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Direct Liquefaction of Coal with Coal-Derived Solvents to Produce Precursors for Carbon Products

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ABSTRACT

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David Fenton

Direct liquefaction (hydrogenation) of coal has frequently been pursued as one avenue for the production of value-added products from coal. In previous work, model solvents such as tetralin were employed as the hydrogen-donor solvent to produce carbon precursors such as pitch directly from coal. The focus of this research was to evaluate five coal-derived liquids as substitutes for tetralin in the coal hydrogenation process. A mid-distillate by-product liquid from the production of high quality char was obtained from Antaeus Technical Services, Inc. and split into three fractions, the original liquid (RACL), its heavy fraction (DACL-H), and its light fraction (DACL-L). The other two liquids were heavy creosote oil (HCO) and carbon black base #1 (CBB) from Koppers Industries, Inc. These liquids were used as hydrogenation solvents under varying reaction conditions such as gas pressure, gas composition, and solvent-to-coal ratio. The products were separated by filtration and vacuum distillation to produce three fractions, the THF insolubles, pitch, and recycle solvent. The coal-alone conversions were calculated for each hydrogenation reaction and the pitch fractions were characterized as possible carbon-product precursors by softening point, ash content, coke yield, elemental analysis, and optical texture. The results showed that DACL-L was the most effective solvent at producing soluble coal species. However, the coke of the pitch fraction showed an isotropic optical texture. The cokes of the pitch fractions for reactions with all the other solvents exhibited an anisotropic optical texture. The coal-alone conversion was slightly increased as the initial gas pressure in the reactor was increased, and the coal-alone conversion was higher using hydrogen rather than argon in the gas phase. The ash content of the pitches was very low (≤ 0.1%) for all the reactions. The coke yield depended linearly on the pitch softening point but showed no dependence on the reaction conditions or the hydrogenation solvent. Finally, the elemental composition of the pitches was similar regardless of the gas pressure or composition, leading to the possibility of pitch production at lower pressures in an inert atmosphere.

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Finally, I would like to dedicate this to my wife, Jennifer, for her sacrifices, understanding, and encouragement throughout this process.

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CHAPTER 1
INTRODUCTION

The element carbon is used in the production of many materials on which our daily lives depend. Examples of such materials are plastics, pharmaceuticals, iron, steel and aluminum. However, the amount of carbon found on earth represents only 0.04% of the total mass of the earth [17]. Half of this carbon is in a non-reactive form, such as carbon dioxide and carbonate materials. The remainder of the earth's carbon is concentrated in various fossil fuels, including coal, petroleum, and natural gas [17]. These fossil fuels are the predominant source of energy and feedstock for the production of chemicals in the world today [32].

Although the major use of fossil fuels is the production of energy, these materials are extremely important in their non-fuel uses. Currently, products derived from the petroleum industry dominate the non-fuel uses of fossil fuels [32]. These products include the production of petrochemicals, asphalt and road tar, waxes, liquefied petroleum gases, and petroleum coke. However, petroleum reserves are declining rapidly, and the concentration of impurities such as sulfur, vanadium, and nickel, in the petroleum reserves is on the rise.

One alternative source of carbon for the production of carbon artifacts could come from coal. The known reserves of coal are expected to significantly outlast those of petroleum. Currently, several non-fuel uses of coal include high-temperature carbonization for the production of metallurgical coke, gasification to produce synthesis gases, activated carbons, coal tar, and coal tar pitch. Most carbon product feedstocks from coal are derived from by-products from the metallurgical coke industry. During the process of high temperature carbonization, the volatiles are captured and condensed into coal tar. The recovered coal tar can then be processed by distillation to carbon feedstock such as tar acids, tar bases, naphthalene, creosote oils, and coal tar pitch.

Coal tar pitch is generally defined as the solid residue remaining after the removal of oils from coal tar by distillation. This pitch has many different uses in industry today. It is used as a binder in the production of carbon electrodes for electric furnaces and anodes for the aluminum industry. Coal tar pitch can be used to impregnate carbon artifacts when high density and strength are necessary. It can also be used as a carbon feedstock for the production of carbon fibers, nuclear graphite, and carbon composites.

One disadvantage to the use of coal tar pitch is that it is derived as a by-product of the carbonization process of coal. The amount of coal tar produced from one ton of coal is on the order of 4 wt% of the original coal (Table 1.1). Moreover, coal tar pitch accounts for only approximately 50 wt% of coal tar, or approximately 2 wt% of the original coal [45]. This disadvantage is magnified by the fact that the production of metallurgical coke by carbonization is declining in the United States by 3-4% per year due to increased imports, decreasing coke demand, and environmental regulations placed on existing coke ovens [1]. In order to compensate for the decrease in pitch derived from coal tar and the dwindling supply of petroleum, these precursors for carbon products could be produced directly from coal.

Table 1.1 Production Yields from Coal Carbonization [34]

Yield from 1 ton of coal	Weight %
1520 lbs coke	76
78 lbs tar	4
20 lbs light oil	1
20 lbs ammonium sulfate	1
280 lbs gas	14
80 lbs miscellaneous	4

One avenue to the production of carbon product precursors from coal is through the liquefaction of coal. Liquefaction has two general methods of producing carbon products: direct and indirect liquefaction. Indirect liquefaction converts coal into synthesis gas: carbon monoxide and hydrogen. These gases are then reformed to produce various hydrocarbons. In direct liquefaction, or hydrogenation, coal is thermally treated in the presence of hydrogen or a hydrogen-rich donor solvent to produce low molecular-weight organic species.

In previous work at West Virginia University, coal-derived pitches have been obtained by combining coal hydrogenation (liquefaction) and solvent extraction [34]. In these experiments, coal was hydrogenated in the presence of tetralin (1,2,3,4-tetrahydronaphthalene). This solvent has been well studied in the past and proven to be a very effective hydrogen donor in the presence of coal. However, during liquefaction reactions tetralin is converted into naphthalene and cannot be used as a recyclable solvent without external separation and rehydrogenation.

One alternative to using tetralin in the liquefaction reactions is to employ a coal-derived liquid as the liquefaction solvent. Making this substitution would have two possible advantages: (1) the possibility of producing a recyclable solvent during the product separation steps thus eliminating the need to supply an external solvent and (2) the process would employ only coal and coal products as starting materials, thus generating a completely coal-derived carbon product precursor. Thus, the evaluation of five coal-derived liquids as liquefaction solvents for the production of carbon product precursors is presented in this thesis report.

1.1 Research Objectives

Five different coal-derived liquids have been collected for testing as liquefaction solvents in order to produce precursors for carbon products. The first three of these liquids are fractions of a process-derived coal liquid from Antaeus Technical Services, Inc. in Alloy, West Virginia. This coal liquid is a mid-distillate by-product from the pyrolysis of an Eastern caking-type bituminous coal to produce high quality char. The fourth and fifth coal liquids are heavy creosote oil and carbon black base #1, obtained from Koppers Industries, Inc. in Pittsburgh, Pennsylvania. Both of these liquids are distillate fractions of coal tar derived from the production of metallurgical coke.

The products of the liquefaction reactions were separated into three different fractions: unconverted coal, carbon pitch, and a possible recycle solvent. The resultant carbon pitch was tested as a precursor of carbon products. This was done using standard test procedures such as softening point, ash determination, coking value, and optical texture. Using these parameters, the products from the direct liquefaction of coal can be compared to cokes and pitches of commercial value today.

CHAPTER 2

BACKGROUND

This chapter is dedicated to explaining some of the general concepts that are pertinent to the present thesis research. A general description of carbon, its properties, types of carbon artifacts, and their importance to industry is discussed. Also a brief review of coal formation, properties, and classification is presented. Finally, the concepts that govern the production of carbon artifacts from coal by direct liquefaction are discussed.

