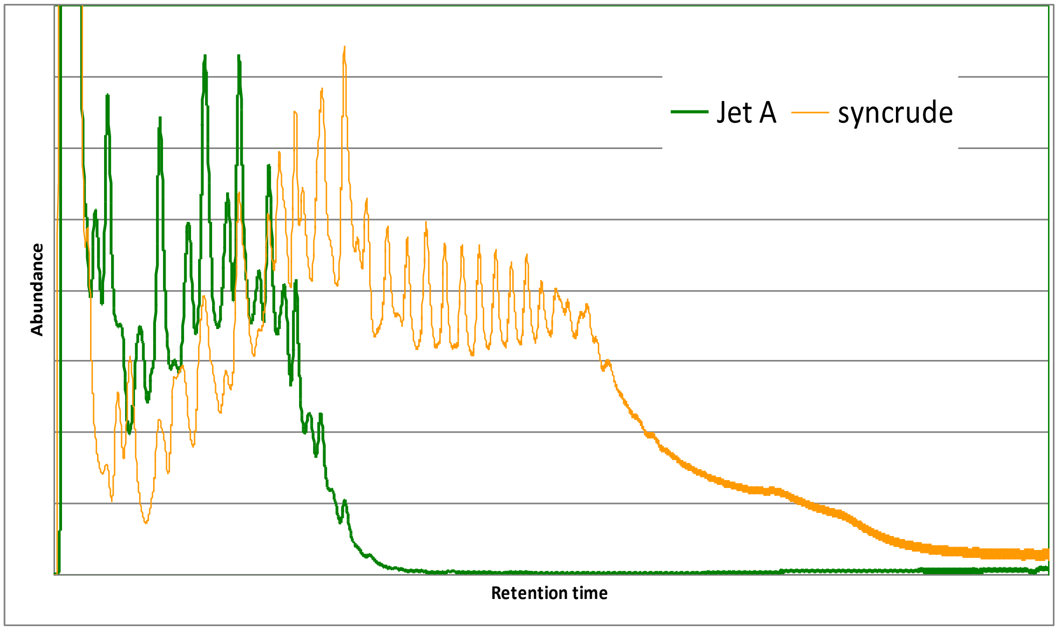


Figure 18 GC Comparison between Jet A fuel and UTA syn oil. The GC chromatogram analysis was recorded in SRI Instruments manufacture GC (model SRI 8610C), the GC was equipped with Flame ionization detector (FID), MXT®-500, 6.0 m, 0.53 mm ID, 0.15 µm Simulated Distillation, toluene as solvent, and Carrier gas: He with 5 psi, 10 mL/min

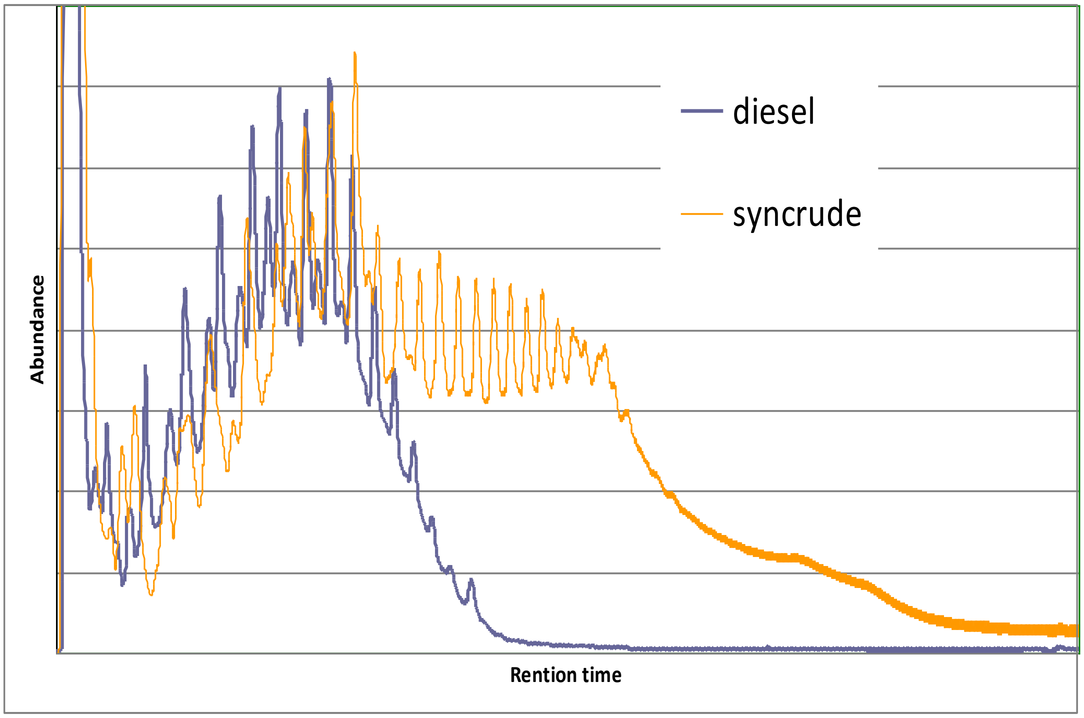


Figure 19 GC Comparison between diesel fuel and UTA syn oil. The GC chromatogram analysis was recorded in SRI Instruments manufacture GC (model SRI 8610C), the GC was equipped with Flame ionization detector (FID), MXT®-500, 6.0 m, 0.53 mm ID, 0.15 µm Simulated Distillation, toluene as solvent, and Carrier gas: He with 5 psi, 10 mL/min

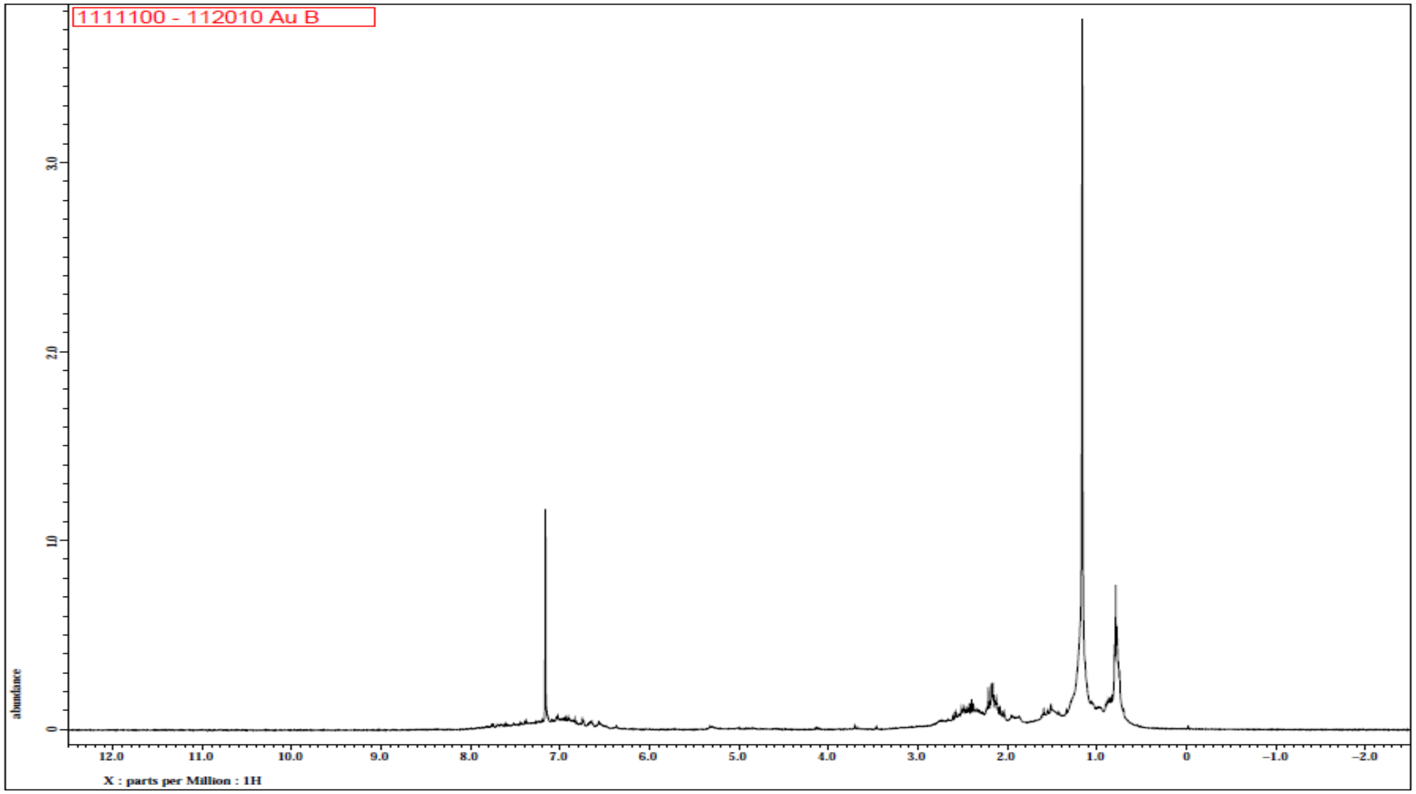


Figure 20 ^{1}H NMR spectra of UTA syn oil. d 0.00 – 2.00 ppm aliphatic protons, d 2.00- 6.00 ppm Olefin protons, and 6.00 – 8.00 ppm Aromatic protons. Solvent CDCL$_3$

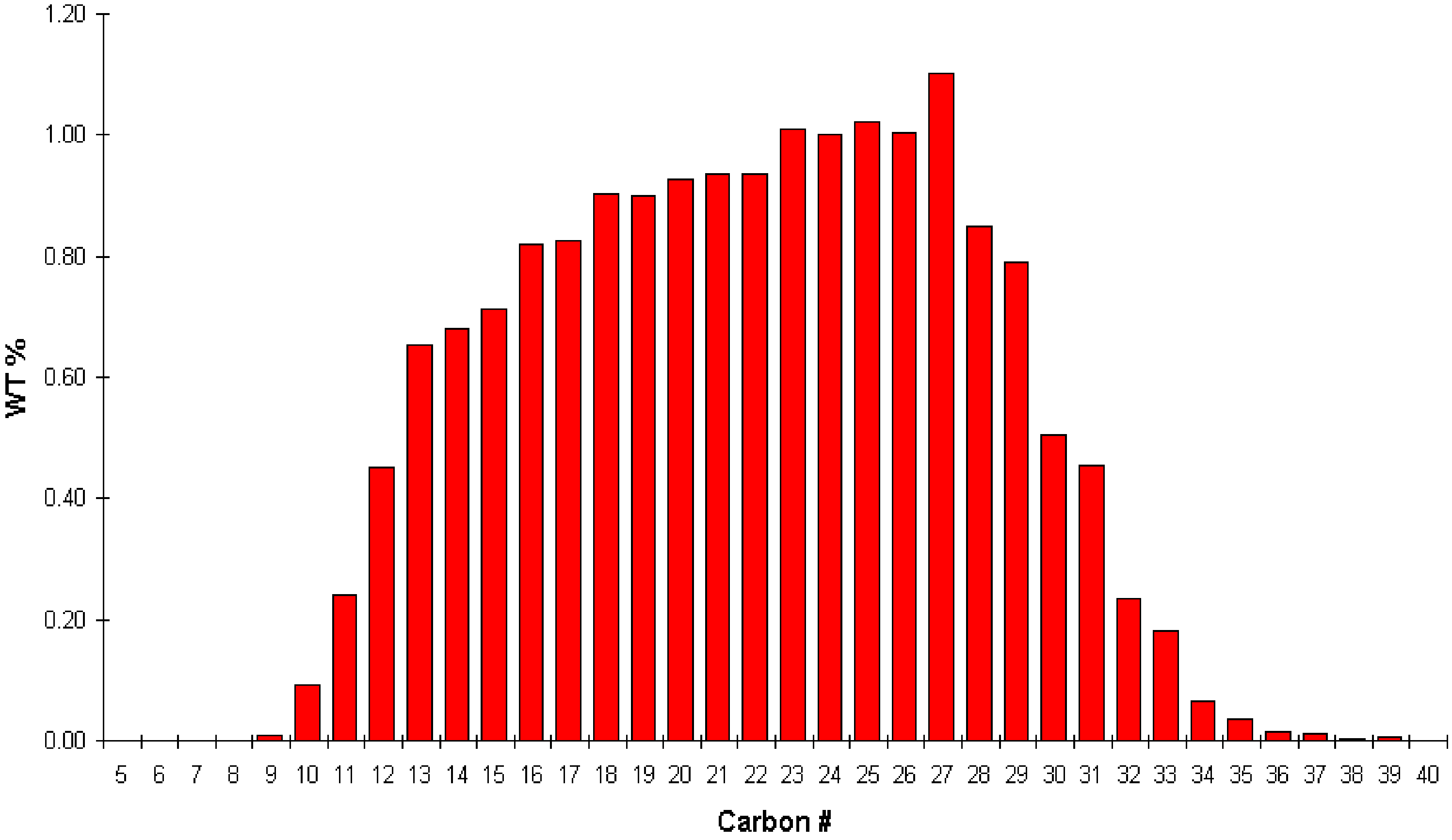


Figure 21 carbons number distribution of UTA syn oil. The test performed by Core laboratories- Houston, report # 206991.

Simulated distillation measurements provide a mass percent vs boiling point distribution of the synoil. Simulated distillation methods are defined specifically by ASTM test methods D5307, D7169 and D2887. ASTM D5307 is used for the determination mass with boiling points under and up to 538 °C (1000 °F), with material boiling above 538 °C being reported as residue. ASTM D5307 was later replaced by ASTM D7169. ASTM D7169 is for the determination by GC of boiling range distribution of crude petroleum through 720 °C (1328 °F). ASTM D2887 covers the determination by GC of the boiling range distribution of petroleum products and fractions having a T.B.P. of 538 °C (1000 °F) or lower at atmospheric pressure.

The simulated distillation curves of UTA synoils obtained by our laboratory are plotted and compared (Figure 22). These five simulated distillation curves represent the five stages that UTA synoil goes through during the UTA process. The stages are called CTD, HCTD, DCTD1, DCTD2, and DCTD3. The simulated distillation data reveals that generally 95% of UTA synoil can be distilled at temperatures below 550°C (1100°F). The slight increase in the T.B.P. curves as the synoil was recycled in the process is believed to be associated with the reduction in the low hydrocarbons fraction of the synoil. Although the synoil simulated distillation procedure provides only an estimate of the yields of the products of various boiling ranges, the results are of great importance for the characterization and commercial trading of synoil. However, there are several areas that can contribute to data variability of the synoil assay distillation procedure. For example, the use of two different consecutive distillation methods with widely different characteristics such as efficiency, column hold-up and pressure drop across the column. Figure 23 represents the simulated distillation of the UTA synoil (ASTM D7169) which were compared to simulated distillation data of Istmo and Maya crude which were obtained from the work of Espinosa-Pena et al.[114-115] The graph shows a lower distillation T.B.P. for the synoil over both Istmo and Maya crudes in the regain above 400°F, this indicates T.B.P. of multiple crude oil as determined by simulated distillation will differ substantially from each other.

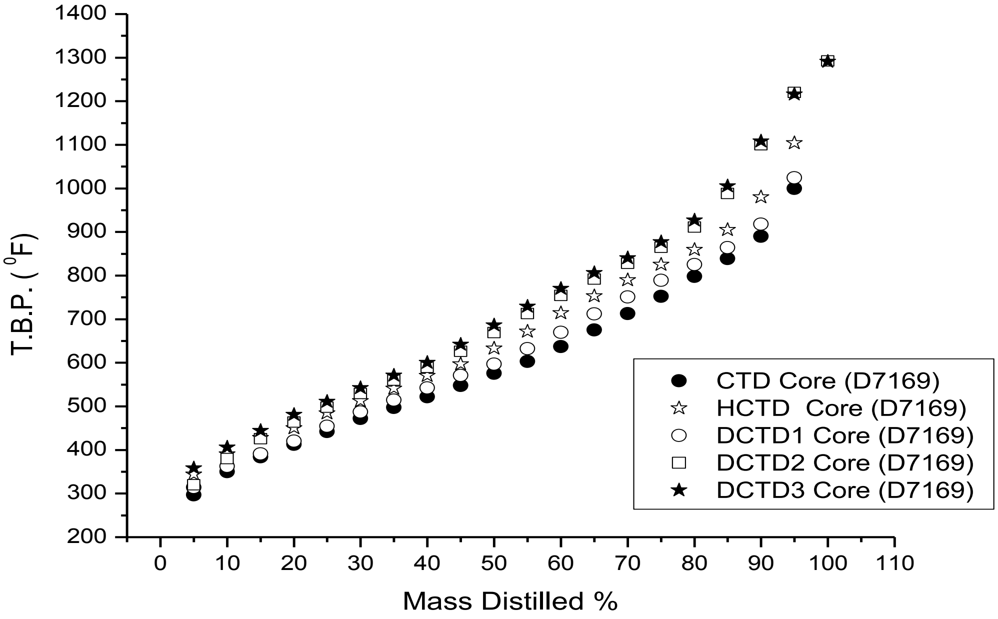


Figure 22 Simulated distillation T.B.P. curve in mass by ASTM D7169 method of UTA syn oil:(dark circle) UTA CTD, (white star) UTA HCTD, (white circle) UTA DCTD1, (white square) UTA DCTD2, and (dark star) UTA DCTD3.

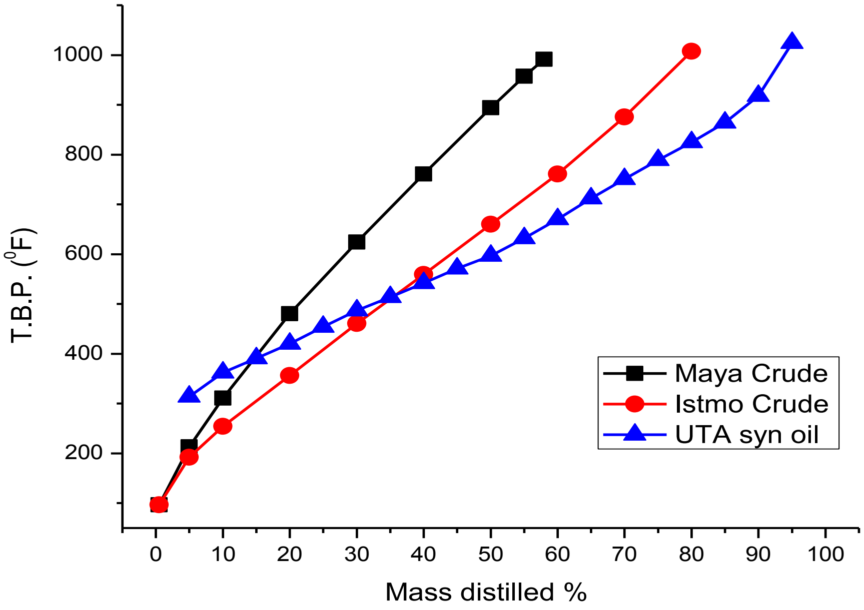


Figure 23 Comparison between the simulated distillation mass curves of UTA synoil (triangle) and Maya crude (square) and Istmo crude (circle). ASTM methods performed on UTA syn oil was D7169, Istmo and Maya crude ASTM D2892.[114]

Ruossis et al.[116] Study the coupling of gas chromatographic simulated distillation with mass spectrometry for the determination of the distillation profiles of light and heavy crude oils.

Figure 24represents the simulated distillation of the UTA synoil (ASTM D5307) which were compared to simulated distillation data five types of crude oil which were obtained from the work of Ruossis et al.[116] In the figure, five type of crude oil sorted as following: Crude A, Crude B, Crude C, Crude D, and Crude

E. crude A been the heaviest and Crude E the lightest. It is seems UTA synoil follow the heavy crude distillation behavior at temperature below 300 0F and slowly adapt the lighter crude distillation behavior at high temperature.

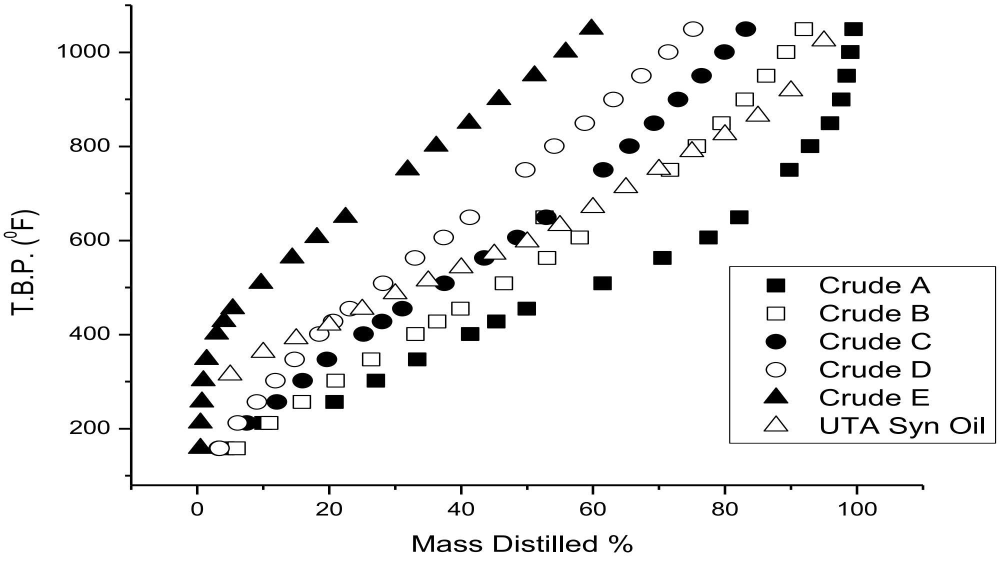


Figure 24 Simulated distillation T.B.P. curve in mass of UTA syn oil compered to five type of crude oil range from light to heavy: (Black square) Crude A, (white square) Crude B, (Black circle) Crude C, (white circle) Crude D, (Black triangle) Crude E, and (white triangle) UTA Syn oil

Conclusion

The chemical and physical properties of UTA synoil play an important part in its price, transportation, and refining and subsequent sale as refined products. It is known that synoil contains some impurities. Sulfur has been identified as one of the impurity, which affects the quality of the final refined product and processing cost. In general, presences of certain impurities such as sulfur and nitrogen, which affect properties of synoil and create many operational and quality issues, which affecting the cost of recovery and refining. A comparison between typical crude and UTA synoil reveal a great similarity in the chemical and physical properties. The 1.40 H/C ratio and the 0.6 % sulfur content are the most important factors in terms of using UTA synoil as refinery feeds. The SARA analysis shows UTA synoil contains, 17.5% wt saturated hydrocarbons, 61.5% wt aromatics, 3.3% wt as resins and 18.0% wt asphlaltenes. UTA synoil average carbon number is 19 with wide distribution range between 9 to 40 C atoms. The GC analysis shows an excellent overlap with diesel and Jet A Fuel.