2.1 Carbon and Carbon Products

Carbon is a unique element that is essential in the industrial world today. In its various forms, carbon is used as a feedstock for chemicals and plastics, a transportation fuel, in the production of anodes and electrodes for metal reduction, carbon fibers, and other applications too numerous to list here. The diversity of uses for carbon stems from its ability not only to form bonds with elements such as hydrogen, oxygen, nitrogen, sulfur, and others, but its amazing ability to form a variety of bonds with itself. The ability for carbon to form bonds is so diverse, that it has spawned its own discipline in chemistry, organic chemistry.

Elemental carbon has the ability to take on three different crystalline forms: diamond, graphite, and fullerenes. The carbon in diamond is tetrahedrally bonded while fullerenes are bonded in the shape of a soccer ball, with hexagons and pentagons of carbon atoms. However, the most naturally occurring form of carbon is in the crystalline structure of graphite. In graphite, the carbon atoms are in a sp^2 spatial arrangement and trigonally bonded in planar sheets. These planar sheets are normally found in the hexagonal ABAB sequence but can occur in the rhombohedral ABCABC sequence (Figure 2.1).

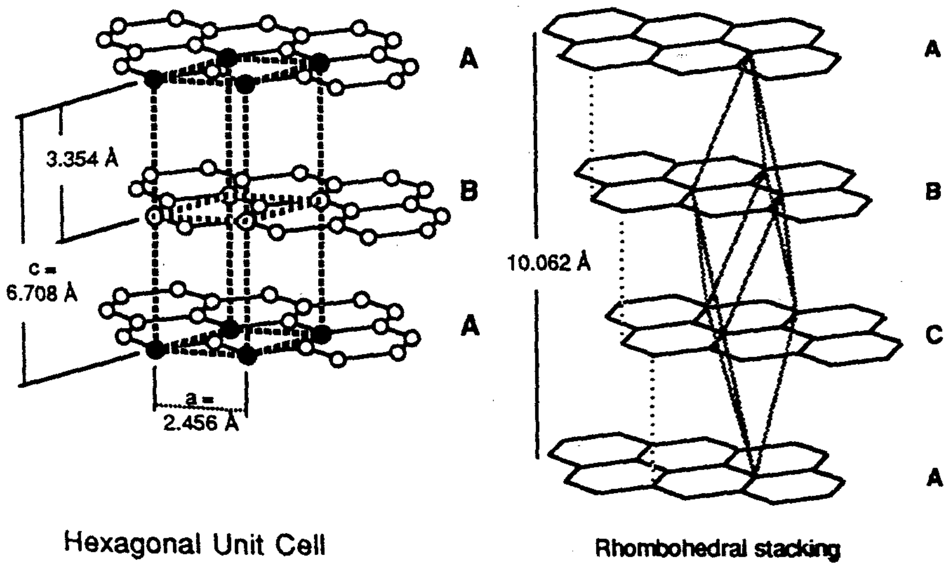


Figure 2.1 Crystalline Structure of Graphite [10]

Graphite in its ideal form would have no faults in its layers of carbon planes. The carbon atoms are held together within the planes by covalent bonds, while the planes are held together by much weaker Van der Waal's forces. The diversity of graphitic properties, such as thermal conductivity, hardness, porosity, electrical conductivity, surface effects, and chemical reactivity, can be attributed to the difference in the parallel and perpendicular bond strengths in graphite. The ability to control the crystal structure allows for the production of different carbon products in industry. Usually artificial graphite is formed by the mixture of a highly-ordered material with amorphous or less-ordered material. The higher the degree of order, or ideally graphitic, the more anisotropic the carbon artifact will be. At the other end of the spectrum is an isotropic artifact with more deviations from the ideal graphite structure. The anisotropy or isotropy can be observed by optical microscopy and is an important property in determining the end use of the carbon artifact. Figure 2.2 shows photomicrographs representing isotropic and anisotropic textures.

Industrial carbon artifacts are based on the graphite structure. Precursors to carbon materials can be considered as being graphitizable or non-graphitizable. Graphitizable carbons are materials that when subjected to a high temperature treatment are converted to graphitic carbons. These materials are usually rich in hydrogen and low in oxygen. Non-graphitizable carbons are those that are not converted to a graphitic structure after heat treatment. These materials are usually low in hydrogen and rich in oxygen and form a rigid disordered structure when heated. Example of such carbons are wood, non-fusing coals, and cross-linked polymers.

2.2 Pitches

Currently, the majority of coal-based carbon pitches are derived as by-products from the production of metallurgical coke in the recovery coke oven. The volatile products of the carbonization process are condensed to form coal tar. Pitch is defined as the substance that is left after distillation of the coal tar to remove the heavy creosote and anthracene oils. Pitch is a complex mixture of organic compounds that are predominately polycyclic aromatic hydrocarbons.

Pitches can also be made from petroleum. One type of petroleum pitch is a by-product obtained from the catalytic cracking process. Petroleum pitch can be produced from these heavy residues by thermal treatment, vacuum or steam stripping, oxidation, or distillation. The types of pitch that are produced depend on the treatment of the residues. Usually, longer treatment times and higher treatment temperatures result in a higher aromatic pitch with a more anisotropic texture.

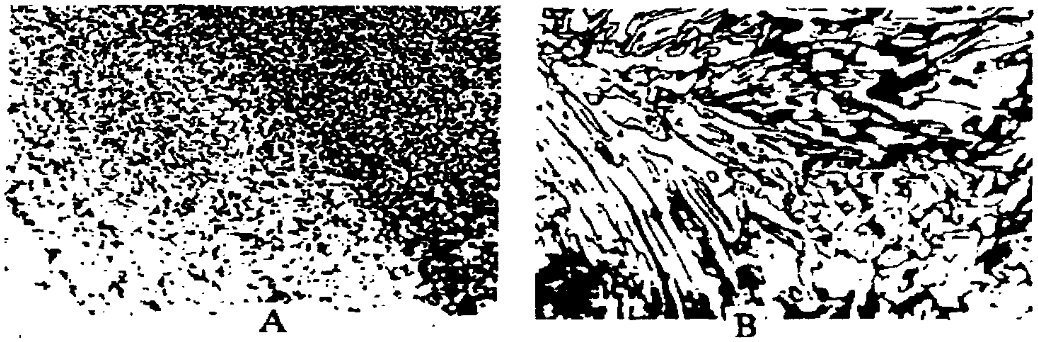


Figure 2.2 Optical Textures of A) Isotropic and B) Anisotropic Semicokes

Another type of pitch that can be formed is mesophase pitch. This pitch exists in a state where the macromolecular components exhibit both an ordered solid state and a fluid liquid. These pitches are highly oriented and can be used to produce high modulus fibers and carbon composites. Mesophase pitches can form when anisotropic pitch is heated above 350 °C. After melting, the pitch undergoes dehydrogenative condensation to increase the pitch aromaticity. The increase in aromaticity produces larger, more planar molecules, which begin to associate with each other. During the early stages of this association, the molecules come together to form tiny anisotropic spheres of liquid crystalline-like materials. These spheres increase in size as the aromatic molecules of the isotropic pitch are incorporated in the growing mesophase sphere. As these spheres collide, they coalesce to form larger spheres in order to minimize surface energy until the pitch becomes 100% bulk mesophase.

The physical and chemical properties of pitch determine its end use. Pitch can be used as a binder in the production of anodes and electrodes to hold coke particles together. This type of pitch needs to have a high-carbon yield and not affect the properties of the finished product. Some characteristic properties of binder and impregnating pitch from coal and petroleum are shown in Table 2.1. Pitch can also be used to reduce the porosity of carbon products where high density and strength are required. This type of impregnation pitch should have a low viscosity and low ash content. The production of carbon fibers is another possible use for carbon. This type of pitch requires a low solids content, a low softening point for ease of spinning, and high reactivity toward stabilization.

2.3 Cokes

Metallurgical coke is produced by high-temperature carbonization of coal. This requires heating of the coal in the absence of air to produce a solid carbon residue. This process also gives off gaseous and condensable hydrocarbon by-products. The solid residue is metallurgical coke and is used to produce pig iron from iron ore in a blast furnace.

Table 2.1 Characteristics of Various Commercial Pitches [13]

	Binder Pitch			Impregnating Pitch		
Supplier	Allied	Aristech	Koppers	Ashland	Kawasaki	Mitsubishi Kasai
Feedstock Base	Coal Tar	Coal Tar	Coal Tar	Petroleum	Coal Tar	Coal
Softening Point (°C)	109.1	109.8	110.3	121.1	99.5	95.3
Coking Value (%wt)	58.5	57.6	58.0	49.1	50.0	44.3
Ash Content (%wt)	0.17	0.16	0.21	0.03	0.00	0.003
Sulfur (%wt)	0.61	0.62	0.59	3.1	0.41	0.43
Carbon (%wt)	93.84	92.84	93.83	91.25	92.70	92.49
Hydrogen (%wt)	3.66	4.42	3.92	5.08	4.44	4.27
$\%H_{aromatic}$	85.4	85.8	86.0	55.5	86.1	82.8

Petroleum coke is produced by upgrading the heavy fractions of crude oil which are formed during petroleum processing. The residue or heavy fractions can be converted to petroleum coke by several coking methods. However, the most common process is the delayed coking process. High-grade coke from petroleum is consumed by the aluminum industry in order to reduce aluminum oxide to aluminum. Petroleum coke can also be used to produce graphite electrodes and some carbon-carbon composites.

The properties of the coke determine its specific end use. There are two different types of coke: anisotropic and isotropic. The anisotropic cokes have large crystallite domain sizes while the isotropic cokes have a fine-grained texture (see Figure 2.2). Anisotropic coke is employed in the manufacture of graphite electrodes, which are capable of carrying large electrical currents at high temperature in the electric-arc furnace. The isotropic cokes are more suited for nuclear graphite. This graphite requires a high chemical purity to avoid the adsorption of low-energy neutrons. Also, because the isotropic coke has no preferred bulk orientation, the graphite will have a high dimensional stability especially when heated.

2.4 Characterization Techniques for Cokes and Pitches

Because the physical and chemical properties of coke and pitch samples determine the end use of that substance, it is important to present a brief discussion on some of the more common characterization techniques. Some of the different techniques are softening point, ash content, coking value, optical microscopy, and x-ray diffraction. However, not all are used in the present thesis research.

2.4.1 Softening Point

Because pitch samples do not exhibit a specific phase transition from a solid to a liquid upon heating, a distinct melting point cannot be ascertained. However, as a pitch is heated, the viscosity of the sample begins to decrease. The softening point is the temperature at which the sample reaches a low enough viscosity to flow a prescribed distance (see Section 3.3.1 for more detail). The measurement gives some insight into the consistency of the sample and can be beneficial in determining its end use. The softening point is a crucial property for pitches, which are used as binders, impregnating agents, and fiber precursors.

2.4.2 Ash Content

The ash content determines the amount of impurities present in the pitch sample. These impurities are derived from the inorganic material present in the original coal sample. These inorganic materials are converted to inorganic oxides during the combustion process of the ash content test (Section 3.3.3). The combustion process removes all the organic matter from the pitch sample and leaves behind the inorganic matter. Because these inorganic oxides are considered impurities in the final carbon artifacts, it is important for the ash content of the pitch to be low.

2.4.3 Coking Value

The determination of a pitch's coking value is extremely important to its possible commercial applications. The coke yield determines the amount of carbon residue remaining after hydrogen and volatile matter are removed by thermal treatment. The heating process (up to 600 °C, see Section 3.3.2) eliminates these volatiles and then the pitch is transformed into a semicoke. The semicoke is then converted to coke when the sample contracts and carbonization is complete. Most commercial applications require a coke yield of 50 to 60 percent by weight.

2.4.4 Optical Microscopy

Once a coke sample has been formed, the optical texture can be determined by optical microscopy with a polarized-light microscope. The optical texture gives some insight into the surface and graphitization properties of the coke sample. The texture can range from an isotropic carbon (small, uniform domains) to anistropic carbon (large, elongated domains). The commercial application of the coke sample depends on where it falls in the range of isotropic to anisotropic texture.

2.4.5 X-ray Diffraction

X-ray diffraction can be used to determine the bulk structure of carbon materials. This technique can also indicate the amount of ordered material present and the crystallite size of the ordered structures. The x-ray diffraction measurement is determined by placing the sample in powder form in a capillary or spread on a flat sample holder. An x-ray beam is then aimed at the sample and the diffracted x-rays are recorded on film or with a diffractometer. This technique can also estimate the average particle size of the sample and give some insight into the amount of strain or defects in the crystal lattice.

2.5 Carbon Products from Coal

In this section, a review of basic concepts defining the art of producing carbon products directly from coal is discussed. In order to accomplish this, one must first have a basic knowledge of coal, including its method of formation, composition, classification, and structure. This section also describes the differences between coal and its major competitor, petroleum. Several different methods of upgrading are discussed, such as pyrolysis, indirect liquefaction, and direct liquefaction.

2.5.1 Coal – Formation, Composition, and Classification

Coal can be defined in many different ways. Gibson's definition, that coal "consists of a complex mixture of organic chemical substances containing carbon, hydrogen, and oxygen in chemical combination, together with smaller amounts of nitrogen and sulphur," describes the chemical composition of coal [17]. On the other hand, Francis [16] describes coal by explaining its origin when he states that coal is "a compact stratified mass of mummified plants which have been modified chemically in varying degree, interspersed with smaller amounts of inorganic matter." Both of these definitions can be related by reviewing coal formation, composition, and classification.

The formation of coal entails two different stages, the diagnetic or biochemical stage and the geochemical stage. The diagnetic stage begins with the formation of peat beds as plant material settles in low, swampy areas. At this stage, bacteria and fungi begin to decompose the plant material by removing oxygen and hydrogen by giving off water, carbon dioxide, and methane. The biochemical stage of coal formation ends as more and more sediment begins to cover the peat layer. As the peat is further submerged and the sediment layer reaches a height of approximately 40 centimeters, bacteria and fungi cease to exist, thus ending the diagnetic stage [37]. During the first stage of coalification, the carbon content of material is raised from 40-45 percent to greater than 60 percent [6].

The second stage of coalification is the geochemical stage. During this stage, the peat bed undergoes further metamorphosis due to temperature and pressure from further layers of sediment depositing on top of the peat bed. Oxygen and hydrogen are again eliminated as methane, carbon dioxide, and water. As this occurs, the carbon content is slowly increased, however, all coals are not subjected to the same amount of coalification. This gives rise to a series of coalification (shown below) that ranges from lignite to anthracite.

peat → lignite→ sub-bituminous → bituminous → anthracite

Because coal is made from different types of organic material from plants, the composition of coal can vary widely. There are two different ways that one can describe the composition of coal, physically and chemically. Physical classification of coal is derived from the observation that one piece of coal is made up of different “banded components.” These components or lithotypes were classified by Stopes in 1919 as vitrain, clarain, durain, and fusain [35]. Lithotypes can be further broken into smaller microscopic entities called macerals. There are three main groups of macerals, vitrinite, exinite, and inertinite. Vitrinite is derived from woody tissues at various levels of decomposition. Exinite or liptinite comes from spores and pollen coats, cuticles, resins, and other fatty secretions. Inertinites are derived from plant tissues that have been partially carbonized in the peat stage of coalification.

Defining the chemical composition of coal entails the use of an ultimate and proximate analysis. Ultimate or elemental analysis is a quantitative determination of the amount of carbon, nitrogen, hydrogen, sulfur, and oxygen that are present in the coal. The proximate analysis assesses the change in the weight of coal as the sample is heated. Proximate analysis determines the amount of fixed carbon, moisture, ash, and volatile matter that is present in the original coal sample. This method of determining chemical composition is significant for its use in classifying coals by rank.

Coal rank varies from anthracite through bituminous and sub bituminous to lignite with anthracite being the highest or most mature rank of coal. The American Society for Testing and Materials (ASTM) classifies coal by the amount of fixed carbon or volatile matter for medium-volatile bituminous through anthracite. The lower ranked coals, lignite through high-volatile A bituminous, are ranked by their heating value. The ASTM classifications can be seen in Table 2.2.