Chapter 5

Conclusion

We concluded that the UTA process developed by the CREST lab for converting coal into synoil is feasible, resulting redactions in the United States dependent in foreign oil, contribute meaningfully to the domestic oil supply and ease the transportation fuel price.

The first part of this dissertation has shown that lignite coals differ significantly in respect to each other. Progress was made in determining how the characteristics of lignite coals and reaction conditions influence coal conversion to liquid products during hydro-liquefaction. The wide variation in lignite coals in rank emphasizes the need for detailed understanding of how specific coal characteristics influence liquefaction reactions and the properties of the liquid product. The heterogeneity and variability of coals makes them a complex feedstock on the one hand and presents major challenges to efforts to identify and quantify those parameters of most significance. Coal liquefaction can be quantified by comparing conversions and yields with the corresponding parameters. The role of temperature, pressure, catalyst, reductant, moisture, proximate analysis, solvent, and loading, reaction cycle, and reaction duration were all studied during the course of this dissertation.

The results presented and discussed in chapter three indicate that the proximate analysis and the reaction parameters are important with regards to total liquid and conversion yields during hydro-liquefaction of such coals. The strong dependence of liquid and conversion on the proximate analysis suggests that the subtleties of variation in chemical composition or structure with change in rank are of great importance. Also the dependence of conversion yields on the ash ratio further suggests that the effects of the mineral matter in the lignite coal liquefaction are important. Low ash content led to higher oil yield and lower conversion yield. In addition, the product and conversion yield from coal feeds decrease with increase in temperature. The product and conversion yields were significantly affected by the changes in hydrogen pressure and reductant type. The improved product and conversion yields were seen when the moisture values were between 10 to 20%. In the presence of the hydrogen-donor solvent it may be easier for the donor solvent itself to stabilize the free radicals from the coal with the catalyst, if present, and hydrogen acting to regenerate the donor capability of the solvent. However, these processes are not well understood and require additional investigation. Synthetic crude yields from reactions involving the hydrogen-donor solvent can contain 60 to 75 percent of the carbon in the coal, and similar yields can be obtained in processes involving an appropriate catalyst and molecular hydrogen.

Maximizing the liquid yield requires a careful balance between temperature, pressure, heat-up time, residence time at elevated temperature, and the addition of an appropriate catalyst. In general, short residence time in the heated zone is favorable to higher liquid yield if the other conditions are satisfactory. The major factors that affect the liquefaction of coal are:

a) Reactivity of coal: Higher the rank of the coal more severe conditions need for liquefaction. Younger, lower rank lignite coals liquefy most readily but give lower yields and lower ratios of liquids to gases.

b) Liquefaction temperature: liquefaction heating temperature should be as rapid as possible to prevent repolymerization of reactive fragments formed from the rupture of the weakest bonds in the coal at temperatures lower than those for which hydrogen transfer becomes rapid. Temperatures to produce liquids range from 320 to 370 °C.

c) Catalyst: iron in BXF1 catalyst act as catalysts in coal liquefaction especially effective in the temperature range in which liquids are formed; similarly, the ash present in the coal probably has catalytic capabilities.

d) Pressure: required pressures for liquids production by hydrogenation range from about 700 to 1400 psi. Rank of coal, liquefaction scheme, desired end product, mineral matter and added catalyst present, and extent of conversion determines the optimum pressure. Lower rank lignite coals can be liquefied at lower pressures.

e) Reaction Time: mixtures of coal and vehicle oil require from about 20 min to 40 min at pressure and temperature of the reaction. Lignite coal has low resistance to maxing time and coal gasification promoted above 45 min.

The second part of the dissertation proved a comprehensive analysis of the chemical composition and evaluation of the coal liquid products. The chemical composition and evaluation data provides extensively detailed hydrocarbon analysis data for refiners, oil traders and producers. In addition, the data helps refineries determine if a synoil feedstock is compatible for a particular petroleum refinery or if the synoil could cause yield, quality, production, environmental and other problems.

Liquid products from coal are generally different from those produced by petroleum refining, particularly as they can contain substantial amounts of phenols. Therefore, there is always a question about the place of coal liquids in refining operations. However, currently there are not many investigations on the characterization of the refinery step processing of coal liquids. And that is assigned to two factors: 1) Thorough and intensive investigations were done during the energy cruses back in the 1980's. 2) Existing refineries can tolerate a wide range of crude oil feed stock specifications in their processes.

Error! Not a valid bookmark self-reference. represents assay values for UTA synoil. The synoil assays evaluate various chemical properties of the synoil. The two most important properties determining a synoil value are its density and its sulfur content. However, other specifications are important to address the place of synoil in the refineries. UTA synoil is considered heavy due to it is high wax content and sweet due to it is low sulfur content (< 0.6% / w/w). The SARA analysis shows that UTA synoil contains 18.0% wt asphlaltenes, 17.5% wt saturated hydrocarbons, 61.5% wt aromatics, and 3.3% wt as resins. PNA analysis of Shows 21.4% wt paraffins, 10.4% wt naphthalenes, and 68.2 aromatics. UTA synoil average carbon number is 19 with wide distribution range between 9 to 40 C atoms. The GC analysis shows an excellent overlap with diesel and Jet A Fuel. Finally, the data presented in Table 12 shows that UTA synoil is compatible with refineries feed stocks, and it can be refined into a wide range of fuel products.

Table 13 The assay values for UTA syn oil.

Assay	UTA Crude (average)
Carbon	81-84 %
Hydrogen	9.88 % (H/C 1.4)
Nitrogen	0.44 %
Oxygen	5.78 % (O/C 0.052)
Sulfur	0.645 %
Density	0.83 g/mL
Viscosity	170 cp
API	39.0°
PNA analysis	21.4% Paraffins, 10.4% Naphthalenes, and 68.2% Aromatics
SARA analysis	18.0 %Saturate, 17.5% Aromatic, 61.2% Resin, and 3.3 % Asphaltenes

UTA method has been shown to be a feasible way of lignite coal liquefaction and it can be commercially deployed in the United States. The practicality of the method depends on using the highly abundant lignite coal, homogenous hydrogen donating solvent, relatively cheap abundant iron catalyst, and mild conditions. In summary liquefaction experiments of lignite coal were carried out in continuously stirred reactor under mild conditions and hydrogen atmospheres. The maximum oil yield of 60% was obtained at final liquefaction temperature of 320 °C with a particle size of 16 mesh, with a heating rate of 15 °C/min, and hydrogen atmospheric pressure of 1000 psi. The oil product was characterized by elemental analysis and various chromatographic and spectroscopic techniques and also compared with currently utilized transport fuels and presented as a syn fuel candidate. For the evaluation of the employment of result oil as a fuel, the following options are recommended:

a) UTA synoil might be used a source of low-grade fuel directly or may be upgraded to higher quality liquid fuels.

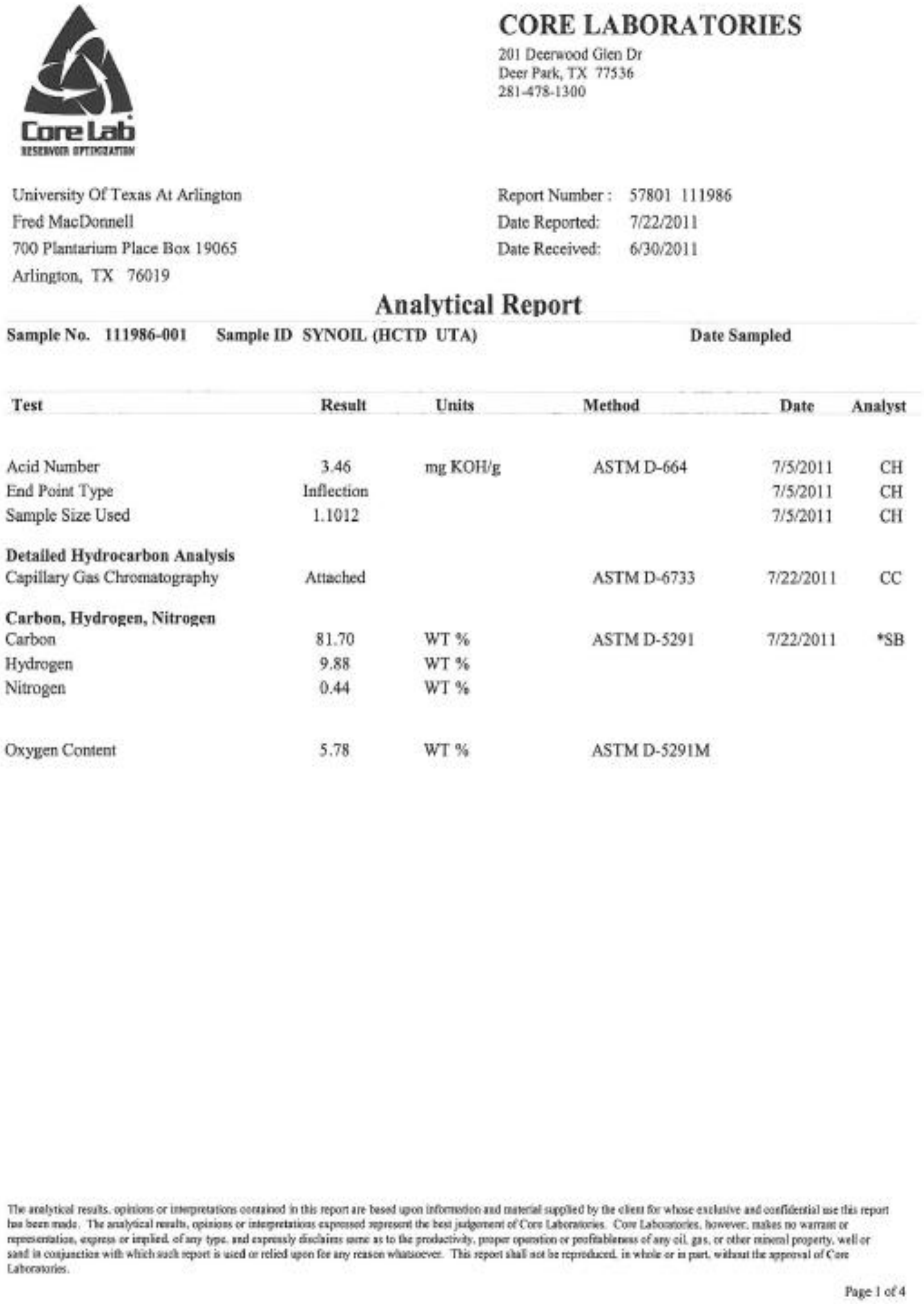
b) UTA synoil seems to be more appropriate for the production of hydrocarbons and chemicals.

c) There is a great potential for United States to exploit lignite coal reserves as possible synthetic petroleum sources.

d) The findings of laboratory-scale studies are encouraging and warrant larger-scale applications of Lignite liquefaction for synthetic fuels.

APPENDIX A

Core Laboratory HCTD Syn Oil Analysis Report # 57801-111986



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Fred MacDonnell
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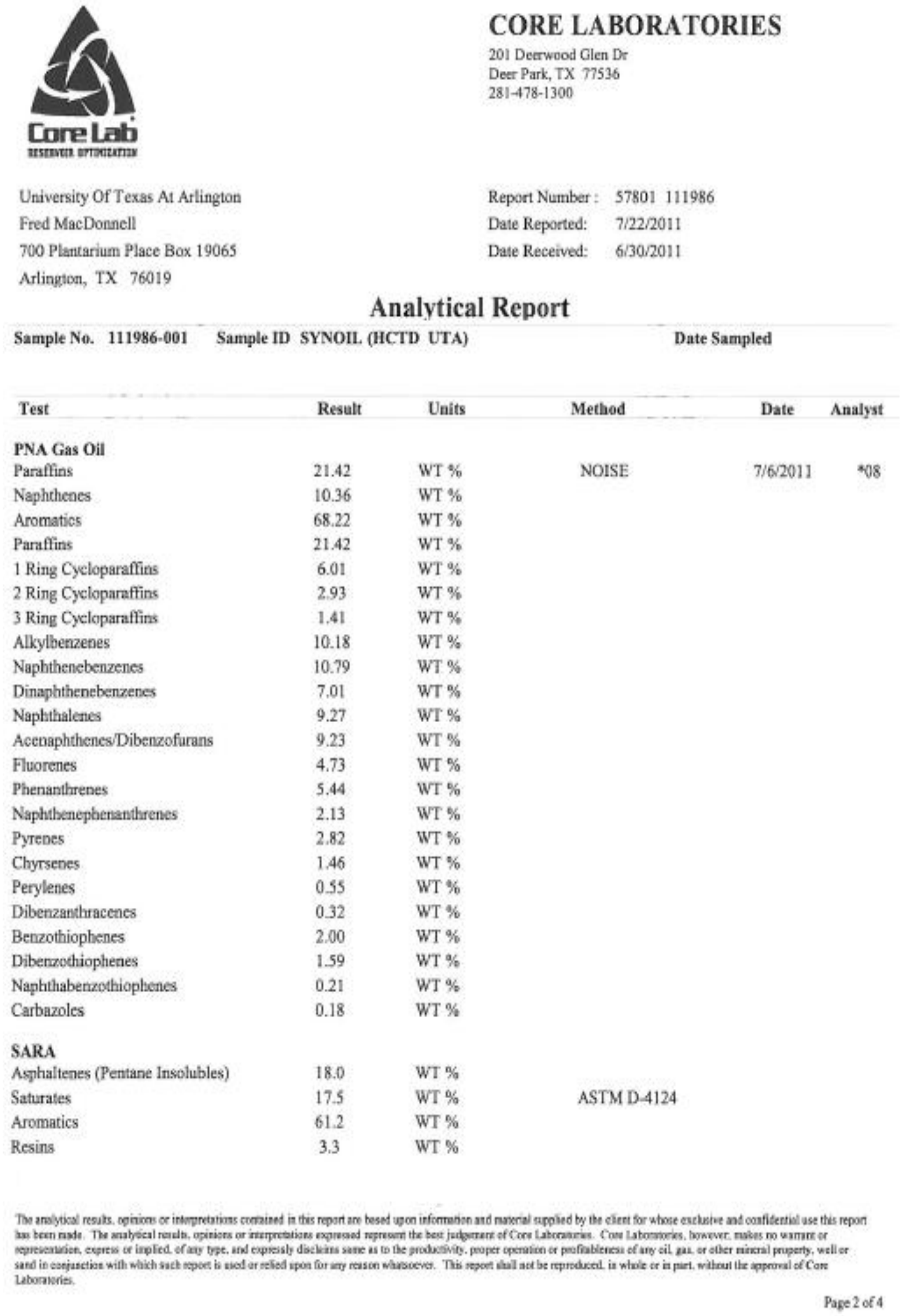
Arlington, TX 76019

Report Number : 57801 111986
Date Reported: 7/22/2011
Date Received: 6/30/2011

Analytical Report

Sample No. 111986-001 **Sample ID SYNOIL (HCTD UTA)** **Date Sampled**

Test	Result	Units	Method	Date	Analyst
Acid Number	3.46	mg KOH/g	ASTM D-664	7/5/2011	CH
End Point Type	Inflection			7/5/2011	CH
Sample Size Used	1.1012			7/5/2011	CH
Detailed Hydrocarbon Analysis					
Capillary Gas Chromatography	Attached		ASTM D-6733	7/22/2011	CC
Carbon, Hydrogen, Nitrogen					
Carbon	81.70	WT %	ASTM D-5291	7/22/2011	*SB
Hydrogen	9.88	WT %			
Nitrogen	0.44	WT %			
Oxygen Content	5.78	WT %	ASTM D-5291M		



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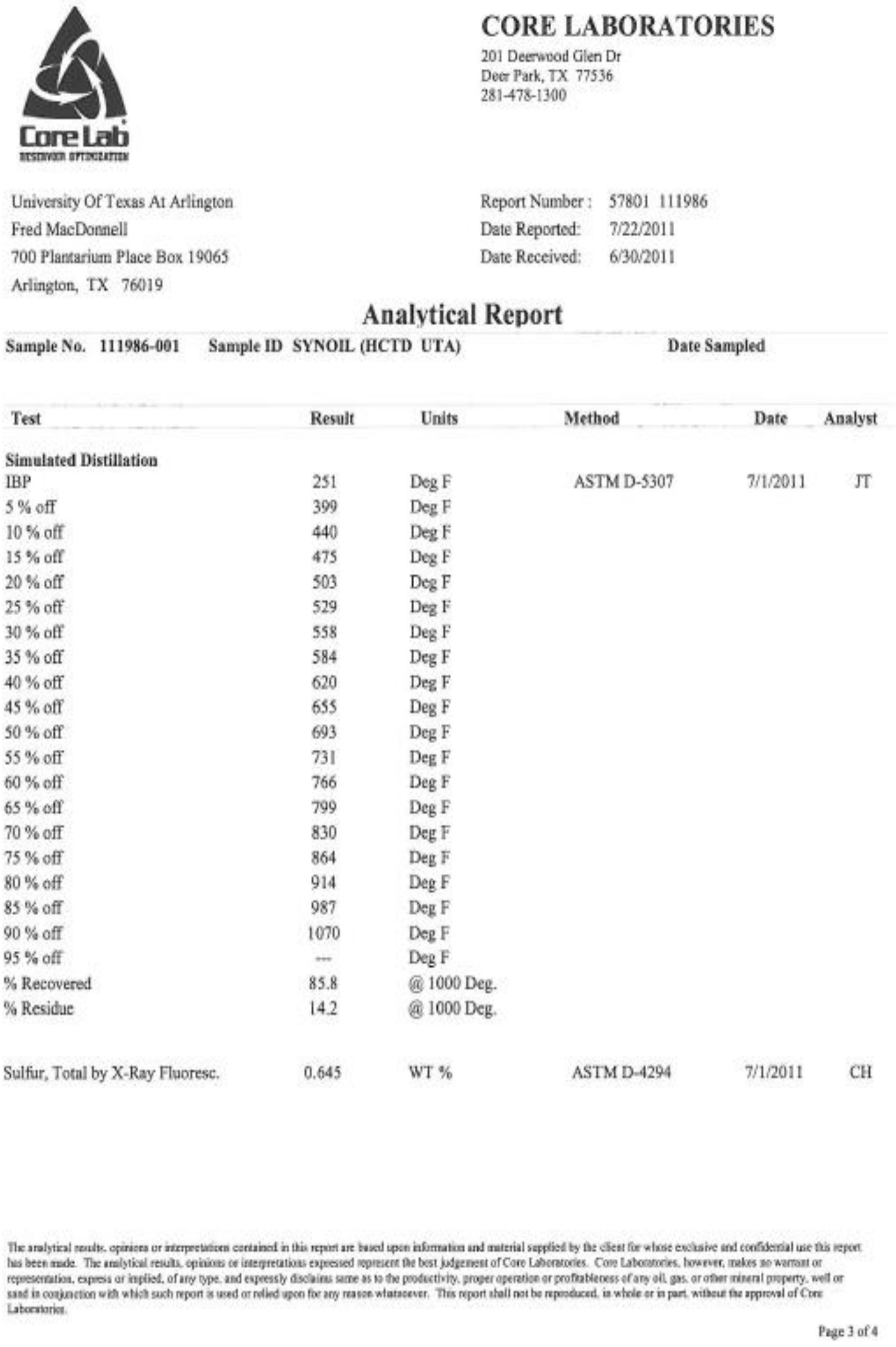
Report Number : 57801 111986
Date Reported: 7/22/2011
Date Received: 6/30/2011

Analytical Report

Sample No. 111986-001 **Sample ID SYNOIL (HCTD UTA)** **Date Sampled**

Test	Result	Units	Method	Date	Analyst
PNA Gas Oil					
Paraffins	21.42	WT %	NOISE	7/6/2011	*08
Naphthenes	10.36	WT %			
Aromatics	68.22	WT %			
Paraffins	21.42	WT %			
1 Ring Cycloparaffins	6.01	WT %			
2 Ring Cycloparaffins	2.93	WT %			
3 Ring Cycloparaffins	1.41	WT %			
Alkylbenzenes	10.18	WT %			
Naphthenebenzenes	10.79	WT %			
Dinaphthenebenzenes	7.01	WT %			
Naphthalenes	9.27	WT %			
Acenaphthenes/Dibenzofurans	9.23	WT %			
Fluorenes	4.73	WT %			
Phenanthrenes	5.44	WT %			
Naphthenephenanthrenes	2.13	WT %			
Pyrenes	2.82	WT %			
Chyrsenes	1.46	WT %			
Perylenes	0.55	WT %			
Dibenzanthracenes	0.32	WT %			
Benzothiophenes	2.00	WT %			
Dibenzothiophenes	1.59	WT %			
Naphthabenzothiophenes	0.21	WT %			
Carbazoles	0.18	WT %			
SARA					
Asphaltenes (Pentane Insolubles)	18.0	WT %			
Saturates	17.5	WT %	ASTM D-4124		
Aromatics	61.2	WT %			
Resins	3.3	WT %			



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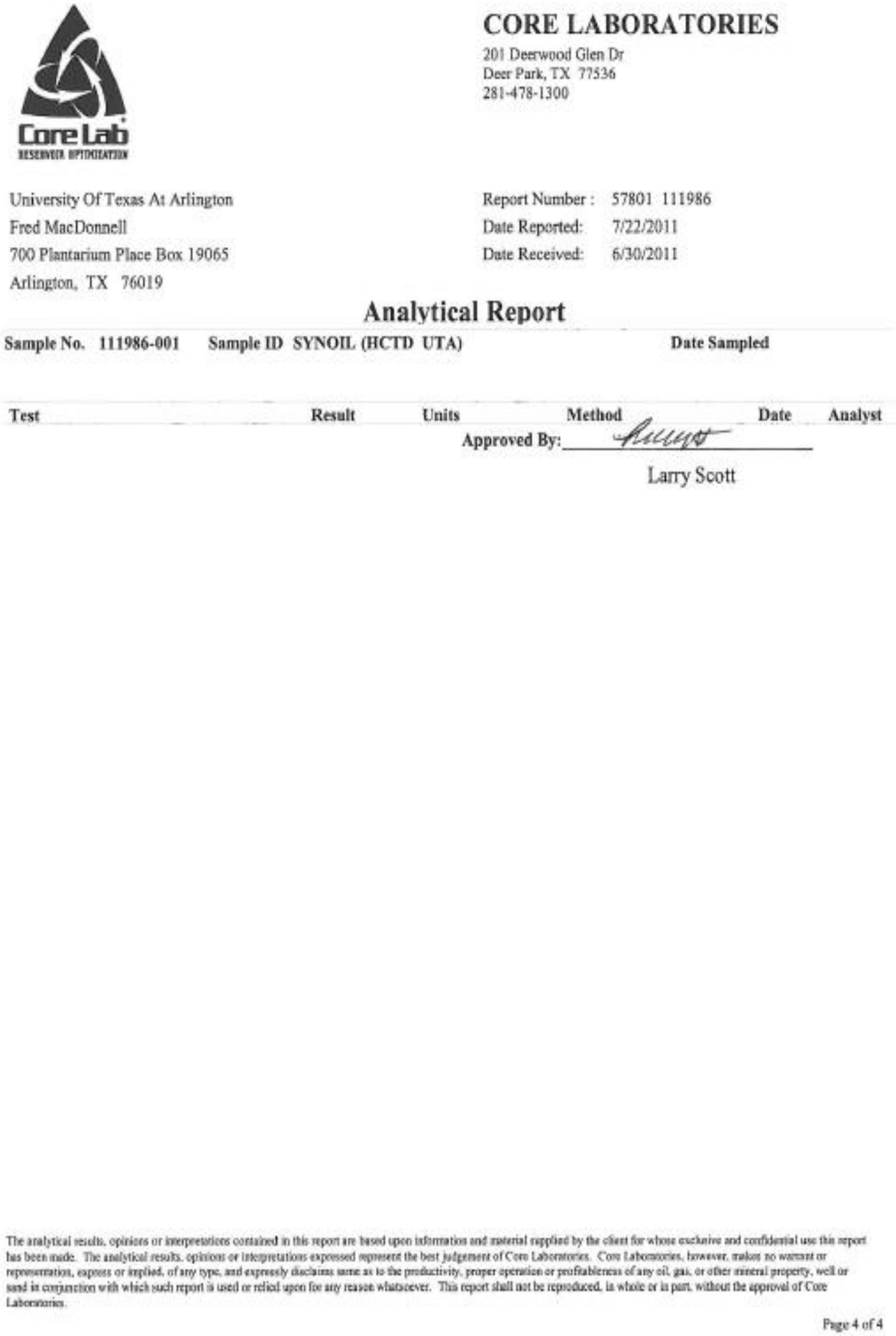
Report Number : 57801 111986
Date Reported: 7/22/2011
Date Received: 6/30/2011

Analytical Report

Sample No. 111986-001 **Sample ID SYNOIL (HCTD UTA)** **Date Sampled**

Test	Result	Units	Method	Date	Analyst
Simulated Distillation					
IBP	251	Deg F	ASTM D-5307	7/1/2011	JT
5 % off	399	Deg F			
10 % off	440	Deg F			
15 % off	475	Deg F			
20 % off	503	Deg F			
25 % off	529	Deg F			
30 % off	558	Deg F			
35 % off	584	Deg F			
40 % off	620	Deg F			
45 % off	655	Deg F			
50 % off	693	Deg F			
55 % off	731	Deg F			
60 % off	766	Deg F			
65 % off	799	Deg F			
70 % off	830	Deg F			
75 % off	864	Deg F			
80 % off	914	Deg F			
85 % off	987	Deg F			
90 % off	1070	Deg F			
95 % off	---	Deg F			
% Recovered	85.8	@ 1000 Deg.			
% Residue	14.2	@ 1000 Deg.			
Sulfur, Total by X-Ray Fluoresc.	0.645	WT %	ASTM D-4294	7/1/2011	CH

Page 3 of 4



CORE LABORATORIES

201 Deerwood Glen Dr
Deer Park, TX 77536
281-478-1300

University Of Texas At Arlington
Fred MacDonnell
700 Plantarium Place Box 19065
Arlington, TX 76019

Report Number : 57801 111986
Date Reported: 7/22/2011
Date Received: 6/30/2011

Analytical Report

Sample No. 111986-001 **Sample ID SYNOIL (HCTD UTA)** **Date Sampled**

Test	Result	Units	Method	Date	Analyst

Approved By: ______________

Larry Scott

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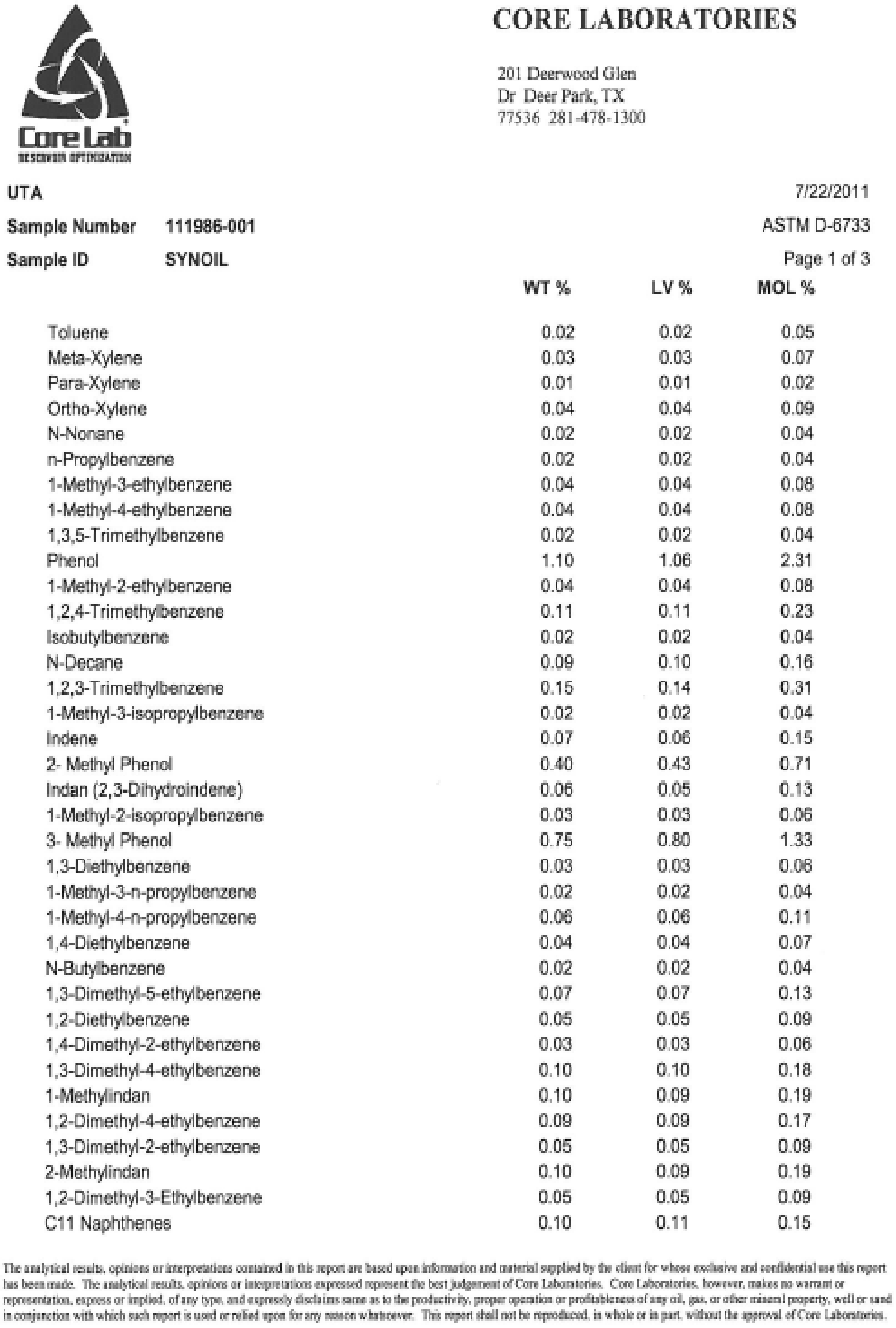
Page 4 of 4



CORE LABORATORIES

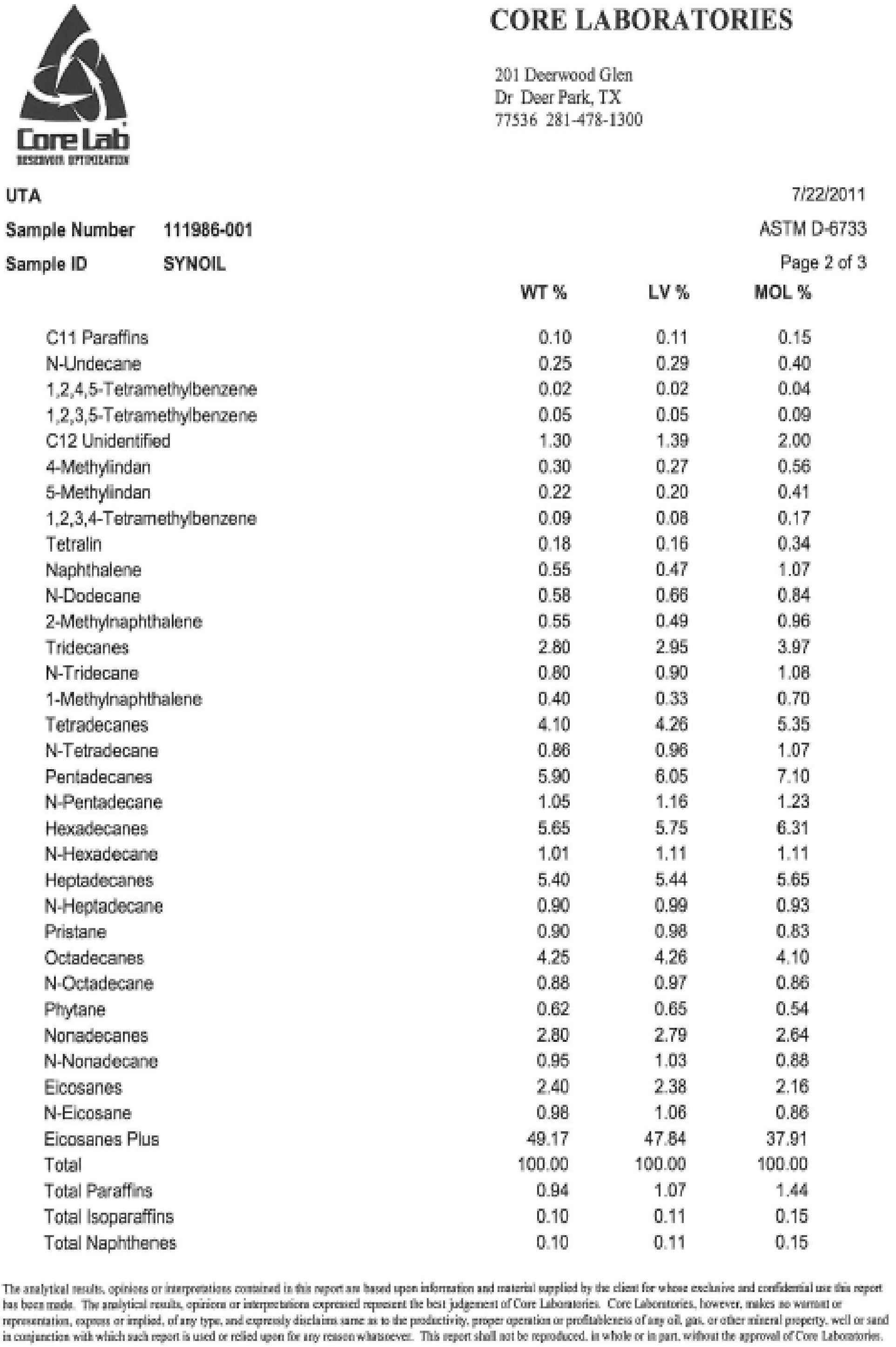
201 Deerwood Glen
Dr Deer Park, TX
77536 281-478-1300

UTA 7/22/2011

Sample Number **111986-001** ASTM D-6733

Sample ID **SYNOIL** Page 1 of 3

	WT %	**LV %**	**MOL %**
Toluene	0.02	0.02	0.05
Meta-Xylene	0.03	0.03	0.07
Para-Xylene	0.01	0.01	0.02
Ortho-Xylene	0.04	0.04	0.09
N-Nonane	0.02	0.02	0.04
n-Propylbenzene	0.02	0.02	0.04
1-Methyl-3-ethylbenzene	0.04	0.04	0.08
1-Methyl-4-ethylbenzene	0.04	0.04	0.08
1,3,5-Trimethylbenzene	0.02	0.02	0.04
Phenol	1.10	1.06	2.31
1-Methyl-2-ethylbenzene	0.04	0.04	0.08
1,2,4-Trimethylbenzene	0.11	0.11	0.23
Isobutylbenzene	0.02	0.02	0.04
N-Decane	0.09	0.10	0.16
1,2,3-Trimethylbenzene	0.15	0.14	0.31
1-Methyl-3-isopropylbenzene	0.02	0.02	0.04
Indene	0.07	0.06	0.15
2- Methyl Phenol	0.40	0.43	0.71
Indan (2,3-Dihydroindene)	0.06	0.05	0.13
1-Methyl-2-isopropylbenzene	0.03	0.03	0.06
3- Methyl Phenol	0.75	0.80	1.33
1,3-Diethylbenzene	0.03	0.03	0.06
1-Methyl-3-n-propylbenzene	0.02	0.02	0.04
1-Methyl-4-n-propylbenzene	0.06	0.06	0.11
1,4-Diethylbenzene	0.04	0.04	0.07
N-Butylbenzene	0.02	0.02	0.04
1,3-Dimethyl-5-ethylbenzene	0.07	0.07	0.13
1,2-Diethylbenzene	0.05	0.05	0.09
1,4-Dimethyl-2-ethylbenzene	0.03	0.03	0.06
1,3-Dimethyl-4-ethylbenzene	0.10	0.10	0.18
1-Methylindan	0.10	0.09	0.19
1,2-Dimethyl-4-ethylbenzene	0.09	0.09	0.17
1,3-Dimethyl-2-ethylbenzene	0.05	0.05	0.09
2-Methylindan	0.10	0.09	0.19
1,2-Dimethyl-3-Ethylbenzene	0.05	0.05	0.09
C11 Naphthenes	0.10	0.11	0.15



CORE LABORATORIES

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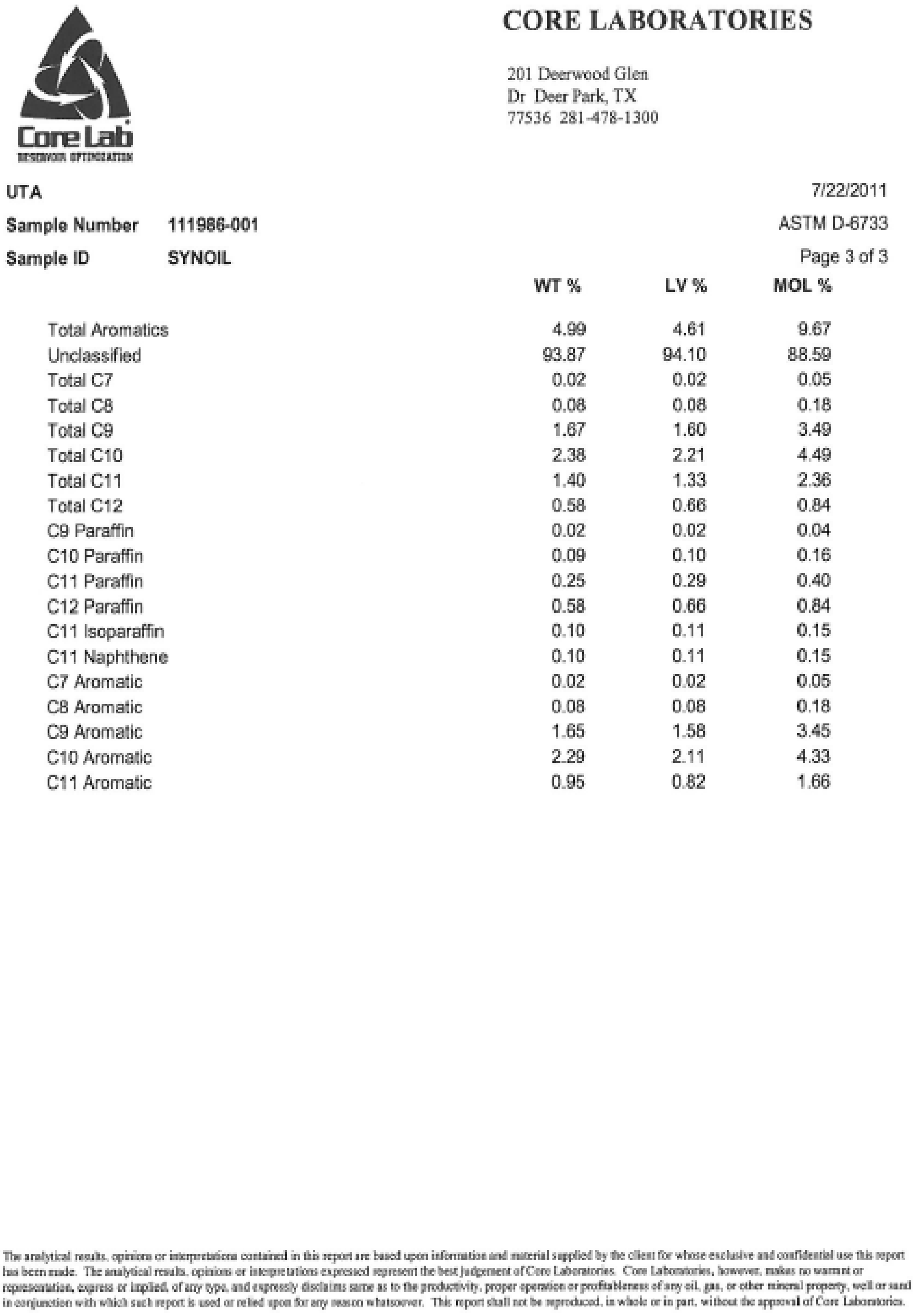
Dr Deer Park, TX
77536 281-478-1300

UTA 7/22/2011

Sample Number **111986-001** ASTM D-6733

Sample ID **SYNOIL** Page 2 of 3

	WT %	LV %	MOL %
C11 Paraffins	0.10	0.11	0.15
N-Undecane	0.25	0.29	0.40
1,2,4,5-Tetramethylbenzene	0.02	0.02	0.04
1,2,3,5-Tetramethylbenzene	0.05	0.05	0.09
C12 Unidentified	1.30	1.39	2.00
4-Methylindan	0.30	0.27	0.56
5-Methylindan	0.22	0.20	0.41
1,2,3,4-Tetramethylbenzene	0.09	0.08	0.17
Tetralin	0.18	0.16	0.34
Naphthalene	0.55	0.47	1.07
N-Dodecane	0.58	0.66	0.84
2-Methylnaphthalene	0.55	0.49	0.96
Tridecanes	2.80	2.95	3.97
N-Tridecane	0.80	0.90	1.08
1-Methylnaphthalene	0.40	0.33	0.70
Tetradecanes	4.10	4.26	5.35
N-Tetradecane	0.86	0.96	1.07
Pentadecanes	5.90	6.05	7.10
N-Pentadecane	1.05	1.16	1.23
Hexadecanes	5.65	5.75	6.31
N-Hexadecane	1.01	1.11	1.11
Heptadecanes	5.40	5.44	5.65
N-Heptadecane	0.90	0.99	0.93
Pristane	0.90	0.98	0.83
Octadecanes	4.25	4.26	4.10
N-Octadecane	0.88	0.97	0.86
Phytane	0.62	0.65	0.54
Nonadecanes	2.80	2.79	2.64
N-Nonadecane	0.95	1.03	0.88
Eicosanes	2.40	2.38	2.16
N-Eicosane	0.98	1.06	0.86
Eicosanes Plus	49.17	47.84	37.91
Total	100.00	100.00	100.00
Total Paraffins	0.94	1.07	1.44
Total Isoparaffins	0.10	0.11	0.15
Total Naphthenes	0.10	0.11	0.15



CORE LABORATORIES

201 Deerwood Glen
Dr Deer Park, TX
77536 281-478-1300

UTA 7/22/2011

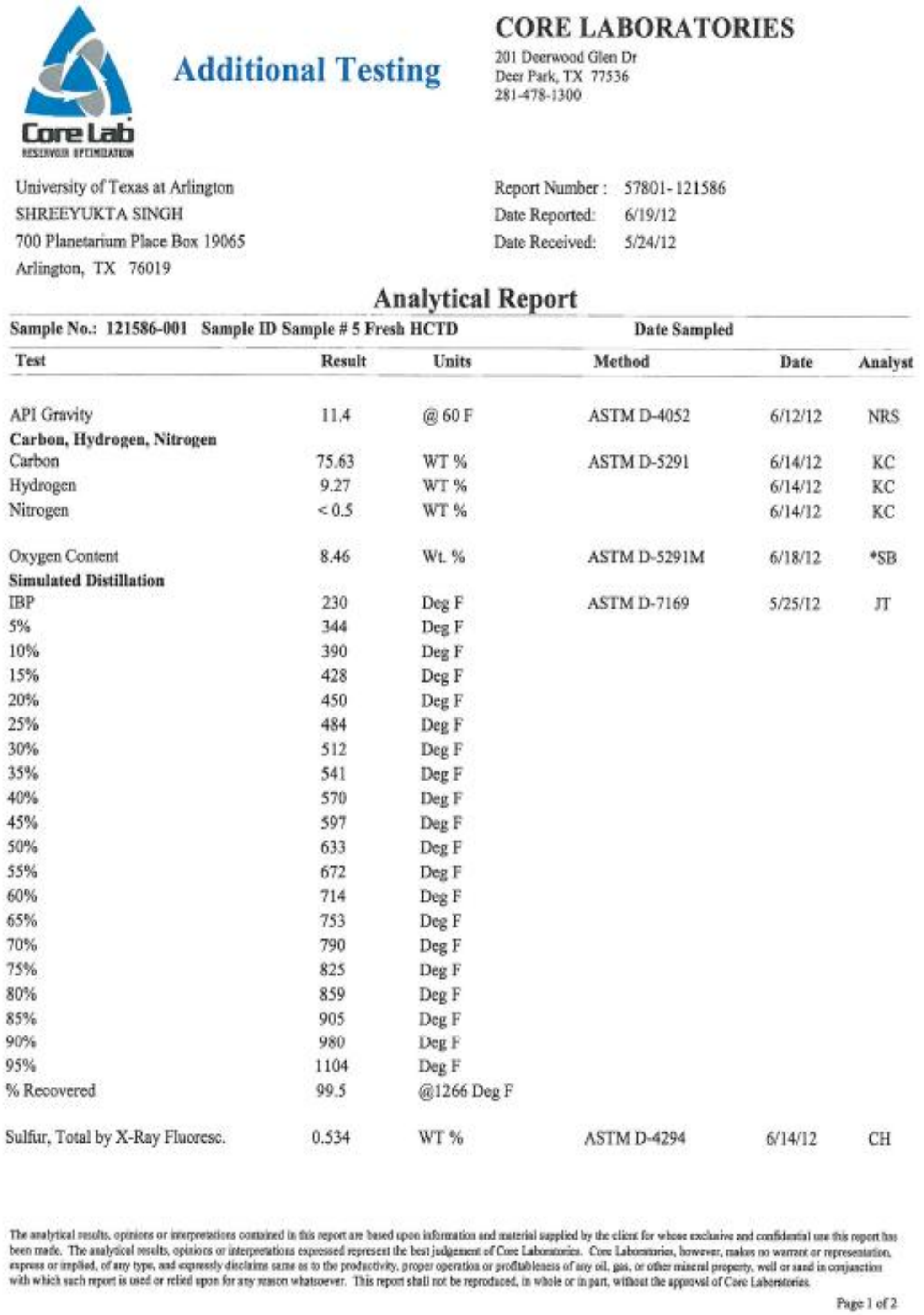
Sample Number **111986-001** ASTM D-6733