As the amount of carbon decreases with decreasing rank, other elements must fill in the remaining structure. The hydrogen and oxygen content increase with decreasing coal rank, but the nitrogen and sulfur content vary little with rank. Instead, the abundance of these two elements depends on where the coal was formed. The elemental composition of coal of varying rank can be seen in Table 2.3. It can be seen as coal rank decreases that the hydrogen-to-carbon ratio increases. Also, the amount of oxygen compared to carbon decreases with increasing rank. However, the levels of nitrogen and sulfur atoms remain low for all ranks of coal. All of these elements are bonded together to form various aromatic rings, aliphatic chains, and functional groups.

The majority of the functional groups that are present in coal are those that include oxygen. These types of functional groups include phenols, alcohols, ethers, carboxylic acids, and carbonyls. There has been significant study in the literature on correlating the mineral- and ash-free carbon content of coal to the relative amount of each of these functional groups. Whitehurst et al. [40] show the outcome of these correlations in Figure 2.3. Using these correlations along with the relative abundance of each atom, a complex model of a basic coal structure was proposed by Wiser [43]. This model is shown in Figure 2.4. Weak bonds in the coal structure are identified by the arrows in Figure 2.4. Coal liquefaction and dissolution requires breaking the molecular structure of coal into small soluble fragments at these weak bonds.

Table 2.2 The ASTM System for Classifying Coals by Rank [31]

Class	Group	Fixed Carbon[a]	Volatile Matter[a]	Heating Value[b]
Anthracite	Metaanthracite	>98	<2	
	Anthracite	92-98	2-8	
	Semianthracite	86-92	8-14	
Bituminous	Low-volatile	78-86	14-22	
	Medium-volatile	69-78	22-31	
	High-volatile A	<69	>31	>14,000
	High-volatile B			13,000-14,000
	High-volatile C			10,500-13,000
Sub bituminous	Sub bituminous			10,500-11,500
	Sub bituminous			9,500-10,500
	Sub bituminous			8,300-9,500
Lignitic	Lignite A			6,300-8,300
	Lignite B			<6,300

Note: This classification system is based on ASTM standard D 388-66, which is published annually by ASTM in their compilation of standards. [a] The fixed carbon and volatile matter, reported as percentages, are determined on a dry, mineral-free basis. The mineral matter is calculated from the ass content by the Parr formula: mineral matter=1.08 [percent ash +0.55 (percent sulfur)] [b] The heating value, reported in British thermal units per pound, is expressed on a moist, mineral-free basis. The moisture content is the bed moisture or equilibrium moisture of the coal after equilibration with nominally 100% relative humidity atmosphere. Some overlap occurs in the heating-value range of sub bituminous A and high volatile C coals. Coals with heating values between 10,500 and 11,500 are classified as high volatile C bituminous if they display caking properties and as sub bituminous A if they do not.

Table 2.3 Percent Elemental Composition of Various Coal Ranks [11]

	Element, %wt (dry ash-free basis)				
Sample	C	H	O	N	S
Meta-anthracite	97.9	0.21	1.7	0.2	-
Anthracite	95.9	0.89	1.8	0.3	1.8
Anthracite	92.8	2.7	2.9	1.0	0.6
Semianthracite	90.5	3.9	3.4	1.5	0.7
Low volatile bituminous	90.8	4.6	3.3	0.7	0.6
Medium volatile bituminous	89.1	5.0	3.6	1.7	0.6
High volatile A bituminous	84.9	5.6	6.9	1.6	1.0
High volatile B bituminous	81.9	5.1	10.5	1.9	0.6
High volatile C bituminous	77.3	4.9	14.3	1.2	2.3
Subbituminous A	78.5	5.3	13.9	1.5	0.8
Subbituminous B	72.3	4.7	21.0	1.7	0.3
Subbituminous C	70.6	4.8	23.3	0.7	0.6
Lignite	70.6	4.7	23.4	0.7	0.6

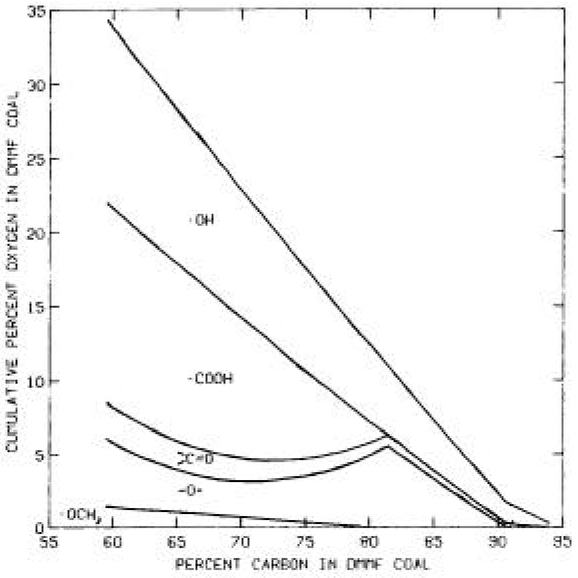


Figure 2.3 Distribution of Oxygen Functionality in Coals as a Function of Rank [40]

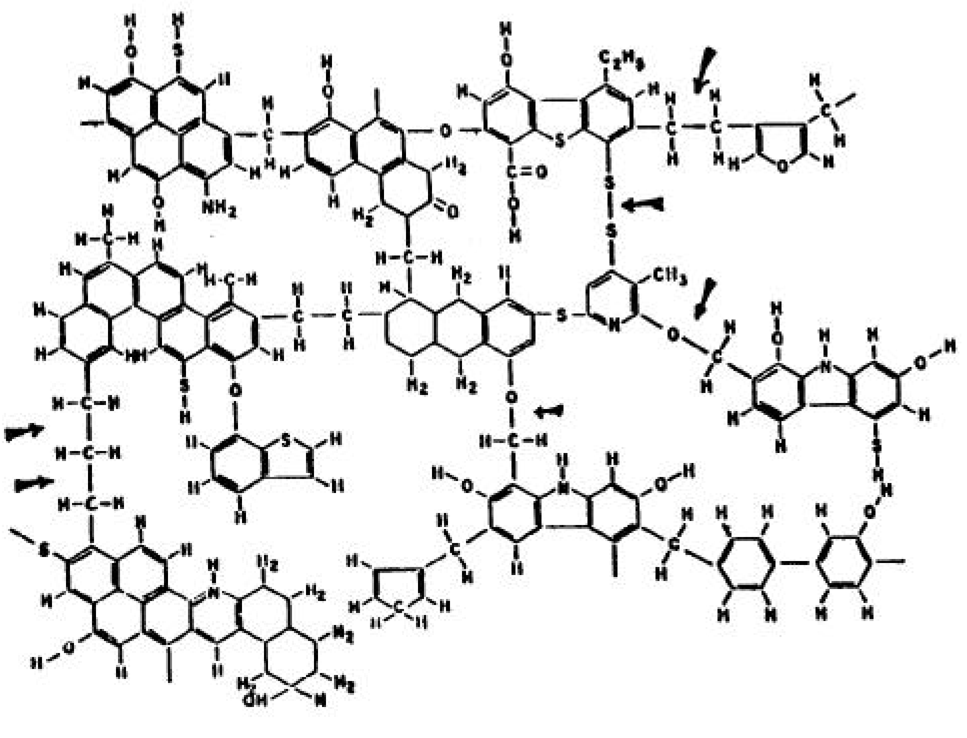


Figure 2.4 One Typical Molecular Unit in Coal [43]

2.5.2 Coal vs. Petroleum

In order for coal to be considered as a possible precursor to high value carbon products, it must be converted so that it has properties similar to that of its main competition, petroleum. For this to happen, one must understand some of the key differences between the structure of coal and oil. The major difference between coal and oil is that the molecular weight of crude oil has a range of 150 to 250 [26], while the average molecular weight of coal usually exceeds 1000. Another major difference between coal and oil is that on average the atomic hydrogen-to-carbon ratio for coal is much lower than that of oil. The typical value for crude oil lies between 1.4 and 1.9, while the average value for coal is only about 0.8 [33]. A list of typical hydrogen-to-carbon atomic ratios for several coals and hydrocarbons, such as asphaltene, toluene, crude petroleum, gasoline, and methane, is given in Table 2.4.