Sample ID **SYNOIL** Page 3 of 3

	WT %	**LV %**	**MOL %**
Total Aromatics	4.99	4.61	9.67
Unclassified	93.87	94.10	88.59
Total C7	0.02	0.02	0.05
Total C8	0.08	0.08	0.18
Total C9	1.67	1.60	3.49
Total C10	2.38	2.21	4.49
Total C11	1.40	1.33	2.36
Total C12	0.58	0.66	0.84
C9 Paraffin	0.02	0.02	0.04
C10 Paraffin	0.09	0.10	0.16
C11 Paraffin	0.25	0.29	0.40
C12 Paraffin	0.58	0.66	0.84
C11 Isoparaffin	0.10	0.11	0.15
C11 Naphthene	0.10	0.11	0.15
C7 Aromatic	0.02	0.02	0.05
C8 Aromatic	0.08	0.08	0.18
C9 Aromatic	1.65	1.58	3.45
C10 Aromatic	2.29	2.11	4.33
C11 Aromatic	0.95	0.82	1.66

APPENDIX B

Core Laboratory HCTD Syn Oil Analysis Report # 57801-121586



Additional Testing

CORE LABORATORIES

201 Deerwood Glen Dr
Deer Park, TX 77536
281-478-1300

University of Texas at Arlington
SHREEYUKTA SINGH
700 Planetarium Place Box 19065
Arlington, TX 76019

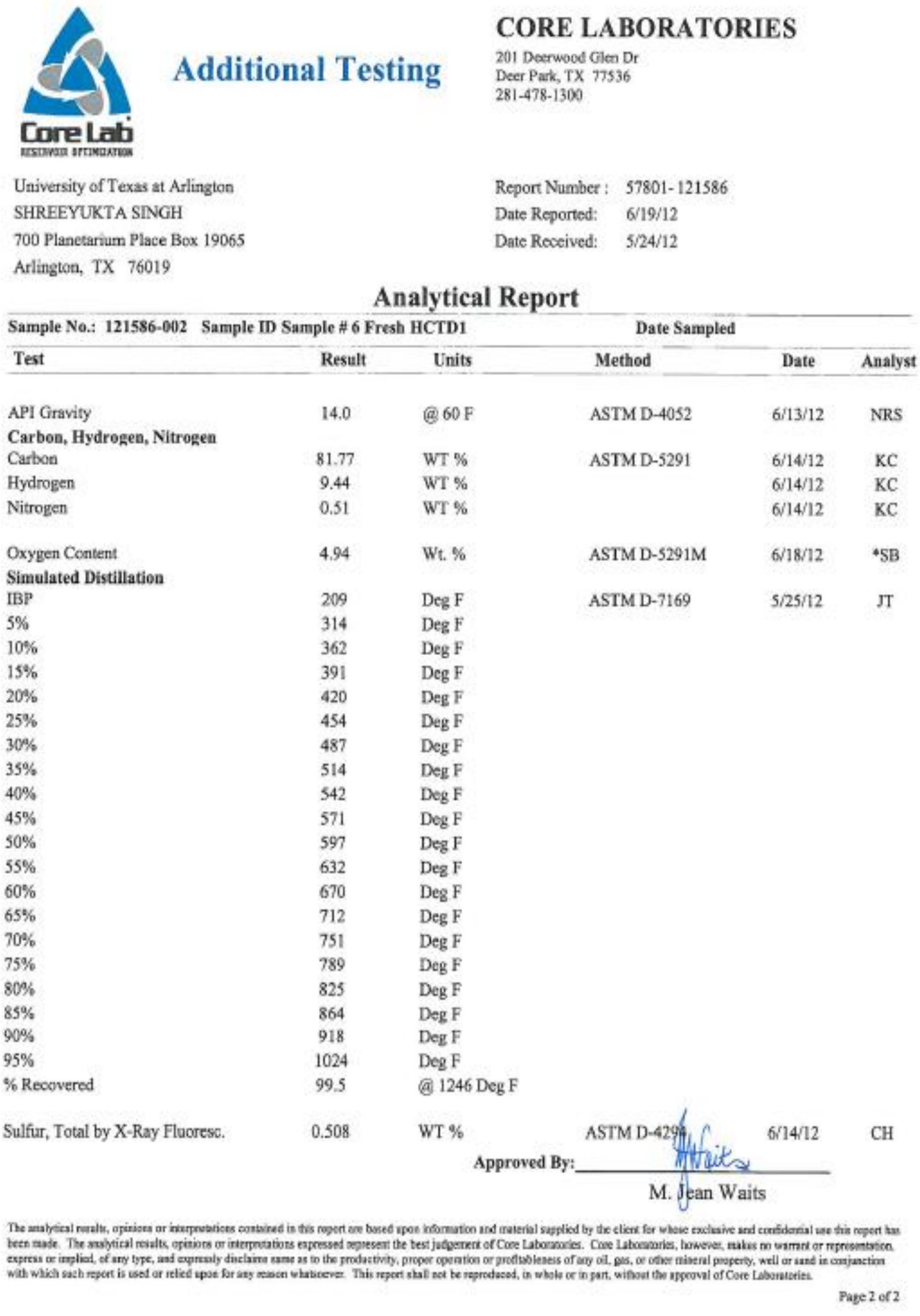
Report Number : 57801-121586
Date Reported: 6/19/12
Date Received: 5/24/12

Analytical Report

Sample No.: 121586-001 Sample ID Sample # 5 Fresh HCTD **Date Sampled**

Test	Result	Units	Method	Date	Analyst
API Gravity	11.4	@ 60 F	ASTM D-4052	6/12/12	NRS
Carbon, Hydrogen, Nitrogen					
Carbon	75.63	WT %	ASTM D-5291	6/14/12	KC
Hydrogen	9.27	WT %		6/14/12	KC
Nitrogen	< 0.5	WT %		6/14/12	KC
Oxygen Content	8.46	Wt. %	ASTM D-5291M	6/18/12	*SB
Simulated Distillation					
IBP	230	Deg F	ASTM D-7169	5/25/12	JT
5%	344	Deg F			
10%	390	Deg F			
15%	428	Deg F			
20%	450	Deg F			
25%	484	Deg F			
30%	512	Deg F			
35%	541	Deg F			
40%	570	Deg F			
45%	597	Deg F			
50%	633	Deg F			
55%	672	Deg F			
60%	714	Deg F			
65%	753	Deg F			
70%	790	Deg F			
75%	825	Deg F			
80%	859	Deg F			
85%	905	Deg F			
90%	980	Deg F			
95%	1104	Deg F			
% Recovered	99.5	@1266 Deg F			
Sulfur, Total by X-Ray Fluoresc.	0.534	WT %	ASTM D-4294	6/14/12	CH

Page 1 of 2



Additional Testing

CORE LABORATORIES

201 Deerwood Glen Dr
Deer Park, TX 77536
281-478-1300

University of Texas at Arlington
SHREEYUKTA SINGH
700 Planetarium Place Box 19065
Arlington, TX 76019

Report Number : 57801-121586
Date Reported: 6/19/12
Date Received: 5/24/12

Analytical Report

Sample No.: 121586-002 Sample ID Sample # 6 Fresh HCTD1 **Date Sampled**

Test	Result	Units	Method	Date	Analyst
API Gravity	14.0	@ 60 F	ASTM D-4052	6/13/12	NRS
Carbon, Hydrogen, Nitrogen					
Carbon	81.77	WT %	ASTM D-5291	6/14/12	KC
Hydrogen	9.44	WT %		6/14/12	KC
Nitrogen	0.51	WT %		6/14/12	KC
Oxygen Content	4.94	Wt. %	ASTM D-5291M	6/18/12	*SB
Simulated Distillation					
IBP	209	Deg F	ASTM D-7169	5/25/12	JT
5%	314	Deg F			
10%	362	Deg F			
15%	391	Deg F			
20%	420	Deg F			
25%	454	Deg F			
30%	487	Deg F			
35%	514	Deg F			
40%	542	Deg F			
45%	571	Deg F			
50%	597	Deg F			
55%	632	Deg F			
60%	670	Deg F			
65%	712	Deg F			
70%	751	Deg F			
75%	789	Deg F			
80%	825	Deg F			
85%	864	Deg F			
90%	918	Deg F			
95%	1024	Deg F			
% Recovered	99.5	@ 1246 Deg F			
Sulfur, Total by X-Ray Fluoresc.	0.508	WT %	ASTM D-4294	6/14/12	CH

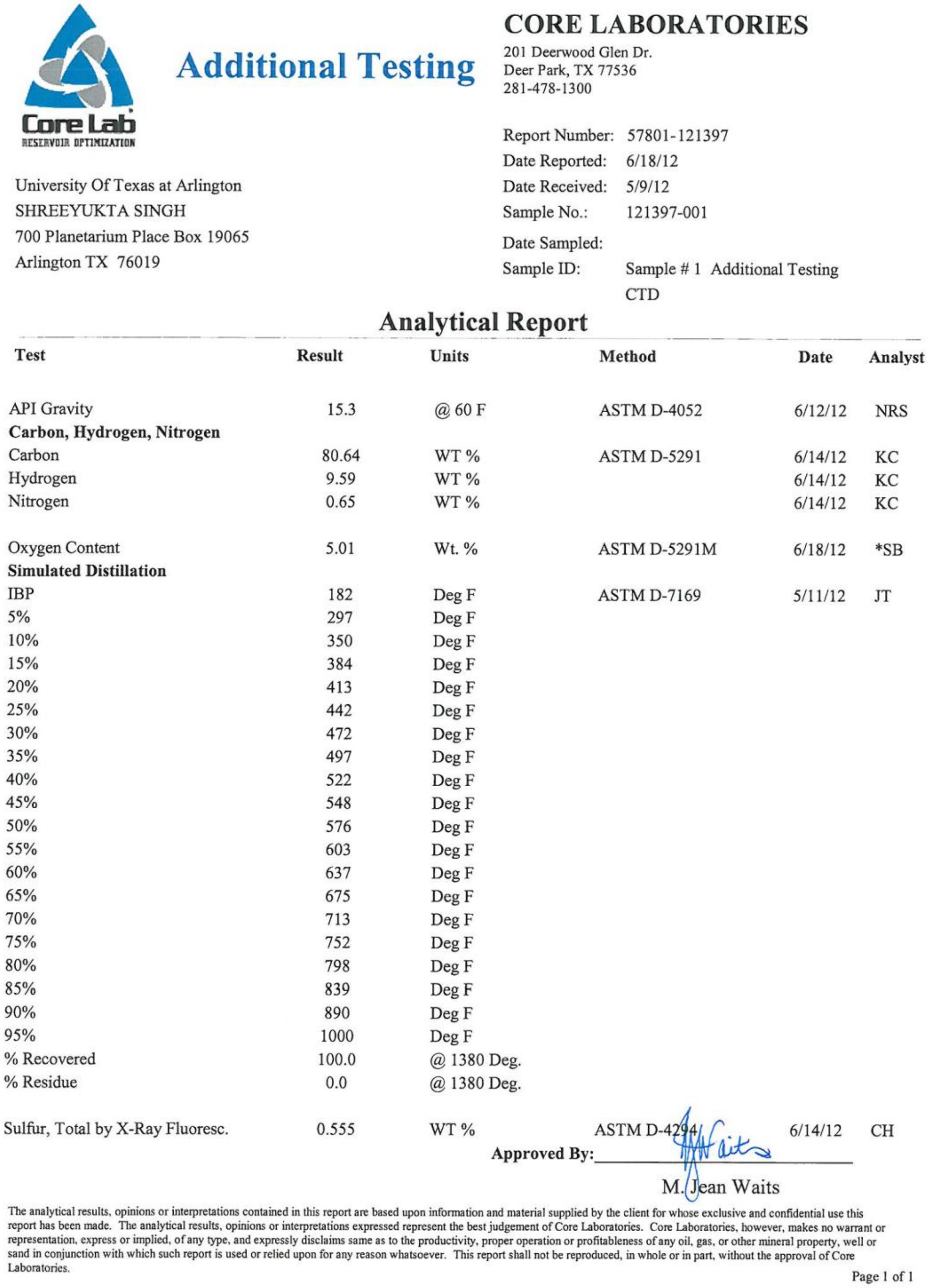
Approved By: MWaits

M. Jean Waits

Page 2 of 2

APPENDIX C

CORE LABORATORY SYN OIL ANALYSIS REPORT # 57801-121397



Core Lab
RESERVOIR OPTIMIZATION

Additional Testing

CORE LABORATORIES
201 Deerwood Glen Dr.
Deer Park, TX 77536
281-478-1300

Report Number: 57801-121397
Date Reported: 6/18/12
Date Received: 5/9/12
Sample No.: 121397-001
Date Sampled:
Sample ID: Sample # 1 Additional Testing
CTD

University Of Texas at Arlington
SHREEYUKTA SINGH
700 Planetarium Place Box 19065
Arlington TX 76019

Analytical Report

Test	Result	Units	Method	Date	Analyst
API Gravity	15.3	@ 60 F	ASTM D-4052	6/12/12	NRS
Carbon, Hydrogen, Nitrogen					
Carbon	80.64	WT %	ASTM D-5291	6/14/12	KC
Hydrogen	9.59	WT %		6/14/12	KC
Nitrogen	0.65	WT %		6/14/12	KC
Oxygen Content	5.01	Wt. %	ASTM D-5291M	6/18/12	*SB
Simulated Distillation					
IBP	182	Deg F	ASTM D-7169	5/11/12	JT
5%	297	Deg F			
10%	350	Deg F			
15%	384	Deg F			
20%	413	Deg F			
25%	442	Deg F			
30%	472	Deg F			
35%	497	Deg F			
40%	522	Deg F			
45%	548	Deg F			
50%	576	Deg F			
55%	603	Deg F			
60%	637	Deg F			
65%	675	Deg F			
70%	713	Deg F			
75%	752	Deg F			
80%	798	Deg F			
85%	839	Deg F			
90%	890	Deg F			
95%	1000	Deg F			
% Recovered	100.0	@ 1380 Deg.			
% Residue	0.0	@ 1380 Deg.			
Sulfur, Total by X-Ray Fluoresc.	0.555	WT %	ASTM D-4294	6/14/12	CH

Approved By:
M. Jean Waits

APPENDIX D

CORE LABORATORY SYN OIL ANALYSIS REPORT # 57801-121672

Core Lab
RESERVOIR OPTIMIZATION

CORE LABORATORIES
201 Deerwood Glen Dr
Deer Park, TX 77536
281-478-1300

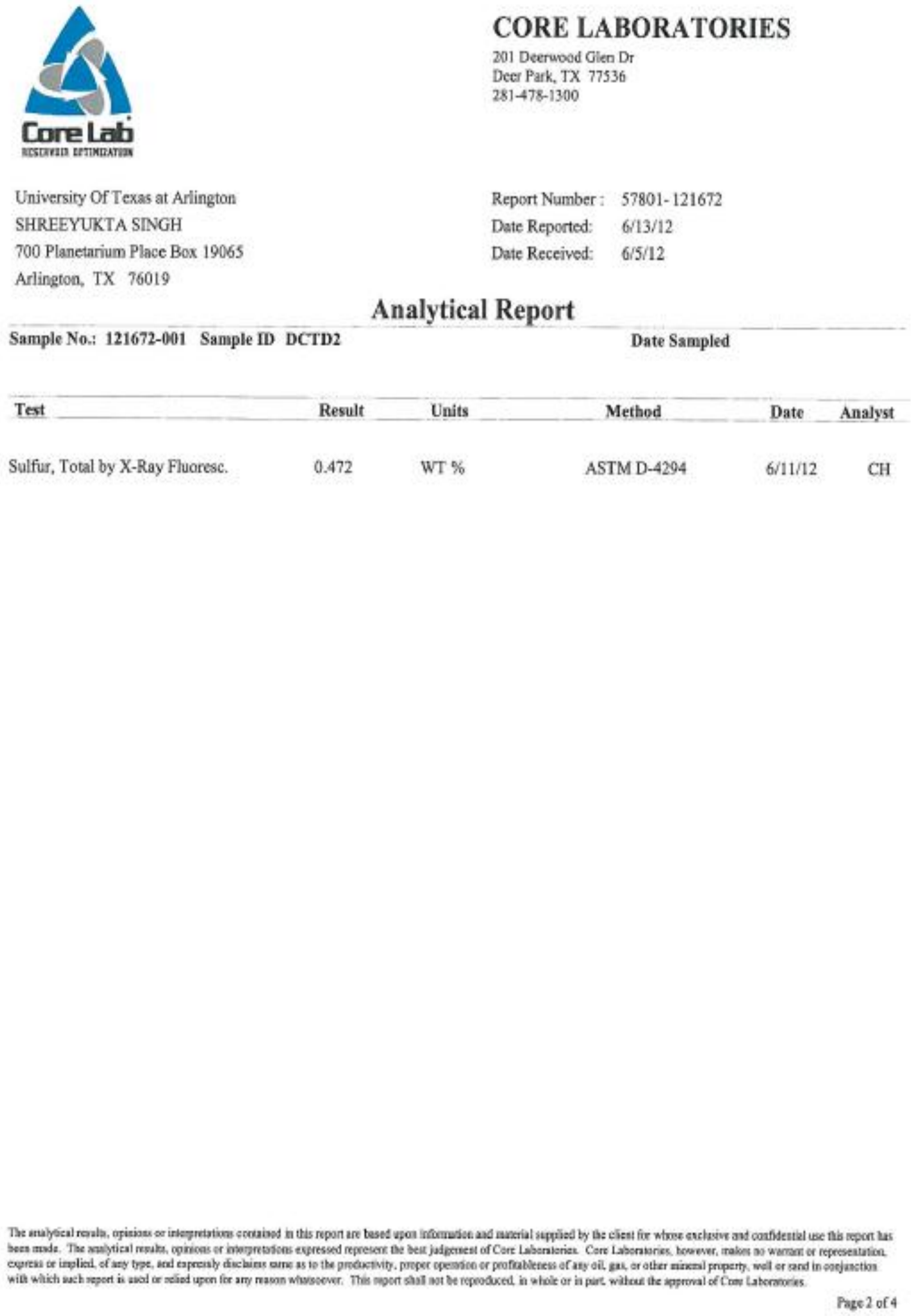
University Of Texas at Arlington
SHREEYUKTA SINGH
700 Planetarium Place Box 19065
Arlington, TX 76019

Report Number : 57801- 121672
Date Reported: 6/13/12
Date Received: 6/5/12

Analytical Report

Sample No.: 121672-001 Sample ID DCTD2 **Date Sampled**

Test	Result	Units	Method	Date	Analyst
Carbon, Hydrogen, Nitrogen					
Carbon	70.99	WT %	ASTM D-5291	6/11/12	KC
Hydrogen	9.12	WT %		6/11/12	KC
Nitrogen	< 0.5	WT %		6/11/12	KC
Oxygen Content	9.88	WT %	ASTM D-5291M	6/12/12	*SB
Simulated Distillation					
IBP	201	Deg F	ASTM D-7169	6/6/12	JT
5%	320	Deg F			
10%	380	Deg F			
15%	426	Deg F			
20%	464	Deg F			
25%	498	Deg F			
30%	529	Deg F			
35%	560	Deg F			
40%	589	Deg F			
45%	626	Deg F			
50%	669	Deg F			
55%	713	Deg F			
60%	754	Deg F			
65%	792	Deg F			
70%	828	Deg F			
75%	865	Deg F			
80%	911	Deg F			
85%	988	Deg F			
90%	1100	Deg F			
95%	1220	Deg F			
FBP	1292	Deg F			
% Residue	0.0	@ 1380 Deg.			
Specific Gravity	1.0581	@60/60 Deg F	ASTM D-4052	6/8/12	NRS



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201 Deerwood Glen Dr
Deer Park, TX 77536
281-478-1300

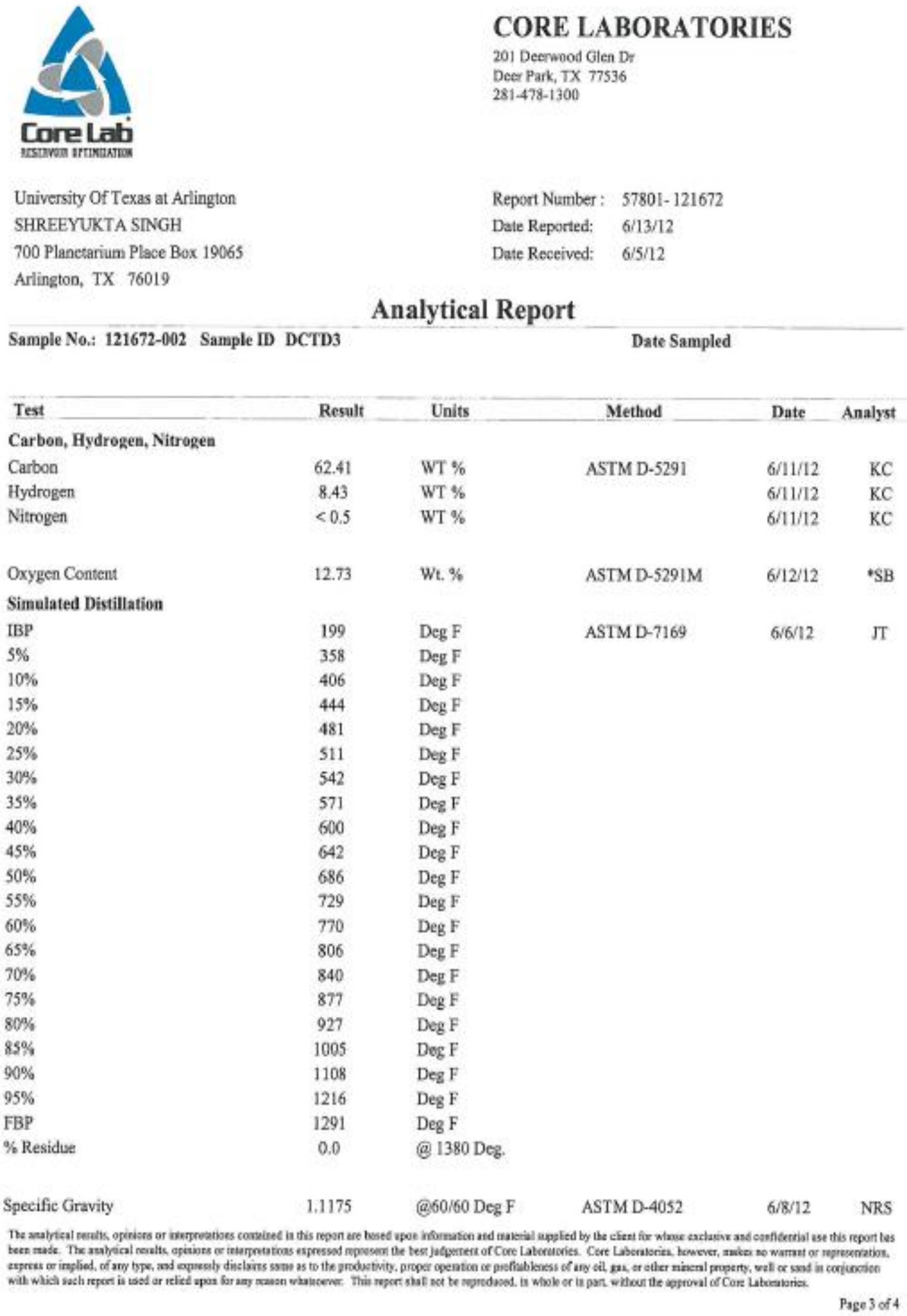
University Of Texas at Arlington
SHREEYUKTA SINGH
700 Planetarium Place Box 19065
Arlington, TX 76019

Report Number : 57801-121672
Date Reported: 6/13/12
Date Received: 6/5/12

Analytical Report

Sample No.: 121672-001 Sample ID DCTD2 **Date Sampled**

Test	Result	Units	Method	Date	Analyst
Sulfur, Total by X-Ray Fluoresc.	0.472	WT %	ASTM D-4294	6/11/12	CH



CORE LABORATORIES

201 Deerwood Glen Dr
Deer Park, TX 77536
281-478-1300

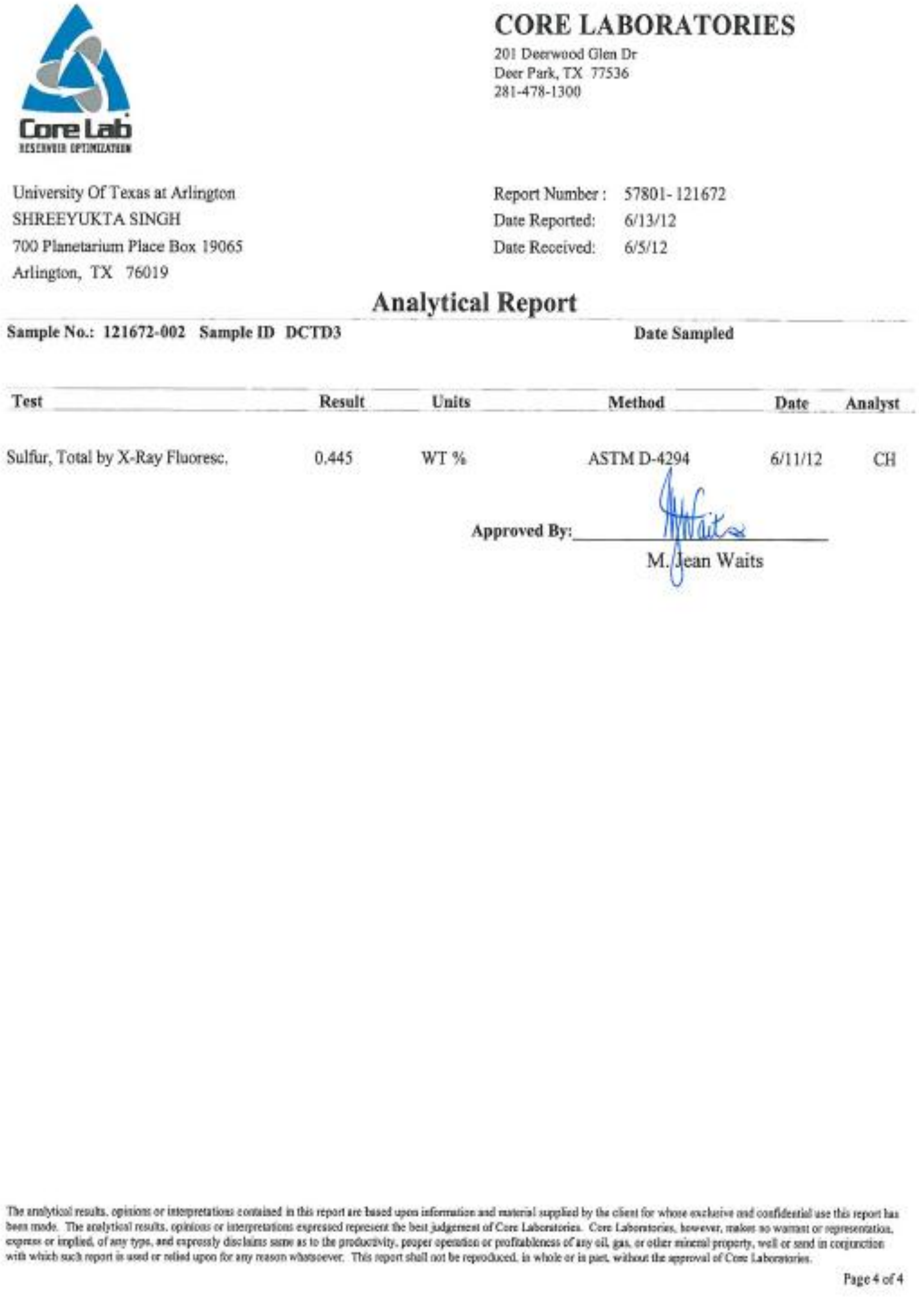
University Of Texas at Arlington
SHREEYUKTA SINGH
700 Planetarium Place Box 19065
Arlington, TX 76019

Report Number : 57801- 121672
Date Reported: 6/13/12
Date Received: 6/5/12

Analytical Report

Sample No.: 121672-002 Sample ID DCTD3 **Date Sampled**

Test	Result	Units	Method	Date	Analyst
Carbon, Hydrogen, Nitrogen					
Carbon	62.41	WT %	ASTM D-5291	6/11/12	KC
Hydrogen	8.43	WT %		6/11/12	KC
Nitrogen	< 0.5	WT %		6/11/12	KC
Oxygen Content	12.73	Wt. %	ASTM D-5291M	6/12/12	*SB
Simulated Distillation					
IBP	199	Deg F	ASTM D-7169	6/6/12	JT
5%	358	Deg F			
10%	406	Deg F			
15%	444	Deg F			
20%	481	Deg F			
25%	511	Deg F			
30%	542	Deg F			
35%	571	Deg F			
40%	600	Deg F			
45%	642	Deg F			
50%	686	Deg F			
55%	729	Deg F			
60%	770	Deg F			
65%	806	Deg F			
70%	840	Deg F			
75%	877	Deg F			
80%	927	Deg F			
85%	1005	Deg F			
90%	1108	Deg F			
95%	1216	Deg F			
FBP	1291	Deg F			
% Residue	0.0	@ 1380 Deg.			
Specific Gravity	1.1175	@60/60 Deg F	ASTM D-4052	6/8/12	NRS



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201 Deerwood Glen Dr
Deer Park, TX 77536
281-478-1300

University Of Texas at Arlington
SHREEYUKTA SINGH
700 Planetarium Place Box 19065
Arlington, TX 76019

Report Number: 57801-121672
Date Reported: 6/13/12
Date Received: 6/5/12

Analytical Report

Sample No.: 121672-002 Sample ID DCTD3 **Date Sampled**

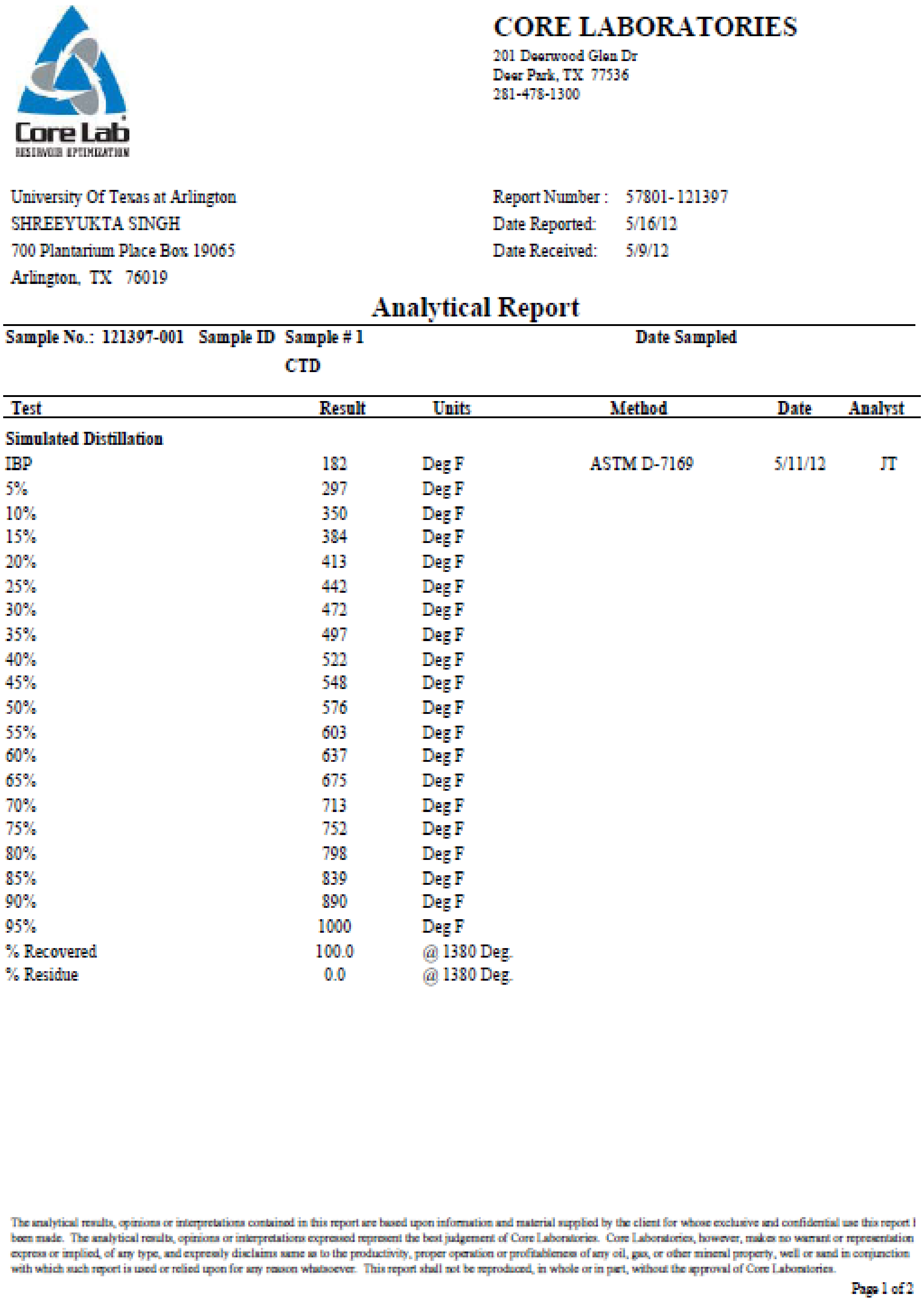
Test	Result	Units	Method	Date	Analyst
Sulfur, Total by X-Ray Fluoresc.	0.445	WT %	ASTM D-4294	6/11/12	CH

Approved By: MWaits
M. Jean Waits

Page 4 of 4

APPENDIX E

CORE LABORATORY SYN OIL ANALYSIS REPORT # 57801-121397



CORE LABORATORIES
201 Deerwood Glen Dr
Deer Park, TX 77536
281-478-1300

University Of Texas at Arlington
SHREEYUKTA SINGH
700 Plantarium Place Box 19065
Arlington, TX 76019

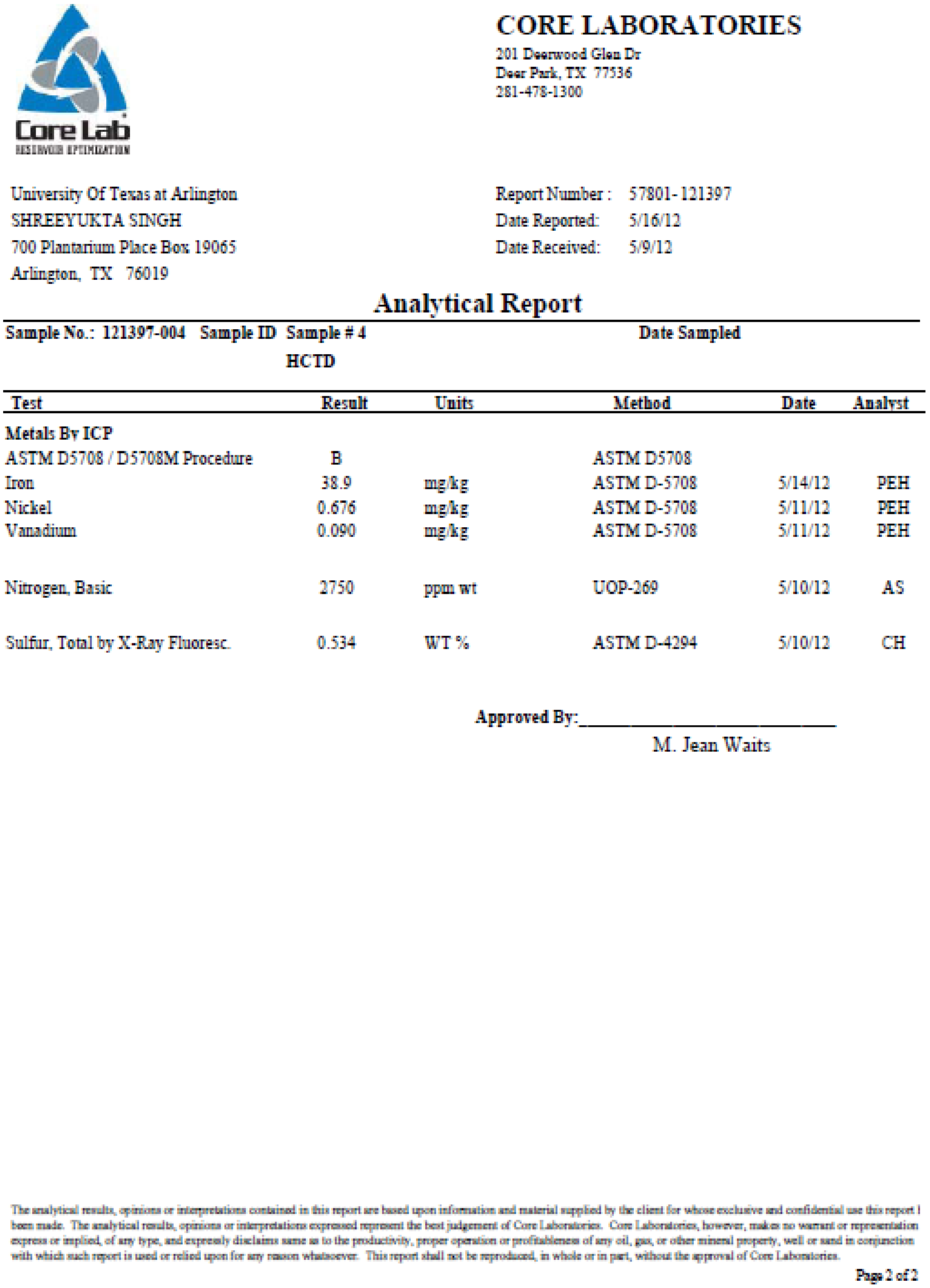
Report Number : 57801- 121397
Date Reported: 5/16/12
Date Received: 5/9/12

Analytical Report

Sample No.: 121397-001 **Sample ID** **Sample # 1** **Date Sampled**
CTD

Test	Result	Units	Method	Date	Analyst
Simulated Distillation					
IBP	182	Deg F	ASTM D-7169	5/11/12	JT
5%	297	Deg F			
10%	350	Deg F			
15%	384	Deg F			
20%	413	Deg F			
25%	442	Deg F			
30%	472	Deg F			
35%	497	Deg F			
40%	522	Deg F			
45%	548	Deg F			
50%	576	Deg F			
55%	603	Deg F			
60%	637	Deg F			
65%	675	Deg F			
70%	713	Deg F			
75%	752	Deg F			
80%	798	Deg F			
85%	839	Deg F			
90%	890	Deg F			
95%	1000	Deg F			
% Recovered	100.0	@ 1380 Deg.			
% Residue	0.0	@ 1380 Deg.			

Page 1 of 2



CORE LABORATORIES
201 Deerwood Glen Dr
Deer Park, TX 77536
281-478-1300

University Of Texas at Arlington
SHREEYUKTA SINGH
700 Plantarium Place Box 19065
Arlington, TX 76019

Report Number : 57801-121397
Date Reported: 5/16/12
Date Received: 5/9/12

Analytical Report

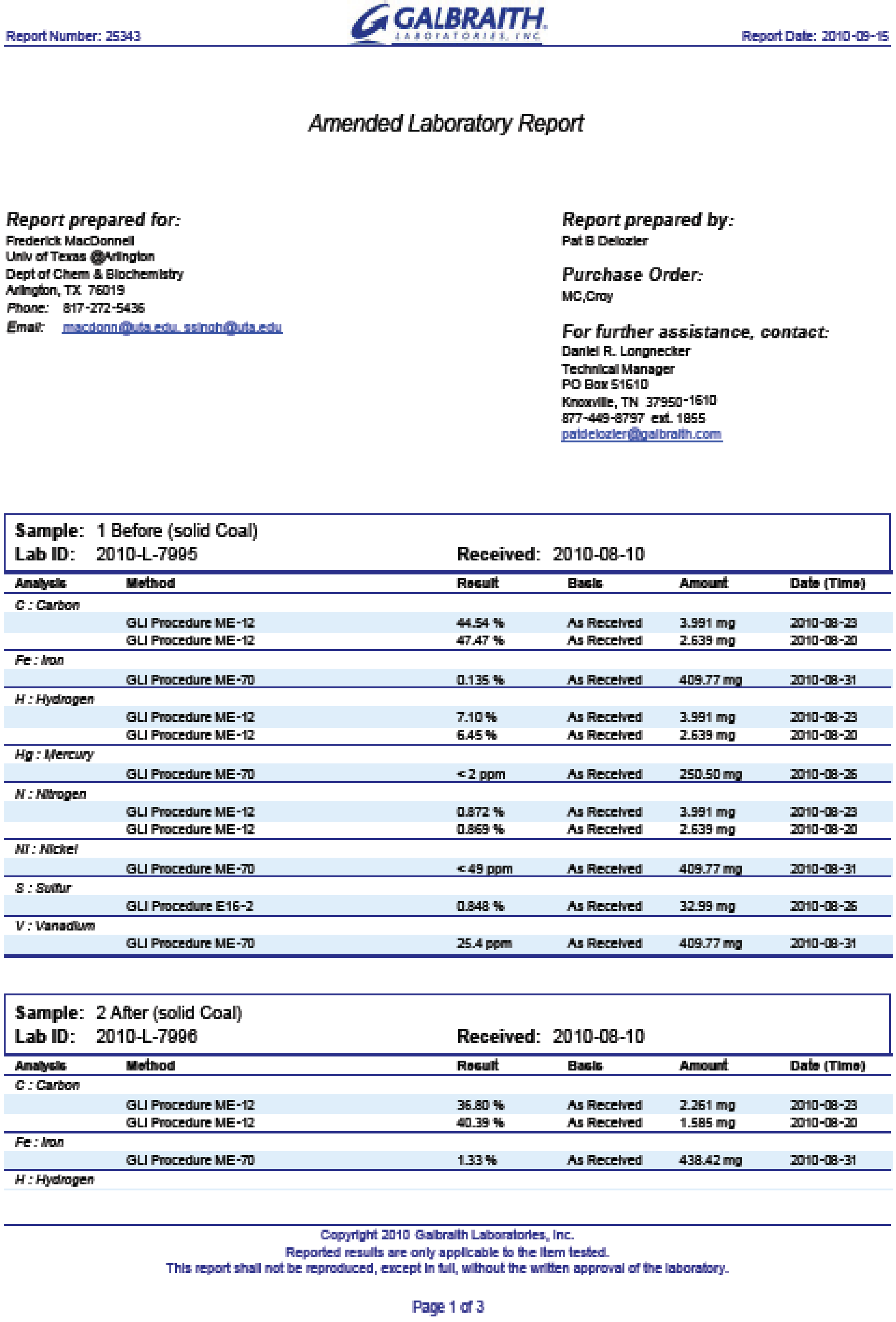
Sample No.: 121397-004 Sample ID Sample # 4 HCTD **Date Sampled**

Test	Result	Units	Method	Date	Analyst
Metals By ICP					
ASTM D5708 / D5708M Procedure	B		ASTM D5708		
Iron	38.9	mg/kg	ASTM D-5708	5/14/12	PEH
Nickel	0.676	mg/kg	ASTM D-5708	5/11/12	PEH
Vanadium	0.090	mg/kg	ASTM D-5708	5/11/12	PEH
Nitrogen, Basic	2750	ppm wt	UOP-269	5/10/12	AS
Sulfur, Total by X-Ray Fluoresc.	0.534	WT %	ASTM D-4294	5/10/12	CH

Approved By:____________________________
M. Jean Waits

APPENDIX F

GALBRITH SYN OIL ANALYSIS REPORT # 25343



Report Number: 25343 GALBRAITH LABORATORIES, INC. Report Date: 2010-09-15

Amended Laboratory Report

Report prepared for:
Frederick MacDonnell
Univ of Texas @Arlington
Dept of Chem & Biochemistry
Arlington, TX 76019
Phone: 817-272-5436
Email: macdonn@uta.edu, ssingh@uta.edu

Report prepared by:
Pat B Delozier

Purchase Order:
MC,Croy

For further assistance, contact:
Daniel R. Longnecker
Technical Manager
PO Box 51610
Knoxville, TN 37950-1610
877-449-8797 ext. 1855
patdelozier@galbraith.com