Table 2.4 Typical Compositions of Coals and Liquid Hydrocarbons[a] [23]

Element	Anthracite	mv Bit.	hvb Bit.	Lignite	Asphaltene	Toluene	Petroleum Crude	Gasoline	Methane
C	93.7	88.4	80.3	72.7	87	91.3	83.0-87.0	86	75
H	2.4	5	5.5	4.2	6.5	8.7	11.0-14.0	14	25
O	2.4	4.1	11.1	21.3	3.5				
N	0.9	1.7	1.9	1.2	2.2		0.2		
S	0.6	0.8	1.2	0.6	0.37		1		
H/C Ratio	0.31	0.67	0.82	0.69	0.9	1.14	1.76	1.94	4

[a] Coal analysis on moisture- and ash-free basis; ash content of coal 3-15 %

In order for coal to be viable as a carbon feedstock, the original hydrogen-to-carbon ratio must be increased. There are two different ways of performing this task: the addition of hydrogen or the rejection of carbon. These two methods are the basis for most coal conversion processes. There are four chief processes that are included here: pyrolysis, indirect liquefaction or gasification, and direct liquefaction with and without a catalyst [23]. These conversion pathways are illustrated in Figure 2.5.

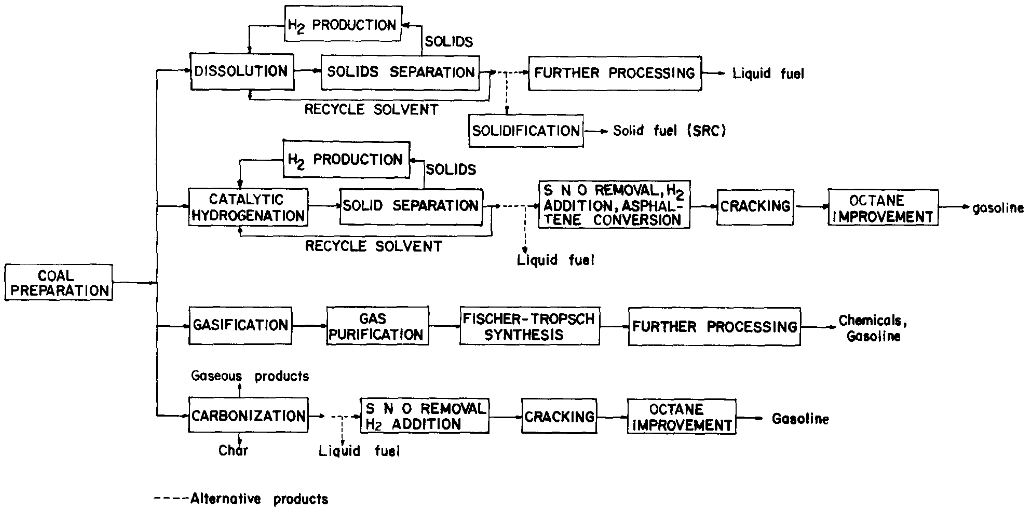


Figure 2.5 Alternate routes for Coal Liquefaction [23]

2.5.3 Pyrolysis

Pyrolysis or carbonization employs the approach of rejecting carbon as its method of increasing the hydrogen-to-carbon ratio of raw coal. This path is illustrated as the bottom process in Figure 2.5. Pyrolysis takes place as coal is heated in the absence of oxygen and thermally decomposed into hydrogen rich liquids and gases and a carbon rich residue (char or coke). This is done in the absence of oxygen, so that undesirable combustion reactions do not take place. As the coal is heated (350 – 400 °C), the bonds or links break between aromatic cluster units. Then the aliphatic side chains, as well as the low molecular weight fragments of coal, break away from the cluster units at 450 – 500 °C. From these the tars and gases are given off. As the sample reaches higher temperatures, the aromatic clusters repolymerize causing the formation of the coke or char [26]. This char contains the mineral matter that was present in the original coal sample. These minerals often act as catalysts in reactions that take place between the char and the product gas [39]. The liquid products, or coal tar, formed from the condensed volatile matter, are processed further by hydrogenation and desulfurization to create valuable products. It is these materials, which are now rich in hydrogen. The yield of these liquids can be optimized by shortening the time that the product is exposed to higher temperatures. This helps minimize the formation of gas as the larger fragments undergo further decomposition [23].

2.5.4 Indirect Liquefaction

Indirect liquefaction or gasification takes place when coal is completely broken down into synthesis gases, mainly carbon monoxide and hydrogen. The general process for indirect liquefaction is shown as the third approach in Figure 2.5. The synthesis gases generated from coal can then be combined in the presence of a Fischer-Tropsch catalyst to form various higher hydrocarbons [23].

An advantage of indirect liquefaction is that because the original coal sample is completely destroyed and only the organic matter is gasified, the amount of mineral matter and impurities in the final product can be minimized. Also, depending on the choice of Fisher-Tropsch catalyst, the products can be highly selective to gas, gasoline, kerosene, diesel fuel, and fuel oil. Products such as methanol and acetone can also be produced depending on the specific type of catalyst. Several types of commonly used catalysts are Fe, Co, Ni, Ru, ZnO_2, and ThO_2. However, in order for the gasification to take place, coal is usually reacted with steam and oxygen to produce carbon monoxide and hydrogen gas. This process creates many by-products that must be removed before further processing into valuable products, such as fuel. Also, the destruction of the original coal structure can be very expensive in terms of thermal efficiency [23].

2.5.5 Direct Liquefaction

Direct liquefaction consists of two different processes, hydrogen-donor solvent reaction and dissolution and catalytic hydrogenation. These two approaches are illustrated as the top two processes in Figure 2.5. In the present research, catalysts are not being used. Therefore, the subsequent discussion of direct liquefaction will only include the hydrogen-donor solvent process and is the focus of the remainder of this chapter.

2.6 Mechanisms of Liquefaction

Curran et al. [9] and Vernon [38] proposed that the transfer of hydrogen to coal from a solvent follows a free radical mechanism. The free radicals are formed by the thermal degradation of the coal structure and are looking to be capped in the most thermodynamically favorable process. Wiser [44] concluded that during each of these ruptures of the covalent bonds, two free radicals are formed, and that these free radicals are capped in one of three ways: (1) addition of atoms (such as hydrogen) or other radical groups to the free radicals, (2) rearrangement of atoms within the free radical, and (3) polymerization of the free radical.

The first method of capping the free radical is the desired method when performing coal liquefaction with a hydrogen donor solvent. This allows the large coal molecules to be thermally degraded, capped with hydrogen, and stabilized as smaller, more soluble and hydrogen-rich species. These species would typically have a molecular weight ranging from 300 to 1000 [40]. The second and third methods occur when there is not a hydrogen donor solvent available. If the free radical species contains an unstable structure such as a hydroaromatic unit, the free radical species could cap itself. Finally, if the free radical species is stable and in the presence of other free radical species, polymerization or retrograde reactions could take place. This is the basis for the formation of coke, char, and other large and insoluble molecular weight species. Therefore, for the formation of low molecular-weight carbon-product precursors, the first method is preferred.

McMillen and Malhotra [24, 25] proposed a slightly different mechanism for the liquefaction of coal. Their theory states that the free radical mechanism is occurring during coal liquefaction, but it does not account for the total amount of conversion. McMillen and Malhotra point out that if a solvent is used to quench radicals, then its ability as a liquefaction solvent should correlate with the weakness of their carbon-hydrogen bonds. However, they found that solvents that are equally effective as radical scavengers, i.e. indane, ethylbenzene, and tetralin, were not equally effective as liquefaction solvents [25]. From this observation, they proposed that solvents not only take a passive role in liquefaction by stabilizing radicals but are also actively participating in bond cleavage. The solvent adds a hydrogen atom into the ipso position of the coal molecule. This addition of a hydrogen atom causes the cleavage of strong coal bonds and the formation of additional coal radicals (Figure 2.6).