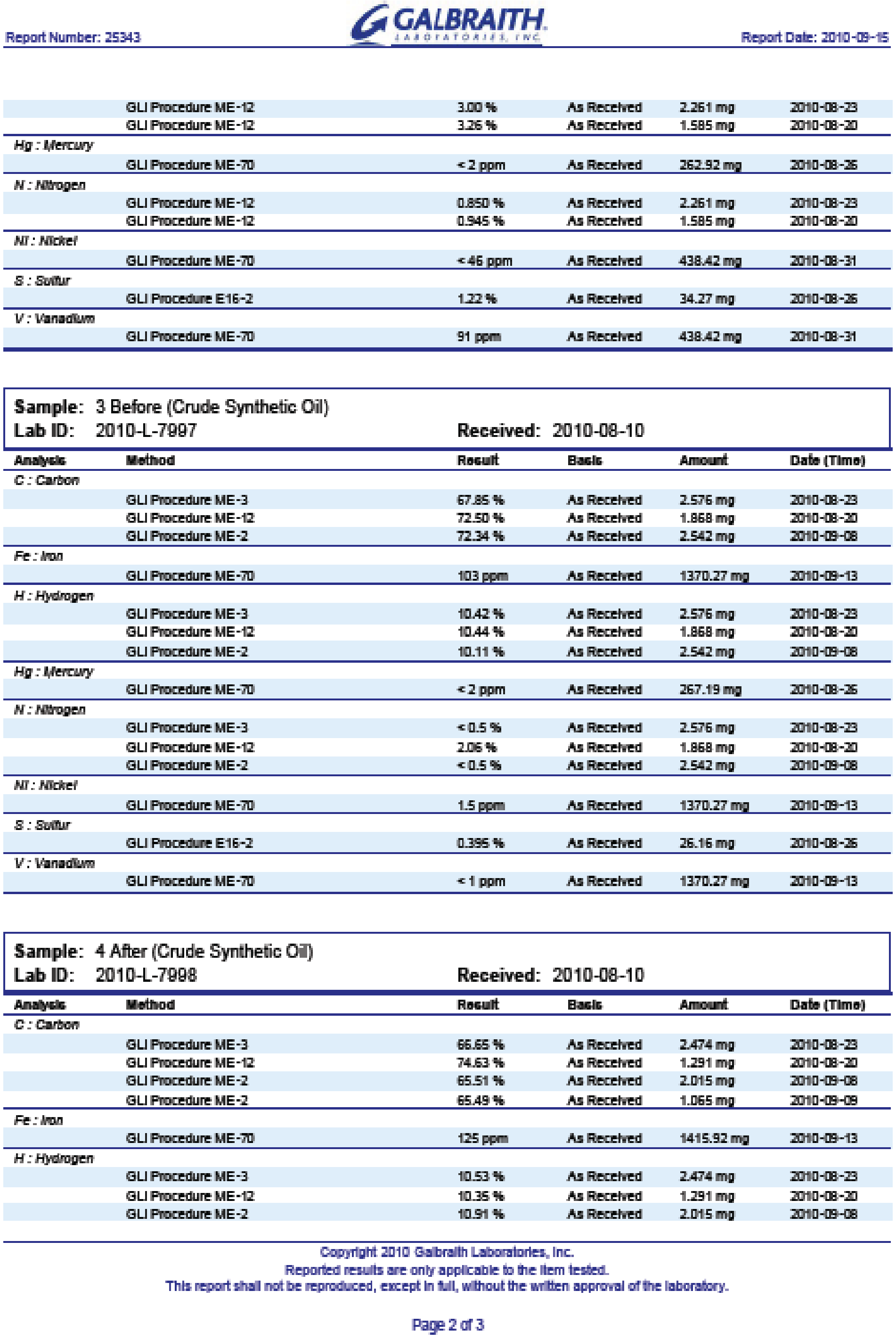
Sample: 1 Before (solid Coal)
Lab ID: 2010-L-7995 **Received:** 2010-08-10

Analysis	Method	Result	Basis	Amount	Date (Time)
C : Carbon					
	GLI Procedure ME-12	44.54 %	As Received	3.991 mg	2010-08-23
	GLI Procedure ME-12	47.47 %	As Received	2.639 mg	2010-08-20
Fe : Iron					
	GLI Procedure ME-70	0.135 %	As Received	409.77 mg	2010-08-31
H : Hydrogen					
	GLI Procedure ME-12	7.10 %	As Received	3.991 mg	2010-08-23
	GLI Procedure ME-12	6.45 %	As Received	2.639 mg	2010-08-20
Hg : Mercury					
	GLI Procedure ME-70	< 2 ppm	As Received	250.50 mg	2010-08-26
N : Nitrogen					
	GLI Procedure ME-12	0.872 %	As Received	3.991 mg	2010-08-23
	GLI Procedure ME-12	0.869 %	As Received	2.639 mg	2010-08-20
Ni : Nickel					
	GLI Procedure ME-70	< 49 ppm	As Received	409.77 mg	2010-08-31
S : Sulfur					
	GLI Procedure E16-2	0.848 %	As Received	32.99 mg	2010-08-26
V : Vanadium					
	GLI Procedure ME-70	25.4 ppm	As Received	409.77 mg	2010-08-31

Sample: 2 After (solid Coal)
Lab ID: 2010-L-7996 **Received:** 2010-08-10

Analysis	Method	Result	Basis	Amount	Date (Time)
C : Carbon					
	GLI Procedure ME-12	36.80 %	As Received	2.261 mg	2010-08-23
	GLI Procedure ME-12	40.39 %	As Received	1.585 mg	2010-08-20
Fe : Iron					
	GLI Procedure ME-70	1.33 %	As Received	438.42 mg	2010-08-31
H : Hydrogen					

Page 1 of 3



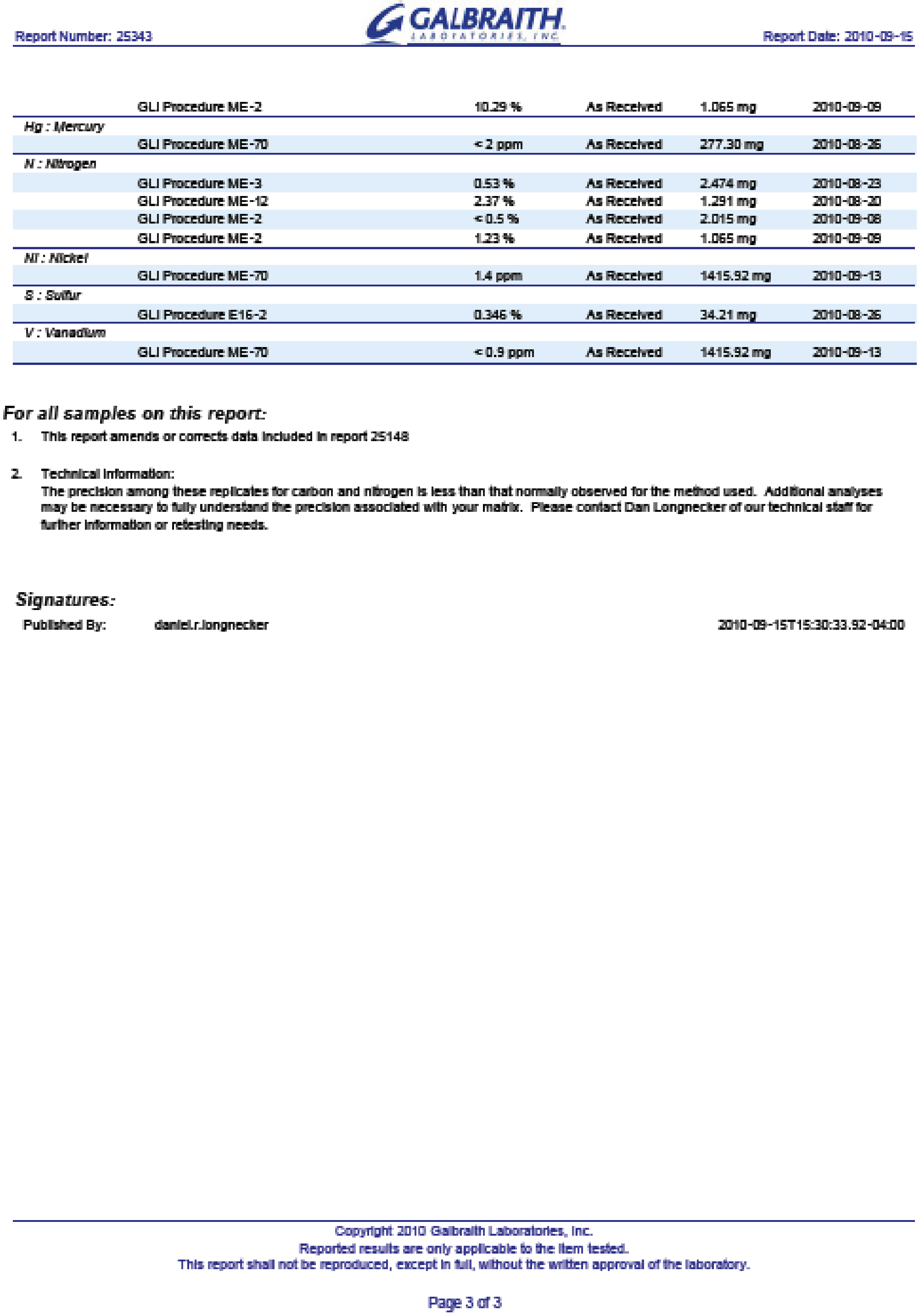
	GLI Procedure ME-12	3.00 %	As Received	2.261 mg	2010-08-23
	GLI Procedure ME-12	3.26 %	As Received	1.585 mg	2010-08-20
Hg : Mercury					
	GLI Procedure ME-70	< 2 ppm	As Received	262.92 mg	2010-08-26
N : Nitrogen					
	GLI Procedure ME-12	0.850 %	As Received	2.261 mg	2010-08-23
	GLI Procedure ME-12	0.945 %	As Received	1.585 mg	2010-08-20
Ni : Nickel					
	GLI Procedure ME-70	< 46 ppm	As Received	438.42 mg	2010-08-31
S : Sulfur					
	GLI Procedure E16-2	1.22 %	As Received	34.27 mg	2010-08-26
V : Vanadium					
	GLI Procedure ME-70	91 ppm	As Received	438.42 mg	2010-08-31

Sample: 3 Before (Crude Synthetic Oil)
Lab ID: 2010-L-7997 **Received:** 2010-08-10

Analysis	Method	Result	Basis	Amount	Date (Time)
C : Carbon					
	GLI Procedure ME-3	67.85 %	As Received	2.576 mg	2010-08-23
	GLI Procedure ME-12	72.50 %	As Received	1.868 mg	2010-08-20
	GLI Procedure ME-2	72.34 %	As Received	2.542 mg	2010-09-08
Fe : Iron					
	GLI Procedure ME-70	103 ppm	As Received	1370.27 mg	2010-09-13
H : Hydrogen					
	GLI Procedure ME-3	10.42 %	As Received	2.576 mg	2010-08-23
	GLI Procedure ME-12	10.44 %	As Received	1.868 mg	2010-08-20
	GLI Procedure ME-2	10.11 %	As Received	2.542 mg	2010-09-08
Hg : Mercury					
	GLI Procedure ME-70	< 2 ppm	As Received	267.19 mg	2010-08-26
N : Nitrogen					
	GLI Procedure ME-3	< 0.5 %	As Received	2.576 mg	2010-08-23
	GLI Procedure ME-12	2.06 %	As Received	1.868 mg	2010-08-20
	GLI Procedure ME-2	< 0.5 %	As Received	2.542 mg	2010-09-08
Ni : Nickel					
	GLI Procedure ME-70	1.5 ppm	As Received	1370.27 mg	2010-09-13
S : Sulfur					
	GLI Procedure E16-2	0.395 %	As Received	26.16 mg	2010-08-26
V : Vanadium					
	GLI Procedure ME-70	< 1 ppm	As Received	1370.27 mg	2010-09-13

Sample: 4 After (Crude Synthetic Oil)
Lab ID: 2010-L-7998 **Received:** 2010-08-10

Analysis	Method	Result	Basis	Amount	Date (Time)
C : Carbon					
	GLI Procedure ME-3	66.65 %	As Received	2.474 mg	2010-08-23
	GLI Procedure ME-12	74.63 %	As Received	1.291 mg	2010-08-20
	GLI Procedure ME-2	65.51 %	As Received	2.015 mg	2010-09-08
	GLI Procedure ME-2	65.49 %	As Received	1.065 mg	2010-09-09
Fe : Iron					
	GLI Procedure ME-70	125 ppm	As Received	1415.92 mg	2010-09-13
H : Hydrogen					
	GLI Procedure ME-3	10.53 %	As Received	2.474 mg	2010-08-23
	GLI Procedure ME-12	10.35 %	As Received	1.291 mg	2010-08-20
	GLI Procedure ME-2	10.91 %	As Received	2.015 mg	2010-09-08



	GLI Procedure ME-2	10.29 %	As Received	1.065 mg	2010-09-09
Hg : Mercury					
	GLI Procedure ME-70	< 2 ppm	As Received	277.30 mg	2010-08-26
N : Nitrogen					
	GLI Procedure ME-3	0.53 %	As Received	2.474 mg	2010-08-23
	GLI Procedure ME-12	2.37 %	As Received	1.291 mg	2010-08-20
	GLI Procedure ME-2	< 0.5 %	As Received	2.015 mg	2010-09-08
	GLI Procedure ME-2	1.23 %	As Received	1.065 mg	2010-09-09
Ni : Nickel					
	GLI Procedure ME-70	1.4 ppm	As Received	1415.92 mg	2010-09-13
S : Sulfur					
	GLI Procedure E16-2	0.346 %	As Received	34.21 mg	2010-08-26
V : Vanadium					
	GLI Procedure ME-70	< 0.9 ppm	As Received	1415.92 mg	2010-09-13

For all samples on this report:

1. This report amends or corrects data included in report 25148

2. Technical Information:
   The precision among these replicates for carbon and nitrogen is less than that normally observed for the method used. Additional analyses may be necessary to fully understand the precision associated with your matrix. Please contact Dan Longnecker of our technical staff for further information or retesting needs.

Signatures:

Published By:	daniel.r.longnecker	2010-09-15T15:30:33.92-04:00

APPENDIX G

UTA Report of Lignite Coal Liquefaction Report

R&D Status Report

HR0011-09-C-0108

Hydrogenation of CTD to HCTD

Run	Starting Material: CH%	T (C)	P (psi)	Catalyst	Time (h)	Yield	CH% After
1 22Oct09	64.6 9.5	300	400	10%Pd/C	12	44	83.2 9.0
2	74.8 9.1	300	1000	10%Pd/alumina	8	63	83.0 8.9
3 5Nov09	80.7 8.3	300	400	10%Pd/alumina	8	??	83.0 9.6
3 11Nov09	72.0 10.0	300	500	10%Pd/alumina	8	70	84.4 10.4
4 14Dec09	72.3 9.89	300	400	10%Pd/alumina	8	80	84.35 10.3
5 12Jan10	72.5 9.3	300	700	25% Ni/Alumina	8	71	84.9 9.9
6 18Jan10	73.2 9.6	300	400	10%Pd/alumina	8	80	83.5 10.2
7 27Jan10	77.9 10.8	300	700	BXF1	8	80	84.0 10.1
8 15Oct 2010 Big Bertha	79.97 9.13	320	1000	BXF1	2	95	85.09 8.7 2.41

9 Oct. 29 2010 Big Bertha	89.07 11.07 3.22	300	560	BXF1	2	97	**84.38** **9.97** **0.88**
10 Dec. 01 2010 Big Bertha	71.78 9.89 2.40	300	1200	BXF1	2	96	**83.83** **9.72** **2.72**
11 Fab. 11 2011 Big Bertha	82.51 8.34 3.50	300	1200	BXF1	2	98	**83.31** **8.63** **5.08**
12 Fab. 23 2011	75.42 9.70 0.95	300	1400	BXF1	2	88	**84.11** **10.26** **3.95**
13 April 28 2011		320	800	BXF1	2	93	
14 June 27 2011 Oil from the 4th Dig. 06132011 d1.1g	82.51 8.34 3.50	320	600	2.50g BXF1	2	95	81.38 8.43 0.45
15 July 05 2011-07-05 Re used DCTD	82.51 8.34 3.50	350	600	11.4g of BXF1	2	96	**81.92** **8.94** **0.33**

16 10-17-2012 Re used DCTD	81.46 8.54 2.99	330	800	9.32g of BXF1	2	97	**82.92** **9.74** **0.43**
17 11-18-2012	82.51 8.56 3.64	320	1000	10.0 g of BXF1	2	94	**83.78** **9.62** **0.54**
18 01-24-2012	79.35 8.98 0.40	320	1000	6.4 g of BXF1	2	96	**78.57** **8.82** **0.34**
19 02-10-2012	Terminated	320	1000	6.01 of BXF1	2	Terminated	Terminated
20 02-11-2012 It shows water in the reactor	83.02 9.46 1.84	320	1000	3.45 of BXF1	2	91	**81.86** **9.04** **0.86**
20 02-13-2012	83.02 9.46 1.84	360	1300	3.20 of BXF1	2	93	**84.34** **8.75** **2.50**
21 05/08/2012	82.56 10.32 3.24	320	800	60.0g of BXF1	2	94.0	**83.32** **11.37** **1.64**
22 06-02-2012	*83.98* 9.56 5.44	320	800	56.0g of BXF1	2	91.2	**83.51** **11.03** **2.64**
23 06-06-2012	80.46 9.59 0.00	320	800	48.0g of BXF1	2	93.5	**85.33** **8.34** **3.67**

24 06-11-2012	82.72 10.43 1.50	320	800	9.02 g of BXF1	2	91.0	**82.96** **11.64** **1.30**
25 06-19-2012	81.78 9.81 3.61	320	800	6.08 g of BXF1	2	93.0	**82.32** **8.99** **5.27**

Proximate Analysis of Lignite Coals

Lignite	% moisture	% volatiles	% fixed carbon	% ash	Theoretical Yield Based on 25 g	Note
Jewett	**31**	**31**	**23**	**15**	13.5	**As received**
LAL (form Jewett)	**23**	**28**	**40**	**9**	17	**As received**
Benton	**34**	**39**	**20**	**7**	14.75	**As received**
Bauxite	**38**	**25**	**21**	**16**	11.5	**As received**
Malvern	**32**	**25**	**18**	**26**	10.8	**As received**
NRG	**24**	**31**	**34**	**11**	16.3	**As received**
Luminant	**32**	**17.5**	**42**	**8.5**	14.9	**As received**
Luminant 1	**29**	**21.8**	**31.5**	**17.7**	13.3	**As received**
Luminant 2	**30**	**29**	**32.5**	**8.5**	15.4	**As received**
Luminant 3	**32**	**7**	**42**	**20**	12.3	**As received**
NRG2	**30**	**23**	**34**	**13**	14.3	**As received**
AU Brown coal	**60**	**18**	**21**	**1**	9.8	**As receive**

						d
Kasse1	**30**	**26**	**30**	**13**	14.0	**As received**
Jewett2 (LAL2) WVU	**10**	**36**	**41**	**13**	19.3	**As received**
Sub1 macoupin clean coal sample 11/11/10	**9**	**30**	**53**	**7**	20.8	**As received**
LUM4 (low ash)	**30**	**26**	**29**	**15**	13.8	**As received**
LUM4 P1	**12**	**30**	**42**	**16**	18.0	**Treated**
LUM4 P2	**20**	**34**	**24**	**22**	14.5	**Treated**
LUM4 P4	**4**	**26#**	**56#**	**14**	20.5	**Treated**
SUB1 P5						**Treated**
PRB as is	**30**	**24**	**41**	**5**	16.25	**As received**
PRB 01/30/12	**10**	**36**	**50**	**4**	21.5	**Treated**
PRB 02/12/12	**5.4**	**36.5**	**51**	**4.5**	21.9	**Treated**
NRG3 7%	**10**	**26**	**26.7**	**37.3**	13.2	**dried**
NRG3 11%	**16.7**	**18.1**	**48.4**	**16.8**	19.1	**dried**
NRG3 14%	**14.2**	**15.5**	**24.1**	**46.2**	9.9	**dried**

 # Incomplete TGA analysis

Digestion Experiments preformed on coal using by UTA process

Run	LAL (g)	Solvent (g)	Solid Rec'd (g)	Oil Recv'd (g)	Max Yield* (g)	Oil Yield** g (%)	HCTD CH% Before	Oil CH% After	CHNS% Inertnite	Notes
1[#]	25.0 LAL (9% ash) (23% H_2O)	-	24 0.00	-	17.0	-	-	not done	-	Predried in air
2[#] 10-29-09	25.0 LAL	~40	5.7 82.6%	-	17.0	-	83.2; 9.0; 1.9	69.0; 8.5 ; 4.1	58.54; 3.34; 2.5	Moisture removed in solvent
3[#] 11-5-09	25.0 LAL	~40	6.1 82.6%	42	17.0	2.0 g (11.8%)	83.0; 8.9; 0.9	80.7; 8.3; 0.8	58.46; 3.58; 1.4	Moisture removed in solvent
4[#] 11-14-09	25.0 LAL	~40	6.0 80.9%	-	17.0	-	84.4; 10.4; 0.7	79.1; 9.6; 0.8	ND	Moisture removed in solvent
7[#] 1-23-10	25.0 LAL	50.0	8.5 66.2%	51.8	17.0	1.8g (10.6%)	84.2; 10.7; 0.5	83.6; 10.4;0.5	64.9; 4.5; 1.5	Moisture removed in solvent
8[#] 2-8-10	25.0 LAL	49.0	~3 97.5%	55.0	17.0	6.0g (35.3%)	83.2; 10.8; 0.3	81.0; 9.9; 0.5	33.1; 2.2; 0.3	BXF1 cat w/H_2O w/H_2
#9	25.0	52.0	~17	50.0	13.5	-2.0	84.8; 10.2;	82.4;	32.9; 3.6;	Moisture

2-13-10	**Jewett**		**0.00%**			**(0.0%)**	**0.5**	**10.1; 0.4**	**0.6**	**removed in solvent**
10$^{\#}$ 2-18-10	**25.0 LAL**	**50.0**	**5.1 86.2%**	**56.4**	**17.0**	**6.4g (38.1%)**	**83.9; 10.6; 0.3**	**83.5; 9.8; 0.5**	**Not done**	**BXF1 cat w/ H_2O w/H_2**
#12 3-2-10	**25.0 LAL**	**50.0**	**5.5 83.8%**	**52.4**	**17.0**	**2.4 (14.1%)**	**84.0; 10.3; 0.6**	**83.9; 10.5; 0.5**	**Not done**	**BXF1cat No H_2O w/ H_2**
#13 3-18-10	**25.0 LAL**	**50.0**	**12 45.6%**	**49**	**17.0**	**-1.0 (0.0%)**	**84.0; 10.3; 0.6**	**65.4; 8.9; 0.6**	**Not done**	**BXF1 cat w/ H_2O No H_2**
# 14 3/28/10	**25 LAL**	**50**	**7.2 73.8%**	**54.0**	**17.0**	**4.0 (23.5%)**	**83.7; 10.3; 0.5; S = 0.5**	**72.6; 9.1; 0.4; S = 2.22**	**ND**	**BXF1 cat; 1mL H_2O; No H_2**
#15 3-31-10	**25.0 LAL (9% ash) (23% H_2O)**	**50.0**	**7.0 75.0%**	**55.2**	**17.0**	**5.2 (30.6%)**	**82.5; 10.1; 0.5; S = 0.5**	**80.5; 9.6; 0.5; S = 0.54**	**60.0; 4.4; 1.5**	**BXF1cat + 1 mL H_2O + H_2**
#16 4-2-10	**25.0 Benton (5%ash) (34%H_2O)**	**50.0**	**4.7 76.5%**	**54.2**	**14.7**	**4.2 (29%)**	**83.6; 10.3; 0.6; S = 0.5**	**82.6; 10.1; 0.4; S = 0.5**	**57.8; 4.3; 1.4**	**BXF1 cat 300 psi H_2**
#17 4-7-10	**25.0 Bauxite**	**50.0**	**10.9 37.3%**	**48.5**	**11**	**-1.5 (0 %)**	**84.6, 10.3, 0.5**	**84.7, 9.6, 1.2**	**44.9; 3.8; 0.9**	**BXF1 cat 300 psi H_2**

	(16%ash) 38%H_2O)									
#18 4-12-10	25.0 Benton	50.0	4.1g 80.6%	54.8	14.7	4.8 (32.6%)	84.6, 10.3, 0.5	84.6, 9.8, 0.5	64.1; 5.3; 1.3	BXF1-BXF1(II) cat 300 psi H_2; At 320 C, H_2 1500 psi for half an hour
#19 4-17-10	25.0 Malvern (25.6%ash, 31.6% H_2O)	50.0	8.9g 47.9%	51.0	10.7	1.0 (9.3%)	84.5, 9.8, 0.5	84.6, 10.3, 0.9	35.9; 2.3; 1.1	BXF1 cat 300 psi H_2
#20 4-19-10	25 NRG (11%ash, 24% H_2O)	50.0	4.9 79.9%	58.0	16.2	8.0 (49.4%)	84.5; 9.8; 0.5	85.0; 10.4; 0.8	65.2; 4.6; 1.6	BXF1 cat 300 psi H_2
#21 4-22-	25 LAL	50	13.2 38.5%	51.5	17	1.5 (8.8%)	86.5; 10.2; 3.8	85.1; 9.9; 4.1	57.7; 3.9; 1.4	BXF2 cat. 300psi H_2,

10										pressure reachedat 1350psi at 340C
#22 4-23-10	25 LAL	50	14 33.8%	42.9	17	-8 0.00	86.5; 10.2; 3.8	84.4; 10.2; 1.7	54.8; 3.7; 1.5	No cat. 320C 1000psi
#23 4-26-10	25 NRG	50	5.1 85.5%	57.5	16.2	7.5 (46.3%)	86.5; 10.2; 3.8	85.1; 9.8; 2.4	68.7; 4.5; 1.7	BXF1-cat, 320 800 psi w/ H_2
#24 4-27-10	25 LAL	50	9.5 57.4%	54.2	17	4.2 (24.7%)	84.6; 9.8; 2.37	84.2; 9.9; 0.6	64.8; 4.2; 1.7	BXF1(1-3 micron), 320 C 800 psi w/ H_2
#25 4-29-10	25 LAL	50	8.0 66.2%	54.5	17	4.5 (26.5%)	84.6; 9.8; 2.37	85.3; 10.8; 0.9	66.7; 4.9; 1.7	BXF1(325 mesh), 320 C 700 psi w/ H_2
#26 5-3-10	25 LAL	52.5	8.5 63.2%	57.2	17	4.7 (27.6%)	84.6; 9.8; 2.37	84.9; 9.4; 0.6	63.4; 4.4; 1.5	BXF1-cat(0.1micron), 320 C 500 psi w/ H_2
#27	25	50	12	52	17	2	84.6; 10.5;	86.3;	71.0; 4.3;	BXF1 cat

5-18-10	LAL		42.6%			(11.7%)	2.09	10.3; 3.6	1.8	(reuse), 300 psi w/H_2, 320C
#28 5-20-2010	25 LAL	50	20 0.00%	50	17	0.0 0.0%	84.6; 10.5; 2.09	85.9; 10.1; 4.2	66.0; 4.4; 1.7	BXF1cat, 1000 psi w/ syngas, 320C
#29 5-31-2010	25 LAL	50	17 13.2%	52	17	2 (11.8%)	84.6; 10.5; 2.09	84.1; 10.2; 0.3	66.3; 4.5; 1.4	BXF1 cat, 1000 psi w/ syngas, 320C Observed 1.5-2mL H_2O
#30 6-1/-10	25 LAL	50	12 42.6%	50.7	17	0.7 (4.1%)	84.6; 10.5; 2.09	84.1; 10.1; 0.6	61.3; 4.4; 1.42	Reduced BXF1-cat(0.1micron), 320, 300w/H_2
#31 6-2-10	25 LAL	50	15 25.0%	51.5	17	1.5 (8.8%)	84.6; 10.5; 2.09	84.7; 9.8; 2.1	60.9; 3.9; 1.3	BXF1 cat (Reduced reuse), 300 psi w/H_2, 320C

#32 6-8-10	**25Luminant (8.5%ash, 32% H_2O)**	**50**	**8.5 56.9%**	**54.0**	**14.8**	**4.0 (27.0%)**	**85.0;9.9; 1.7**	**85.5; 10.0;2.6**	**69.9; 3.76; 1.79**	**BXF1 cat 300 psi H_2**
#33 6-15-10	**25 LAL**	**50**	**13 36.8%**	**52**	**17**	**2.0 (11.7)**	**84.8, 8.7, 5.6**	**85.9, 10.8, 3.5**	**66.6, 4.7, 1.6**	**BXF1-cat(>50nm), 320 C 300 psi w/ H_2**
#34 6-20-10	**25 NRG*****	**50**	**5.6 82.4%**	**57.3**	**16.2**	**7.3 (45.1%)**	**84.8, 8.7, 5.6**	**84.9, 10.3, 2.0**	**65.9, 4.3, 1.6**	**BXF1-cat, 320 300 psi w/ H_2 With slow rpm**
#35 6-21-10	**25 NRG**	**50**	**13 36.7%**	**50**	**16.2**	**0.0**	**84.8, 8.7, 5.6**	**84.5, 10.8, 3.1**	**67.5, 4.3, 1.9**	**BXF1-Cat, 150 psi w/H_2, 320, regular rpm (150)**
#36 6-23-10	**25 NRG**	**50**	**5.8**	**60**	**16.2**	**10 (61.7%)**	**84.8, 8.7, 5.6**	**85.2, 10.8, 4.5**	**61.6, 3.8, 1.7**	**BXF1-Cat, 300 psi w/H_2, 320, regular rpm**

										(150), fast heating(30-40 min)
#37 6-25-10	25 NRG	50	7	57	16.2	7 (43.2%)	84.8, 8.7, 5.6	85.1, 10.2, 5.5	27.7, 2.6, 0.8	BXF1-Cat, 300 psi w/H_2, 320, regular rpm (150), Catalyst added after removing H_2O
#38 6-29-10	25NRG ***	50	7	52	16.2	2 (12.3)	84.8, 8.7, 5.6	84.1, 10.4, 2.1	27.9, 2.1, 0.6	BXF1-Cat, 300 psi w/H_2, 320, regular rpm, Fast heating and fast cooling. Added extra 100 psi of H_2
#39	25NRG	50	7.2	60	16.2	10	84.8, 8.7,	84.5,	51.6, 4.2,	BXF1-

6-30-10	*******					**(61.7)**	**5.6**	**10.5, 2.6**	**1.0**	**Cat, 300 psi w/H_2, 320, regular rpm, Fast heating and fast cooling.**
#40 7-7-10	**25NRG *****	**50**	**16**	**54**	**16.2**	**4 (24.7)**	**85.2, 10.0, 2.7**	**84.9, 10.4, 1.3**	**30.0, 2.1, 1.3**	**1g BXF1-Cat, 300 psi w/H_2, 320, regular rpm, normal heating and cooling. Wet HCTD**
# 41 7-8-10	**25NRG *****	**50**	**17**	**52**	**16.2**	**2 (12.3)**	**85.2, 10.0, 2.7**		**37.31, 2.6, 1.4**	**2g BXF1-Cat(old catalyst , 300 psi w/H_2, 320, regular rpm, fast heating**

										and cooling. Old cat.
# 42 7-14-10	**25NRG *****	**50**	**16**	**53**	**16.2**	**3 (18.5)**	**85.2, 10.0, 2.7**	**83.9, 10.5, 3.8**	**40.8, 2.9, 1.1**	**2g BXF1-Cat(fresh catalyst , 300 psi w/H_2, 320, regular rpm, fast heating and slow cooling. Fresh cat.**
# 43 7-15-10	**25NRG *** 16 mesh coal**	**50**	**16**	**54.5**	**16.2**	**4.5 (28%)**	**85.2, 10.0, 2. 7**	**85.4, 10.2, 3.3**	**63.2, 4.2, 1.5**	**3g BXF1-Cat(fresh catalyst , 300 psi w/H_2, 320, regular rpm, regular heating and cooling**
#44 7-23-10	**Luminant 2**	**50**	**6**	**59.1**	**15.4**	**9.1 (59.0%)**	**85.2 10.25 4.67**	**81.17 9.01 0.53**	**59.41 4.23 1.47**	**3g BXF1-Cat(fresh catalyst ,**

										300 psi w/H_2, 320, regular rpm, regular heating and cooling
#45 7-29-10	NRG 16 mesh	50	7	56.8	16.2	6.8 (42%)	85.2 10.25 4.67	81.17,9.01,0.53	40.02,2.77,1.15	2g BXF1-Cat(fresh catalyst , 300 psi w/H_2, 320, regular rpm, regular heating and cooling
#46 8-2-2010	Luminant 2 16 mesh	50	5.9	65	15.4	15 (97%)	85.2 10.25 4.67	83.14 9.89 4.03	63.34,4.54,1.57	3.8g BXF1-Cat(fresh catalyst , 300 psi w/H_2, 320, regular rpm, regular

										heating and cooling
#47 8-9-10	Luminant 2 16 mesh	40.0	11.0	47.0	15.4	7 (48%)	85.2, 10.25, 4.67	85.69,9.02,6.51	66.28,4.00, 1.62	3.0g BXF1-Cat(fresh catalyst , 300 psi w/H_2, 320, regular rpm, fast heating and cooling
#48 8-9-10	Luminant 2**** 16 mesh	50.0	11.3	53	15.4	3 (19.5%)	85.2, 10.25, 4.67	68.28,8.10,2.98	63.20,4.36, 1.67	3.0 g BXF1-Cat on(SiO_2)fresh catalyst , 300 psi w/H_2, 320, regular rpm, fast heating and cooling
#49 8-11-	Luminant 2	50.0	6.1	59	15.4	9 (58.5)	85.2, 10.25, 4.67	84.3,8.95,5.92	63.95,3.96, 1.65	3.0 g BXF9-Cat

10	**16 mesh**									**fresh catalyst , 300 psi w/H_2, 320, regular rpm, fast heating and cooling**
#50 8-11-10	**Luminant 2 16 mesh**	**50**	**9.0**	**51**	**15.4**	**1 (6.5)**	**85.2, 10.25, 4.67**	**78.61,9.57,0.59**	**49.21,3.12, 1.34**	**3g BXF1 cat, 320 C heated first(650psi) and then added H_2 200psi more , regular rpm, fast heating and cooling**
#51 8-12-10	**Luminant 2 16 mesh**	**50**	**9.0**	**51**	**15.4**	**1.0 (6.5**	**85.2, 10.25, 4.67**	**84.66,10.21,4.01**	**59.21,4.05, 1.45**	**6g Reuse BXF1 cat 300 psi w/H_2, 320, regular**

										rpm, fast heating and cooling
#52 8-12-10	**Luminant 1 16 mesh**	**50**	**10**	**54**	**15.4**	**4.0 26%**	**85.2, 10.25, 4.67**	**83.05,9.82,0.90**	**35.85,2.67, 1.02**	**3g BXF1 cat, 320 C, regular rpm, fast heating and slow cooling,**
#53 8-16-10	**Luminant 2 16 mesh**	**50**	**6**	**58**	**15.4**	**8 52%**	**85.2, 10.25, 4.67**	**85.69 9.02 6.51**	**65.59,4.30, 1.62**	**3g BXF1 cat, 320 C, regular rpm, fast heating and slow cooling, Dry coal 0.00% water**
#54 8-16-10	**Luminant 2 16 mesh**	**50**	**9**	**55**	**15.4**	**5 32%**	**85.2, 10.25, 4.67**	**81.6,9.00,2.68**	**67.91,4.06, 1.83**	**3g BXF1 cat, 320 C, regular rpm, fast heating and slow**

										cooling Dry coal addition of 5.00% water
#55 8-25-10	**25/18 dry Luminant 2 16 mesh**	**50**	**13**	**48**	**15.4**	**-13%**	**83.88, 8.61, 0.93**	**83.58, 8.07,4.79**	**66.79,4.10, 1.42**	**3g BXF1 catalyst , 3h resident time , addition of 250psi H2 at 200C , Fast heating slow cooling**
#56 09/02/10	**25/18 dry Luminant 2 16 mesh**	**50**	**15**	**53**	**15.4**	**3 20%**	**83.88, 8.61, 0.93**	**84.84,9.15,3.95**	**67.59,4.30, 1.62**	**4 g BXF1 catalyst, Fast heating normal cooling**
# 57 09/07/2010	**25/18 dry Luminant 2**	**53**	**12g**	**59**	**15.4**	**6 40%**	**83.88, 8.61, 0.93**	**81.19,8.63,0.77**	**65.59,4.30, 1.82**	**4 g BXF1 catalyst, Fast heating**

	16 mesh									normal cooling
#58 09-20-10	25/18 dry Luminant 2 16 mesh	50	9g	59	15.4	9 58.5%	84.40, 10.01, 2.33	77.16,8.20, 1.79	64.59,4.26, 1.70	3 g of BXF1 Fast heating normal cooling ^{1}H NMR was taking in every step of the way
# 59 09-27-10	25/18 dry Luminant 2 16 mesh	50	7g	59	15.4	9 58.5%	83.88, 8.61, 0.93	81.90, 8.00,1.07	49.31,3.45, 1.12	4 g of BXF1 Fast heating normal cooling ^{1}HNMR was taking in every step of the way

# 60 10-07-10	**Dry 25 Au Coal**	**50**	**18.1**	**50.0**	**15.75**	**0 0.00%**	**83.88, 8.61, 0.93**	**84.10; 7.82; 3.85**	**69.09; 1.85; 1.39**	**3 g of BXF1 Fast heating normal cooling**
# 61 10-08-10	**Dry L2**	**50**	**18.0**	**50.0**	**15.4**	**0 0.00%**	**83.88, 8.61, 0.93**	**84.29; 9.14; 3.58**	**65.59; 3.13 ; 1.69**	**3 g of BXF115 Fast heating normal cooling**
# 62 10-12-10	**Sponge Cake**	**50**	**25.0**	**50**	**XXX**	**0.00**	**83.88, 8.61, 0.93**	**84.98; 8.13; 5.33**	**89.62; 2.92; 1.64**	**swelled over HCTD for two days 3 g of BXF1**
# 63 10-18-10	**Australian Brown**	**50**	**11.0g**	**57.0**	**15.75**	**11 g 69.8**	**83.88, 8.61, 0.93**	**82.82;7.84; 5.42**	**68.17; 3.93; 1.10**	**Dried over H2 on parr**

	Coal									reactor for 3 hours 3g BXF1
# 64 10-22-2010	Large scale reactor 750g of 30+mesh wet L2	1500 g	450g	1200	462	-300 -65%	84.04,10.22,1.12	85.20,9.65,4.54	61.21,4.50,3.76	90g of BXF1: Experiment terminated after reaching pressure of 1200 psi
#65 10-27-2010	16+ L3 16.5/25 wet/dry	50	8	54		4	84.04,10.22,1.12	81.30,8.37,1.67	66.91,4.76,1.35	3g of BXF1
#66 10-28-10	+16 mesh Au coal dry 18 dry coal	50	13	54	15.75	4	84.04,10.22,1.12	84.35,9.75,4.53	70.94,3.48,1.31	3g of BXF1
#67 11-01-	+40mesh L2	56	9	52.6	15.4	2.6	85.59 9.83	84.03 8.97	51.67 2.29	3g BXF1

2010	**coal 1% Dry 18/25 g**						**3.91**	**2.19**	**1.4**	
#68 11-02-2010	**+40mesh L2 coal 1% Dry 296/411 g**	**850**	**Terminated due to oil spill**	**XXX**	**253**	**XXX**	**Terminated due to oil spill**	**Terminated due to oil spill**	**Terminated due to oil spill**	**50g BXF1**
# 69 11-03-2010	**+40mesh NRG coal 2% Dry 18/25 g**	**50**	**15**	**56**	**9.25**	**6 64.9%**	**85.59 9.83 3.91**	**83.85 10.25 3.26**	**5242 3.22 1.18**	**3g BXF1**
#70 11-03-2010	**+40 mesh NRG coal 2% Dry 300/415 g**	**823.4**	**280**	**1121.3g**	**148g**	**220g**	**85.59 9.83 3.91**	**85.87 1019 0.68**	**55.51 3.58 1.22**	**50g BXF1**
#71 11-11-2010	**25g of 16+mesh Au coal (56.54 2.95**	**50**	**12 42.1%**	**58**	**19g**	**8g 42.1%**	**85.59 9.83 3.91**	**82.35 9.54 3.43**	**56.50 2.49 0.89**	**3g BXF1**

	0.91)									
#72 11-16-2010	Mix mesh 104 dry NRG 0.7% 25g (28.15 2.29 0.78)	50	22	50	20	2 10.0%	85.59 9.83 3.91	81.64 9.50 2.20	62.70 3.56 1.54	3g BXF1
# 73 11-23-2010	400g of +40 mesh NRG2 20% H_2O (28.15 2.29 0.78)	812.4g	173	922.9	225g	110.5 49%	85.59 9.83 3.91	82.54 8.97 4.76	62.52 3.10 1.70	48g BXF1
# 74 11-23-2010	25g of +40 mesh NRG2 20% H_2O (28.15	50.0	16 26.7%	53	15g	3 20%	85.59 9.83 3.91	84.67 9.49 3.92	55.12 2.08 1.54	3g BXF1

	2.29 0.78)									
# 75 11-29-2010	25g of 20% Au +16 mesh	50.7	12 45.0%	59.2	19	8.5 44.7%	83.83 9.72 2.72	84.10 8.08 5.10	72.62 3.47 1.00	3.03 g BXF1
# 76 12-09-2010 SS	25g 15% NRG2 +40 mesh RT dried	50.0	19	51.5	13.75	1.5 10.9%	83.83 9.72 2.72	84.42 9.48 2.75	22.0 1.22 0.68	3.7g BXF1
#77 12/09/2010 LS	400g 15% NRG2 +40 mesh RT dried	818.9g	236	932.9	220	114 51.8%	83.83 9.72 2.72	81.22 9.28 2.43	49.85 1.97 1.06	48.0 g BXF1
# 78 01-05-2011 SS	25.1g of NRG22 +16-+40 RT drid0	49.9 g	21.1g	49.9	13g	0.00 0.00%	83.49 7.77 1.34	81.58 8.03 0.98	65.40 4.25 1.59	+170 mesh 3.00 g BXF1
#79	25.1g of	50.0	21.5	50.0	13.0g	0.00	83.49	83.98	46.77	+170

01-10-2011	**NRG22 +16-+40 RTdrid**					**0.00%**	**7.77 1.34**	**9.52 3.66**	**2.82 1.22**	**mesh 3.00 g BXF1**
#80 01-12-2011	**25g Sub 1**	**50.0**	**- - - -**	**- - - - -**	**21.5g**	**- - - - - -**	**83.49 7.77 1.34**	**84.03 9.15 4.40**	**47.60 2.22 1.40**	**+170 mesh 3.03g BXF1 No pre treatment**
# 81 01/19/2011	**25g Mesh +40 Sub**	**50.0**	**14g**	**52.2**	**21.5g**	**2.2g 10%**	**83.49 7.77 1.34**	**83.61 7.82 2.50**	**43.25 3.10 0.90**	**+170 mesh 3.00g BXF1**
#82 01/24/2011	**25g Mesh +40 NRG2**	**50.1**	**19**	**44.93**	**13.75**	**-5.07g**	**83.49 7.77 1.34**	**85.01 7.60 5.41**	**46.84 2.92 1.54**	**Mix mesh 3.01g BXF1-15**
#83 01/26/2011	**25g +40 mesh Sub**	**50.0**	**14.0g**	**55.9**	**21.5g**	**5.90 27.44%**	**83.49 7.77 1.34**	**84.08 9.06 2.89**	**71.24 2.69 10.15**	**+170 mesh 3.00g BXF1**
# 84 02/07/2011 A	**25.0g +40 mesh Sub**	**50.0**	**30.5**	**22.2**	**21.5g**	**-27.8**	**83.49 7.77 1.34**	**85.82 8.79 2.60**	**74.28 2.69 1.64**	**450C +170 mesh 3.00g BXF1**

# 85 02/07/2 011 B	**25.0g +40 mesh Sub**	**50.0**	**18.0g**	**54.5**	**21.5g**	**4.5g 21.0%**	**83.49 7.77 1.34**	**82.11 8.70 0.89**	**71.22 2.74 2.11**	**350C +170 mesh 3.00g BXF1**
#85 02/17/2 011	**25.0g 12-20 mesh Kasse1**	**50.0**	**17.1**	**49.0**	**15.5g**	**-1.0 0.00**	**83.49 7.77 1.34**	**83.58 9.71 0.37**	**54.07 3.61 1.05**	**+170 mesh 3.00g BXF1 800 psi 320C 30.0 min**
#86 02/18/2 011	**25.0g 12-20 Kasse1**	**50.0**	**20.0g**	**50.0**	**15.5**	**0.00 0.00%**	**83.49 7.77 1.34**	**83.41 10.00 0.33**	**60.55 3.00 1.18**	**+170 mesh 3.00g BXF1 1000 psi 320C 30.0 min**
#87 02/21/2 011	**25.1g Jewatt 2**	**50.1**	**19**	**50.0**	**19.25g**	**0.00**	**83.49 7.77 1.34**	**84.77 10.31 2.09**	**57.84 3.41 1.22**	**3.03 g BXF1 1000 psi 320 C 30.0 min**
# 88 02/24/2 011	**25.0g Jewett 2**	**50.0**	**20**	**50.0**	**19.25**	**0.00**	**84.11 10.26 3.95**	**82.26 10.30 2.09**	**65.02 4.47 1.42**	**3.00 g BXF1**