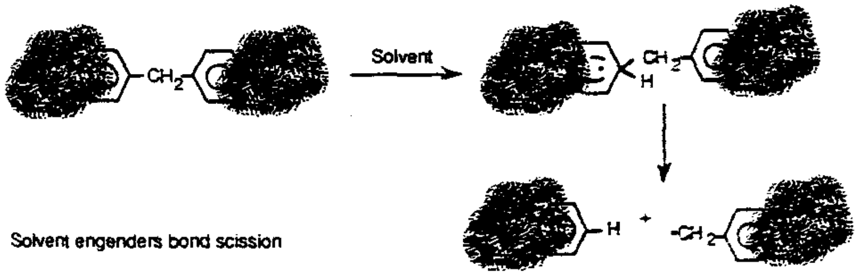


Figure 2.6 Solvent Mediated Hydrogenolysis of a Strong Linkage in Coal [25]

On a macroscopic level, the conversion of coal to liquid hydrocarbons can be visualized as a progressive hydrogenation through a series represented by the following:

$$\text{Coal} \rightarrow \text{Preasphaltenes} \rightarrow \text{Asphaltenes} \rightarrow \text{Oils (Carbenes + Carboids)} \qquad (2\text{-}1)$$

The definition of these liquids is shown in Table 2.5. However, Berkowitz [5] states that the hydrogenation process is much more complicated than the progression illustrated in Equation 2-1 and contains some reversible processes. This schematic is shown in Figure 2.7 and entails two different steps. The first step is “coal solubilization, which depends on the nature and intensity of pyrolytic and H-transfer reactions in the reactant system” [5]. The second occurs when secondary hydrogenation takes place. Secondary hydrogenation depends on the specific reaction conditions and drives the products toward lower molecular weight species [5].

Table 2.5 Definition of Primary Liquids from Berkowitz [5]

	Soluble In	Insoluble In
Carbenes	Carbon disulfide	n-Pentane
Carboids	n-Hexane	Carbon disulfide
Asphaltenes	Benzene and toluene	n-Hexane
Preasphaltenes	Tetrahydrofuran	Benzene

Most of the information that has been obtained concerning the chemistry and kinetics of coal liquefaction has been determined from reactions with coal and a model hydrogen donor such as tetrahydronaphthalene (tetralin). However, these data are still somewhat fragmentary and contradictory.

One hypothesis for the reaction of coal and tetralin is illustrated in Equation 2-2.

$$\text{coal} + \text{tetralin} \Rightarrow \text{coal-derived products} + \text{naphthalene} \qquad (2\text{-}2)$$

This reaction mechanism gives a way to correlate the solubilization of the coal by hydrogen transfer by quantifying the conversion of tetralin to naphthalene at varying reaction conditions [28]. However, this is not the only possible reason for the formation of naphthalene from tetralin. The tetralin could undergo dehydrogenation that results in the formation of hydrogen gas. Or the tetralin could be converted by isomerization to methylindane as well as hydrogen donation to form naphthalene [12].

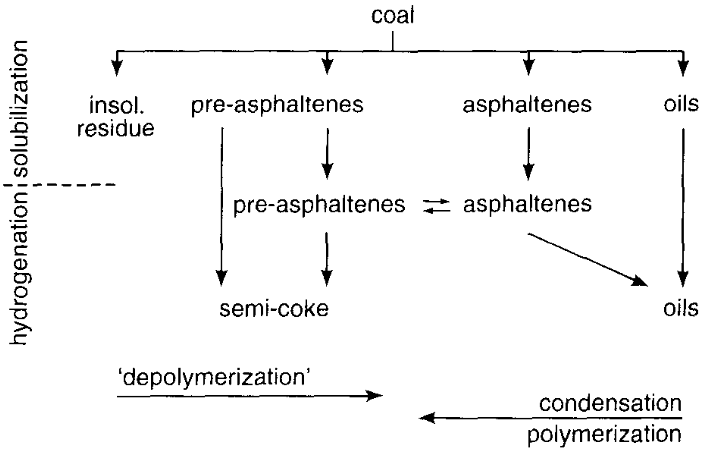
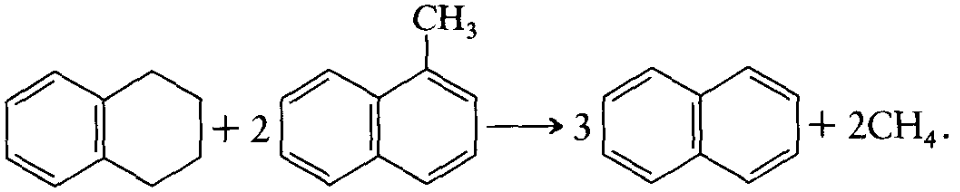


Figure 2.7 Conceptual Reaction Sequences in Coal Liquefaction [5]

Berkowitz [5] also points out that naphthalene can be formed in other possible liquefaction reactions. Using methylnaphthalene to represent a structure found in the coal macromolecule, naphthalene can be formed from the reaction illustrated in Equation 2-3.



(2-3)

As illustrated above and due to the complexity of the coal macromolecule, the chemistry of coal liquefaction has a significant amount of diversity. However, through laboratory studies and pilot plant operations, properties of coal that affect liquefaction results have been compiled and are summarized below in Table 2.6.

Table 2.6 Fundamental Properties Important in Coal Liquefaction [5]

Property	Influence	Desired level
Rank	Liquids yield	Medium
Ash content	Operations and handling	Low
Moisture content	Thermal efficiency	Low
Hydrogen content	Liquids yield and hydrogen	High
Oxygen content	Gas make and hydrogen consumption	Low
Extractability[a]	Liquids yield and quality	High
Aliphatic character	Liquids yield and quality	High
Reactive macerals[b]	Liquids yield	High
Particle size	Operations	Fine/very fine

[a] In effect, “solubility” in potent solvents

[b] Principally vitrinites and exinites

2.7 Coal Liquefaction Parameters

In this section some of the different factors that affect the ability of coal to be processed by direct coal liquefaction will be investigated. These include the coal composition, the type of solvent, the mineral matter in the coal, and the presence or absence of hydrogen gas.

2.7.1 Coal Composition

The effect of coal rank on the process of liquefaction has been extensively studied in the past with very different results. One reason for such discrepancies is the fact that the same rank of coal could be very different according to the geographical region in which it originated and the petrographic composition of the coal. The petrographic composition refers to the vegetation components that go into the process of making coal. These components depend on the types of vegetation present in the area, as well as the amount of biochemical degradation of organic matter before the coalification process of coal formation has started. Several studies that explored this trend are outlined below.

Fisher et al. [15] investigated the influence of coal rank on coal conversion while considering the effects of petrographic composition. They found that coals with more than 89% carbon content were unsuitable for hydrogenation and give a low liquid yield because of their large, condensed polynuclear structure. High volatile bituminous coals were the best for liquefaction, and low rank coals such as lignite and sub bituminous gave lower liquid yields. Also, the low rank coals were affected more by the reaction conditions. The results of this study can be seen in Figure 2.8. These results were confirmed by Given et al. [18] when they found that high volatile bituminous coals gave the highest yields during direct liquefaction.

Neavel [28] found that coal conversion to benzene solubles (asphaltenes and lighter hydrocarbons) decreased as coal rank increased. This experiment was performed using hydrogenated creosote oil as the hydrogen donor solvent at approximately 400 °C. Neavel's results are shown in Figure 2.9. However, Gorin [19] reports heavily divergent liquefaction yields depending on the original coal rank. These differences were attributed to the geographic region from which the coal was mined. Finally, a study by Yarzab et al. [46] attempted to correlate coal properties of over 100 U.S. coals and conversion. These coals were split into three different populations according to 15 coal characteristics. The result of this study was that a correlation demanded a different set of properties for each population.