										1000 psi 320 C 30.0 min
# 89 02/28/2011	25.0g LAL	50.0	19	49.0	17.0	-1 0.00%	83.49 7.77 1.34	83.63 10.45 0.39	55.71 3.57 1.00	3.00 g OLD BXF1 1000 psi 320 C 30.0 min
# 90 03/04/2011	25.0G AU RT DRY	50.0	12.2g	62.1g	24.4	12.1 49.6%	83.49 7.77 1.34	81.65 10.12 3.83	67.31 2.80 1.01	3.00 g OLD BXF1 1000 psi 320 C 30.0 min
#91 03/07/2011	25.0g AU RT DRY	50.0	19.7	50.0	24.4	0.00	83.49 7.77 1.34	81.79 10.79 0.99	67.92 4.54 0.98	3.00 g NEW BXF1 1000 psi 320 C 30.0 min
#92 03/09/2011	AU RT Dry 25.02 g	50.0	22.9	50.0	24.5	0.00	83.49 7.77 1.34	83.90 11.50 2.54	70.64 4.57 0.90	3.01 g BXF1 + 1.02g as is $CaCO_3$
#93	AU RT	50.0	19.6	50.0	24.5	0.00	83.49	82.08	69.96	3.01 g

03/10/2011	**Dry 25.01 g**	**3**					**7.77 1.34**	**10.91 1.38**	**2.08 1.41**	**BXF1 45 min run time**
#94 03/14/2011	**Au RT Dry 25.03g**	**50.7 g**	**18.0**	**51.0**	**24.5**	**0.3 1.22%**	**83.49 7.77 1.34**	**82.71 11.23 2.78**	**65.37 3.51 1.01**	**3.55 g (BXF1 + 25% Na2CO3)**
#95 03/15/2011	**Au RT Dry 25.03g 12% moisture**	**50.00**	**12.7 60.5%**	**58.1**	**21**	**8.1 38.9%**	**83.49 7.77 1.34**	**79.60 10.61 0.68**	**71.5 2.41 1.49**	**3.00 g (frash BXF1)**
#96 03-21-2011	**Au RT Dry 25.00g 12% moisture**	**50.00**	**13.1**	**58.0**	**21**	**8.00 38.1%**	**83.49 7.77 1.34**	**78.00 9.21 0.82**	**71.45 1.69 1.10**	**3.01 g (frash BXF1)**
#97 03-23-2011	**Au RT Dry 25.03g 12% moisture**	**50.00**	**15 28.6%**	**51.5**	**21**	**1.5 7.0%**	**83.49 7.77 1.34**	**84.43 10.40 4.48**	**73.03 1.01 1.05**	**3.01 g (frash BXF1) 420C, 1 min**
#98 03/24/2	**Au RT Dry**	**50.2**	**15 28.6**	**55.1**	**21**	**5.1 24.28%**	**83.49 7.77**	**82.24 10.39**	**43.41 1.02**	**3.01 g (frash**

011	25.00g 12% moisture						1.34	2.75	0.76	BXF1) 420C, 5 min
#99 03/31/2011	Au RT Dry 25.01g 12% moisture	50.1 g	16 24.%	51.0	21	1.00 4.76%	83.49 7.77 1.34	82.92 11.30 2.72	78.10 3.20 1.14	3.01 g (frash BXF1) 420C, 15 min
# 100 04/06/2011	Au RT Dry 25.01g 12% moisture	50.1	12.1	59.1	21	9.1 45.8%	83.49 7.77 1.34	83.50 11.12 3.84	69.88 3.12 1.15	3.00 BXF1 -170mesh 1200psi
#101 04/08/2011	Au RT Dry 25.01g 12% moisture	50.1	15.2	55.6	21	5.5 21.2%	83.49 7.77 1.34	77.90 10.08 0.70	53.65 1.69 1.09	3.00 BXF1 + 5% CaO
#102 04/20/2011	LUM4 25.00g	50.0	15.0	50.0	13.75g	0.00	83.49 7.77 1.34	83.24 9.81 0.56	47.29 3.63 1.07	Normal conditions

#103 04/26/2011	**LUM2 25.00g**	**50.0**	**19.0**	**54.0**	**17.0 10% water**	**4.0 20.0%**	**83.49 7.77 1.34**	**83.06 10.34 0.49**	**64.96 5.04 1.36**	**3.65 BXF1(04262011) cata wasn't fully ready Normal conditions**
#104 04/27/2011	**LUM4 25.00g**	**50.0**	**18.9**	**53.0**	**17.0 10% water**	**3.00 17.6%**	**83.49 7.77 1.34**	**81.54 9.62 0.56**	**56.47 4.10 1.14**	**3.00 BXF1(04272011) Normal conditions**
# 105 05-03-2011	**NRG2 25.00g**	**50.0**	**15.0**	**52.0**	**13.75**	**2 14.5%**	**83.49 7.77 1.34**	**82.30 10.22 0.54**	**48.31 3.31 1.12**	**4.00 BXF1 not fully reduced Under normal conditions**
# 106 05-04-2011	**LUM4 25.00g**	**50.0**	**18**	**53.0**	**17.0**	**3 17.6%**	**83.49 7.77 1.34**	**82.11 10.14 0.50**	**66.69 4.37 1.59**	**3.00 BXF1 Under normal conditions slow cooling**

#107 05-10-2011	LUM4 25.00g	50.0	18.0	52.0	17.0	2.00 11.8%	83.49 7.77 1.34	80.85 9.45 0.48	66.43 4.66 1.53	3.00 BXF1+ 1.25g of CaO (5% of Coal mass) Under normal conditions slow cooling
# 108 05-12-2011	LUM4	50.0	17.0	53.0	17.0	3.00 17.6%	84.38 10.14 0.61	81.46 10.35 0.51	62.68 4.35 1.33	7.00g BXF1 Normal conditions
#109 05-16-2011	LUM4	50.0	16.0		17.0	3.50g	84.38 10.14 0.61	81.92 10.11 0.51	65.94 4.20 1.61	3.00 fresh BXF1 + 1.75g of Alum Normal conditions
#111 05-23-2011	AUC 25.0 40%H2O	50.0	9.09	52.0	15g	2.0 13.0%	84.38 10.14 0.61	80.12 1019 0.45	72.93 4.61 1.01	Normal conditions Pressure went high to 1300psi
#112 05-26-	LUM4 25.0	50.0	18.0	53.0	17.0	3.0 17.6%	84.38 10.14	80.30 9.59	52.81 3.81	Pre-swelling

2011							**0.61**	**0.49**	**1.26**	**at 80C for 3 hours**
#113 05-31-2011	**LUM4 25.0**	**50.0**	**19.0**	**50.00**	**17.0**	**0.00 0.0%**	**84.38 10.14 0.61**	**83.21 9.98 0.46**	**64.14 4.77 1.44**	**360C at 1000psi**
#114 06-01-2011	**LUM4 25.0**	**50.0**	**18**	**50.0**	**17.0**	**0.00 0.0%**	**84.38 10.14 0.61**	**71.99 9.15 0.45**	**70.87 4.60 1.33**	**Pre-swelling at 80C for 16 hours**
#115 06-04-2011	**AUC 25.0**	**50.0**	**11.0**	**57.4**	**12.5**	**7.4 60.0% Based on the V.M only**	**84.38 10.14 0.61**	**83.33 9.98 0.48**	**53.25 1.72 1.08**	**Oil quality trials 1st Dig. d. 0.81g\ml**
#116 06-06-2011	**AUC +16**	**50.0**	**12**	**56.7**	**12.5**	**6.7g 53.0 Based on the V.Monly**	**83.33 9.98 0.48**	**82.21 9.55 0.45**	**54.65 1.79 1.12**	**Oil quality trials 2nd Dig. d. 0.87g\ml**
# 117 06-08-2011	**AUC +16**	**50.0**	**13**	**56.0**	**12.5**	**6.0g 48.0% Based on the V.M only**	**82.21 9.55 0.45**	**79.60 8.65 0.29**	**68.23 3.52 0.74**	**Oil quality trials 3rd Dig. d. 0.96g\ml**

#118 06-13-2011	AUC +16	47.8	12.5	55.0	12.5	5.0g 40.0% Based on the V.M only	79.60 8.65 0.29	75.91 8.90 0.30	70.83 4.40 0.66	Oil quality trials 4th Dig Pyridine Soluble solid (7%) d. 1.01g\ml
#119 06-14-2011	24.0g P1 $HClO_4$ 12% Moi. 16.91%	50.0	11.51	57.9g	17.6g	7.9g 45.0%	84.38 10.14 0.61	77.03 8.83 0.53	53.67 3.86 1.22	Low ash treatment normal conditions
#120 06-15-2011	25.0g P4 HF	50.0	7.33	59.50g	20.0	9.5g 47.5%	84.38 10.14 0.61	77.87 9.09 0.60	44.17 3.26 0.88	Low ash treatment normal conditions
#121 06-22-2011	25.0g P2	50.0	7.50	60.0	15.0	10.0 66.7%	84.38 10.14 0.61	76.04 7.97 0.49	27.71 2.30 0.49	Low ash treatment normal conditions
#122 06-27-2011	25.0 SUB1 P5 HF	50.0	25	50.0		0.00 0.00%	84.38 10.14 0.61	81.38 8.43 .45	77.62 5.05 2.19	Low ash treatment normal conditions (HF\HNO

										3)
#123 07-07-2011	**25.0G LUM4 H2SO4 washed**	**50.0**	**14**	**54.0**	**17**	**4.0 24.0%**	**81.92 8.94 0.33**	**79.08 8.81 0. 47**	**65.36 4.38 1.40**	**Low ash treatment normal conditions (H2SO4 for 24h)**
#124 07-11-2011	**25.0g of H2SO3 treated LUM4**	**50.0**	**9**	**58.0**		**8.0g**	**81.92 8.94 0.33**	**76.90 8.00 0.44**	**50.98 3.69 1.23**	**Low ash treatment normal conditions (H2SO3 for 24h)**
#125 07-13-2011	**25.0g of AUC**	**50.0 of WTI d. 0.882**	**15**	**46g d. 0.912 g/ml**		**0.00**	**83.46 11.52 0.22**	**85.15 11.48 0.35**	**67.50 4.31 0.78**	**Normal conditions**
#126 07-14-2011	**25.0g of AUC**	**50.0 of Used car oil**	**20**	**50.0**		**0.00**	**81.92 8.94 0.33**	**81.15 8.48 0.35**	**63.61 4.64 0.71**	**Normal conditions**
# 127 07-22-2011	**25.0g LUM4 HF treated**	**50.0 g**	**18g 30%**	**54.0**	**20g**	**4.0 20%**	**81.92 8.94 0.33**	**80.0 8.95**	**69.74 4.42 4.06**	**Normal conditions BXF1**

	07-18-2011									
# 128 07-25-2011	25.0g LUM4 HF treated 07-18-2011	50.0 g	17 35%	55.0	20g	5.0 25%	81.92 8.94 0.33	80.16 9.79	67.43 3.91 4.50	Normal conditions BXF9
#129 07-26-2011	25.0g LUM4 HF treated 07-18-2011	50.0	15 45%	53.0	20.0	3.0 15.0%	81.92 8.94 0.33	79.87 9.45	67.01 3.18 3.25	360C
#130 07-27-2011	25.0g LUM4 HF treated 07-18-2011	50.0	17.0 35%	53.0	20.0	2.0 10.0%	81.92 8.94 0.33	76.30 8.28	70.96 3.24 3.65	410C
#131 08-02-2011	25.0g LUM4 HF treated 07-18-2011	50.0	14.0 50%	56.0	20.0	6.0 30.0%	81.92 8.94 0.33	77.73 9.36	68.94 3.59	45 min rxntime
#132 08-03-	25.0g LUM4	50.0	15.0 45%	55.0	20.0	5.0 25.0%	81.92 8.94	77.88 9.72	68.49 4.78	15 min rxn time

2011	HF treated 07-18-2011						0.33			
#133 08-04-2011	25.0g LUM4 HF treated 07-18-2011	50.0	16.0 40%	54.4	20.0	4.4 22.0%	81.92 8.94 0.33	78.62 10.26	69.38 4.04	60 min rxn time
#134 08-05-2011	25.0g LUM4 HF treated 07-18-2011	50.0	17.0 35%	53.0	20.0	3.0 15.0%	81.92 8.94 0.33	79.34 10.00	71.88 3.75	1400 Psi H2
#135 08-08-2011	25.0g LUM4 HF treated 07-18-2011	50.0	19.0 25%	52.5	20.0	2.5 15.0%	81.92 8.94 0.33	78.37 9.74	65.05 3.59	700 Psi H2
#136 08-09-2011	25.0g LUM4 HF treated 07-18-2011	50.0 WTI	20.0 20%	40.0	20.0	0.0 0.00%	81.15 11.96 0.33	83.01 10.79	70.72 3.41	Normal conditions BXF1

#137 08-28-2011	25.0g AUC3 Dried to 0.00% Pallet (D)	50.0 Reused DCTD	11.0 48.0%	60	21.0	10.0 48.0%	83.29 9.33 0.41	81.36 9.71 0.25	60.04 3.39 1.34	BXF1 normal conditions
#138 08-31-2011	25.0g AUC3 Dried to 0.00% Bricks (H)	50.0 Reused DCTD	15.0 28.5%	55.0	21.0	5.0 24.0%	83.29 9.33 0.41	81.77 9.71 0.20	39.69 1.75 0.93	BXF1 normal conditions
#139 09-09-2011	25.0g of P9 10.0% water 16mesh	50.0		57.8		7.8	83.29 9.33 0.41	77.67 8.01 0.44	PND	Done by Abe
#140 09-16-2011	25.0g thac oaks coal As received dried to 10	50.0					83.29 9.33 0.41	61.45 7.01 0.34		Done by Abe

	moisture									
#141	25.0g thac oaks coal HF treated						83.29 9.33 0.41			Done by Abe
#142 12-05-2011	25.0g HF treated caol 14% ash 5% water	50.0 g of Xylene	19.0	50.8	20.3	0.8 3.9%	88.9 11.1 0.0	84.86 11.55 0.27	66.71 3.55 1.30	BXF1 normal conditions (New Workup)
# 143 12-07-2011	25.0g HF treated caol 14% ash 5% water	50.0 g of Xylene	18.0 27.1%	46.0g	20.3	0.00 Weight difference shows it have 3 g of oil	88.9 11.1 0.0	83.37 10.66 0.25	64.97 4.07 1.29	BXF1 normal conditions (old workup)
# 144 12-07-2011	25.0g HF treated caol	50.0 g of Diesel	21.0 12.3%	49.1	20.3	0.00 0.00%	82.73 13.51 0.28	84.73 13.43 0.08	64.03 3.38 1.01	BXF1 normal conditions

	14% ash 5% water	Fuel								
#145 01-25-2012	25.0g of 16 mesh PRB coal (as recived) 52.79 4.82 0.68	50.4 g of PRB HC TD	13.7	51.9	16.3	1.5 9%	78.57 8.82 0.34	80.05 9.11 0.33	68.22 3.78 1.14	2.97 g Fresh BXF1 normal conditions
#146 01-27-2012	25.0g of 16 mesh PRB coal (as recived) 52.79 4.82 0.68	50.0 g of PRB HC TD	11.8	52.2	16.3 + 2.98g after the 2nd filtration	2.2 13.5% 2nd filtration by coffee filter 2.98g	78.57 8.82 0.34	80.70 9.65 0.26	69.33 4.29 1.21	2.98 g Fresh BXF1 normal conditions
# 147 02012012 Run 4	25.0G 16 mesh PRB 10% H2O 62.61	50.0 g LiginteHCTD	9.40 60.7%	54.5 + 10.1g LHC + 0.55g wate	21.4g	14.6 68.2%	83.29 9.33 0.41 LHC 79.60	82.25 9.76 0.45 LHC 79.60 9.55	26.03 1.67 0.38	3.01 g Fresh BXF1 normal conditions

	4.86 0.82			r			9.55 0.30	0.30		
# 148 02012012 Run 3	25.0G 16 mesh PRB 10% H2O 62.61 4.86 0.82	50.0 g PRB HC TD	21.3	39.2 + 10.1g LHC +2.2 g water	20.4g	-0.7 0.00	78.57 8.82 0.34	79.42 9.09 0.32 LHC 82.26 10.14 0.27	71.50 4.06 1.13	3.01 g Fresh BXF1 normal conditions
#149 02072012 Run 5 The reactor was not heating as it should and the gage dead	25.0G 16 mesh PRB 10% H2O 62.61 4.86 0.82	50.0 g PRB HC TD	22.1	32.7 13.0g LHC + 1.64 H_2O	20.4	-2.66 0.00%	78.57 8.82 0.34	82.62 9.09 1.35 LHC (82.11 9.49 1.18)	71.26 4.23 -0.80	3.01 g Fresh BXF1 normal conditions
#150 02122012	25.0gof 16 mesh PRB	50.0 g of HC	18g	40.8g + 10.0g	20.4	0.8 3.90%	81.86 9.04 0.86	82.86 8.80 0.82	69.72 3.40 -1.97	3.01 g Fresh BXF1 at

	6% H2O	TD PRB		of LHC				LHC 83.84 9.92 1.28		400 C Pressure reached 1550 psi
# 151 02142012	25.0 g of 10% H2O PRB 16 mesh coal	50.0 g of 370 C HC TD PRB	19.6	33.0 + 14.2L HC + 1.6g water	20.4	-2.8 0.00%	84.34 8.75 2.50	81.21 9.92 1.69 LHC 82.12 9.29 0.87	66.79 4.26 -2.24	3.01 g Fresh BXF1 at 360 C Pressure reached 1150 psi
#152 02-20-2012	25.0 g of Acid treated Coal	50.0 g of 370 C HC TD PRB	20.5g	35.7 13.5g LHC + 1.8 H_2O	22.4	-0.80 0.00%	84.34 8.75 2.50	82.0 9.11 4.49 LHC 82.37 9.32 0.85	67.66 4.55 1.17	Temperature 320 Pressure 1000psi Time 30 min

#153 02-24-2012	24.99 g of Acid treated Coal H_2O_2 treated coal	50.3 g of Reused HCTD PRB	18.3	48.5 6.08g LHC + 2.02g H_2O	21.5 2.99g gasified	3.2g 14.9 % Show same THF (1.00g)	82.86 8.80 0.82	80.94 9.22 2.48 LHC 82.39 10.24 0.36	69.44 3.39 1.08	Normal conditions H_2O_2 treated coal
#154 02-27-2012	25.0g PRB coal 5.4 % water 1g of NaOH	50.0 g Reused DCTD	23.5	37.7 10.55 LHC and 1.41g water	22.5	48.25g 0.00%	82.62 9.09 1.35	80.16 8.59 0.56 LHC 81.02 10.14 1.62	68.04 3.62 1.19	Normal conditions NaOH treated coal
# 155 2-29-2012	25.0G 16 mesh PRB 5.4% H_2O 62.61 4.86	50.0 g LiginteHCTD	11.6g	54 (still drying over N_2) + 3.56g	22.5	7.5 33.5%	83.29 9.33 0.41	79.81 9.05 1.04 LHC 78.92 10.71 2.39	68.97 3.42 1.12	3.00 g BXF1 Freshly hydrogenated in the reactor and used

	0.82			LHC + 4.45g water						immediately for digestion 320° C Pressure reached 750 psi Time 30 min
# 156 03-06-2012	25.0G 16 mesh PRB 5.4% H2O 62.61 4.86 0.82	50.0 g Of tetraline solvent	20.0	44.7 7.24g of LHC	22.5	1.9 8.4%	90.90 9.09 0.00	87.33 9.65 2.67 LHC 91.10 10.01 3.72	70.33 4.23 1.06	Normal conditions Max pressure 800 psi
# 157 03-23-2012	500.0g of 16 mesh NRG As is	1000 g of Lignite HC TD	463.9g		300		84.34 8.75 2.50	83.49 9.67 5.70	68.49 4.00 0.92	Normal conditions
# 158 03-29-	400.0g of 16	800 g of			240		PND	PND	PND	Normal conditions

2012	mesh NRG As is	Lignite HC TD								
# 159 04-05-2012	350.0g of 16 mesh NRG As is	700g of Lignite HC TD			210		PND	PND	PND	Normal conditions
#160 05/16/2012	25.0g of NRG3 15% moisture*	50.0g of HC TD d 0.95 g/ml	17.9g	49.9 (5.37 g gasified)	15.0g	0.00 1.7g by diff 11.3%	84.34 8.75 2.50	83.35 9.28 5.74	64.81 4.75 1.55	Normal conditions
#161 05/17/2012 DCTD 1	500.g of NRG3 15% moisture*	933.3g of HC TD d 0.95 g/ml	326.2 g	608g drain through (d 0.995 g/ml)	300g		83.32 11.37 1.64	83.68 9.61 5.63	65.02 3.81 0.62	60.0 g BXF1
#162	450.g of	927.	326.9	D.			83.68	69.13	62.16	54.0 g

05/29/2012 DCTD2	**NRG3 6% moisture***	**5g of DCTD1**	**g**	**1.05g / mL**			**9.61 5.63**	**8.01 0.44 (85.09 9.14 4.55 refiltered)**	**3.51 1.28**	**BXF1**
#163 06/01/2012 DCTD3	**350.g of NRG3 10.5% moisture***	**730.5g of DCTD2**	**XX**	**D. 1.11g / mL**			**69.13 8.01 0.44**	**64.34 6.81 3.84 (83.98 8.76 5.41refiltered)**	**60.78 3.66 1.18**	**42.0 g BXF1**
# 164 06/06/2012	**25.21g Of 11% moisture NRG3**	**50.21g HCTD**	**21.5g**	**46.2**			**82.96 11.64 1.30**	**83.49 9.99 4.81**	**35.55 1.07 0.00**	**3.00g of 10% BXFI**
# 165 06/11/2012 DCTD4	**25.00g Of 10% moisture NRG3**	**50.15 G HCTD**	**18.67g (XX.X)**	**48.82g (47.59g + 1.23g of LHC)**	**13.2**	**0.00 0.00**	**64.34 6.81 3.84**	**61.80 7.53 2.18 (82.61 8.98 6.14 refiltered)**	**66.71 4.00 1.18**	**3.00g of 10% BXFI**

								D = 1.00 g/ml		
# 165 06/21/2012	25.15g Of NRG23	50.13 G HC TD	21.83	3.80g water 6.26g LHC 42.83 g oil	16.3 g	0.00 0.00	82.96 11.64 1.30	83.62 10.26 3.82	67.28 4.03 1.27	3.01 g of BXFI
# 166 06/26/2012	25.31g Of NRG23	50.42 G HC TD 3	19.71	47.02 g +7.12 LHC +3.60 water	16.3 g	3.72 g 22.8%	83.98 8.76 5.41	83.52 9.88 3.65	29.83 2.29 0.64	3.02 g of BXFI 30 min at 800 psi Reheated from 230C and run For 10 min at 1000psi
#167 06/28/2012	25.35 NRG 23	50.10 gHC TD	19.82		16.3g					3.01 g of 20% BXFI

Est total carbon in sample (volatile +fixed); ** Yield is X g oil recovered/Max carbon, ***Time and Pressure graph, * 25% Fe on SiO_2 (150-200 mesh).**

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