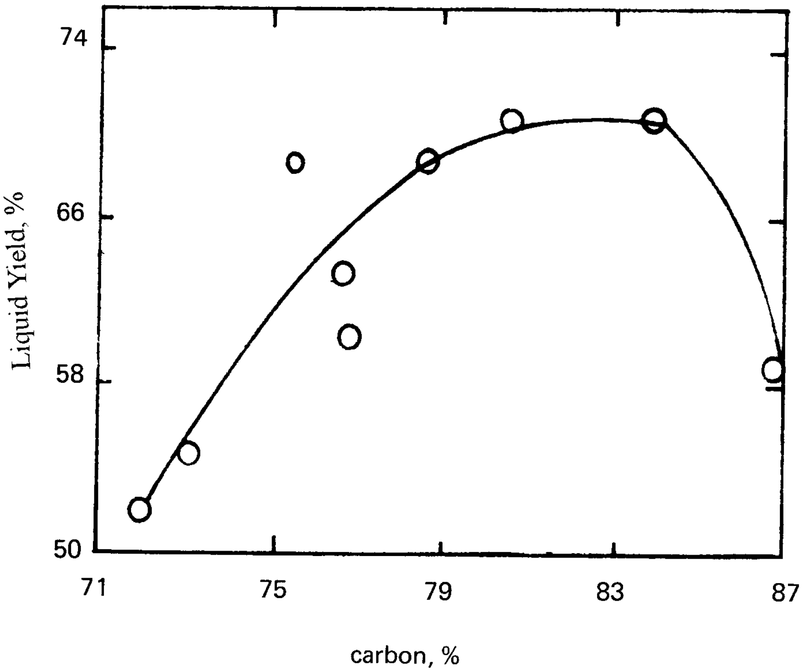


Figure 2.8 Effect of Carbon Content on Liquid Product Yield [15]

Keogh and Davis [21] found that coal rank can also affect the mechanism of coal liquefaction. They found that both bituminous and sub-bituminous coals have two distinct stages of liquefaction. For bituminous coals, during the first stage as conversion increases, the production of asphaltenes and preasphaltenes increases while the production of oils and gases remains stable. In the second stage, as a maximum in conversion is achieved, then the asphaltenes and preashaltenes are converted to oils and gases. For sub-bituminous coals, the first stage includes an increase in conversion, asphaltenes and preasphaltenes, and oils and gases. The second stage is the same as for bituminous coals as the asphaltenes and preashaltenes are converted to oil and gas.

The success of coal liquefaction not only depends on coal rank but also depends on the petrographic composition of the coal. Each type of maceral has a different behavior when subjected to liquefaction conditions. Keogh et al. [22] used density gradient centrifugation to separate and study the behavior of each maceral group from a single parent coal. They found that at lower temperatures (385 °C) conversions are similar. However, as temperature increases, liptinites were converted more than vitrinite which was converted more than inertinite. Finally, they showed that the weighted conversion of the individual macerals did not add up to the total amount of conversion of the parent coal, suggesting some synergistic effects of the combined maceral groups.

Cloke and Wang [8] also studied the effect of maceral composition on liquefaction behavior using hydrogenated anthracene oil. They found that most of the vitrinite was hydrogenated by 350 °C. The increase of temperature from 300°C to 375 °C showed little effect on the conversion of liptinite, however, most of the liptinite was converted by 400 °C. Finally, inertinite could be partially hydrogenated above 400 °C. However, this is not always beneficial because the rate of repolymerization outweighs the rate of hydrogenation.

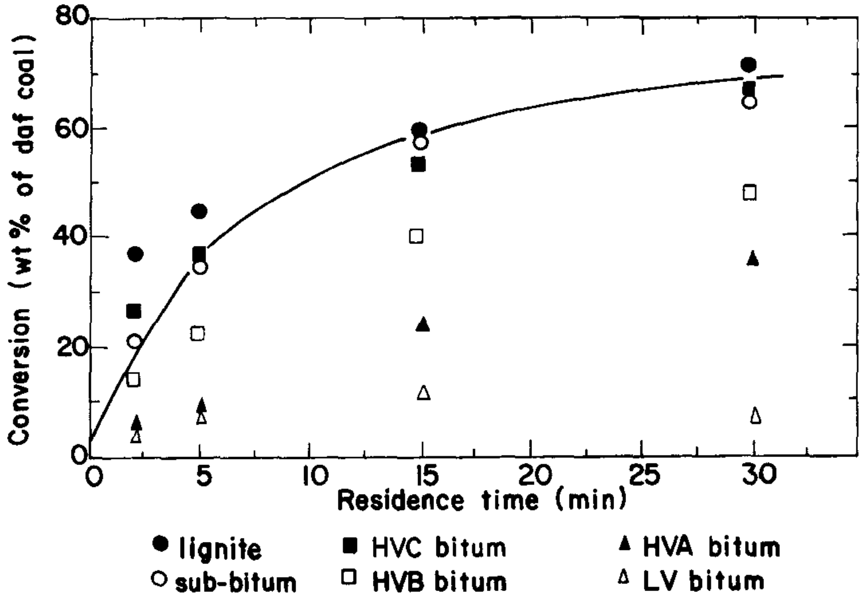


Figure 2.9 Variation in the yield of benzene solubles with rank and reaction time [28]

2.7.2 Liquefaction Solvents

The choice of liquefaction solvent can have an enormous effect on the success of direct coal liquefaction. The choice not only affects the conversion, but also the amount of hydrogen consumed, the degree and quantity of retrograde reactions, and the quality of liquid products [20]. As stated above, the process of liquefaction thermally decomposes the macromolecules of coal into smaller, free radical units. At this point, if hydrogen is added, the free radicals will be stabilized and the small molecules will become stable and soluble. The liquefaction solvent is chosen so that the most efficient transfer of hydrogen to these free radicals can be achieved.

Whitehurst et al. [40] lists four chemical properties that influence the ability for a solvent to be used in coal liquefaction. These are: (1) the hydrogen donor capacity of the solvent, (2) the physical solubilization of coal products, (3) hydrogen transfer capability (the ability to shuttle hydrogen from the coal molecule itself to cap the free radical), and (4) the presence of species that promote the production of char.

Oele et al. [29] defined four different types of solvents based on their effects on coal: non-specific solvents, specific solvents, degrading solvents, and reactive solvents. Of these four types, only specific and reactive solvents are of interest to direct liquefaction. Specific solvents dissolve 20-40% of the original coal at temperatures about or below 200° C. These solvents are electron donors and the process is a physical solution. Some solvents that fall into this group are N-methylpyrolidone (NMP) and pyridine.

A reactive solvent actually undergoes a chemical reaction with the species that is being dissolved. This is the common solvent used in high temperature direct liquefaction reactions. The solvent reacts with coal by donating hydrogen to the free radicals that are formed. Tetralin is one such solvent.

Orchin and Storch [30] performed some liquefaction experiments in order to determine the ability of several reactive solvents to convert coal to benzene solubles. These reactions were carried out at 400 °C under a hydrogen atmosphere that was initially at atmospheric pressure. The results are shown in Table 2.7. The least effective solvent was a high boiling aromatic compound or a hydroaromatic compound that dehydrogenates slowly at the reaction temperature and low pressure. The most effective solvents contained an aromatic hydroxyl group as well as a hydroaromatic ring.

Table 2.7 Effectiveness of Some Solvents for Hydrogenation [30]

Solvent	Benzene Soluble (%, maf coal basis)
o-Cyclohexylphenol	81.6
1,2,3,4-Tetrahydro-5-hydroxynaphthalene	85.3
Tetralin	49.4
Cresol	32.1
Dicyclohexyl	27.2
Naphthalene	22.2
o-Phenylphenol	19.6
Diphenyl	19.4

[a] With 1 atm initial (cold) hydrogen pressure without catalyst. The reaction time is 0.5 hr at 400°C with a 4:1 solvent/coal ratio.

2.7.3 Mineral Matter in Coal

There have been many studies performed on the catalytic effect that mineral matter in coal may produce during liquefaction. Most of the catalytic activity has been ascribed to the presence of pyrite (FeS_2) or the reduced form of pyrite, pyrrhotite (FeS_x, x = 1.0 to 1.14) [40].

Mukherjee and Chowdhury [27] characterized the ash content of a high-vitrinite coal in order to study the catalytic effect of the mineral matter in liquefaction. The hydrogenation reaction took place in the absence of a donor solvent, but specific minerals were added to coal. The results showed that the best correlation of catalytic activity was obtained using added sulfur (organic plus pyritic). Other minerals that showed a correlation with benzene solubles were iron, titanium, and kaolinite.

Whitehurst et al. [40] studied the effect of iron pyrite on the solvent-solvent interactions that occur during the liquefaction of coal. These results showed that the rate of solvent-solvent hydrogen transfer reactions occurred at a higher rate in the presence of coal (containing pyrite) than in solvent-solvent reactions alone.

Another way to study the effect of mineral matter in coal is to remove the mineral matter content without altering the organic composition of the coal before reaction [40]. The mineral matter present in coal can be selectively removed depending on the type of pretreatment. Two kinds of coals were pretreated so that in one experiment all mineral matter was removed except pyrites, and the other set was pretreated to remove all pyrites. In order to remove all mineral matter except pyrite, the coal was treated with HCl followed by HF and then treated again with HCl. The pyrite can be removed by using the Meyers Process. This process uses an aqueous ferric sulfate solution as a leachant to remove the pyrite [41]. After the pretreatment of these coals to remove the ash content, the coal conversion dropped with lower ash content (see Figure 2.10) and the hydrogen consumption dropped with lower ash content signifying that some catalytic activity can be attributed to the presence of pyrite [40].

2.7.4 Hydrogen Pressure

The exact role of a hydrogen atmosphere is not specifically known, however, the presence can greatly benefit the production of soluble coal. The hydrogen at high pressure could donate hydrogen and stabilize the coal free radicals in one of two ways: (1) directly donate hydrogen to the free radical or (2) transfer hydrogen to the donor solvent, which can then be transferred to the coal particle. Yen et al. [47] showed that when tetralin was used as a donor solvent, the yield of benzene insolubles was 25.3% when a nitrogen atmosphere was employed. When the atmosphere was changed to hydrogen, a positive effect on coal conversion was observed as the yield of benzene insolubles decreased to 13.8% indicating more conversion to benzene solubles. Tomic and Schobert [36] also observed an increase in the amount of conversion when a hydrogen atmosphere was used instead of an inert atmosphere during liquefaction without solvents or catalysts. This increase in conversion was believed to occur as hydrogen reduced the amount of retrograde reactions at high temperature [36]. Finally, Artok [2] states that without a catalyst, but with a solvent present, the efficient use of hydrogen during liquefaction is difficult.

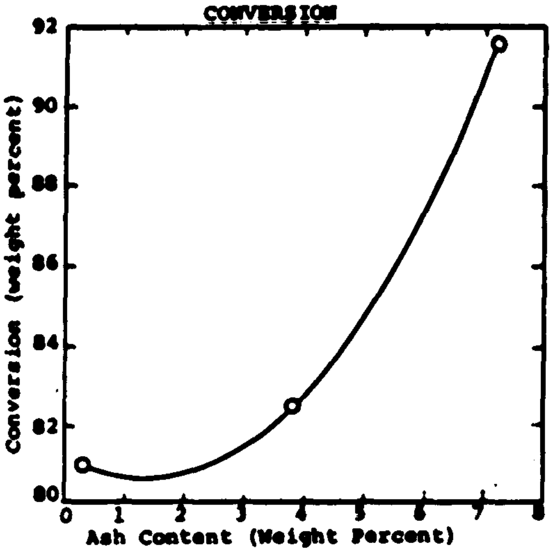


Figure 2.10 Wyodak Coal Conversion vs. Ash Content [40]

The presence of a hydrogen atmosphere on conversion is not the only subject of importance. Another major issue is the exact mechanism that hydrogen undergoes in liquefaction. Finseth et al. [14] state that the bulk of the hydrogen consumed from an uncatalyzed solvent liquefaction above 400 °C is consumed by gas generation, heteroatom removal, and hydrogenolysis of the coal matrix. Wilson et al. [42] report that hydrogen is consumed by alkyl fission and hydrogenolysis, not with hydrogenating aromatic rings. Chawla et al. [7] state that at long times (greater than 15 minutes) hydrogen is consumed by secondary reactions of as asphaltenes and preasphaltenes are converted to oil and gas.

2.8 Summary of Background Remarks

The above discussion has focused on elemental carbon, carbon artifacts, the production of carbon artifacts from coal, and the principles and parameters governing the effectiveness of direct coal liquefaction. By changing the liquefaction reaction parameters, a different set of reaction products could be isolated. Each of these could potentially exhibit different properties when tested as carbon product precursors. It is the goal of this thesis report to understand the effect that several of the discussed reaction parameters (solvent, pressure, and gaseous atmosphere) would have on the quantity and properties of the resultant pitch fraction and its subsequent use as a carbon-product precursor.

CHAPTER 3
EXPERIMENTAL

In this chapter, all of the materials and equipment in the experiments are discussed along with the process of performing the hydrogenation reactions, extracting the products, and testing the final products.

3.1 Materials

Various chemicals and gases were used during the course of this investigation. The supplier and purity are listed below for each of the chemicals and gases.

Tetrahydrofuran (THF) was used as a solvent during the product separation steps of the experiments. THF was obtained from Fisher Scientific and was the histological grade with purity listed as 99% or greater. It was used during all experiments as delivered.

Argon and hydrogen were used as the gaseous atmosphere for the hydrogenation experiments. Nitrogen was used as an inert purge gas during vacuum drying. They were obtained as standard laboratory grade from AirGas of West Virginia.

A medium-volatile bituminous coal (WVGS 13421) was obtained from the West Virginia Geological Survey. A proximate analysis was performed to determine its amount of moisture, fixed carbon, volatile matter, and ash. The results of this analysis along with some other characteristics of WVGS 13421 are shown in Table 3.1. An ultimate analysis was performed to determine the elemental composition of the coal and this can be seen in Table 3.2. The coal was ground to -20 mesh and dried overnight in a vacuum oven. The vacuum oven was set at 110°C with a nitrogen purge (100 cc/min) and a vacuum of 25-30 in Hg.

Three coal-derived solvents were obtained for testing as hydrogenation solvents. The first is a mid-distillate coal liquid obtained from Antaeus Technical Services, Inc. This coal liquid was produced as a by-product from the production of a high quality char and is referred to in this thesis as the Raw Antaeus Coal Liquid (RACL). This coal liquid was a very viscous fluid at ambient temperatures. The second is a heavy creosote oil (HCO), and the third is a carbon black base (CBB). The latter two samples were obtained from Koppers Industries, Inc and are considered to be similar but were obtained from Koppers at different times. However, the elemental composition was slightly different for the two Koppers' samples, and so they were treated as separate solvents. The elemental composition of each raw material is

Table 3.1 Characteristics of WVGS 13421

Coal Bed	Powellton
County	Raleigh
ASTM rank	mvb
Mean-maximum reflectance of vitrinite	1.111
Proximate analysis (as received)	
Moisture	0.98
Fixed carbon	67.87
Volatile matter	27.96
Ash	3.19
Petrographic composition (% volume)	
Vitrinite	63.3
Exinite	5.7
Inertinite	30.0

Table 3.2 Elemental Compositions[a] of WVGS 13421 and Coal-Derived Solvents

	WVGS 13421	RACL	DACL-L	DACL-H	HCO	CBB
C	81.59 %	86.67 %	80.51 %	88.51 %	93.41 %	91.85 %
H	4.56 %	6.76 %	7.74 %	5.72 %	5.14 %	5.51 %
N	1.10 %	1.22 %	0.94 %	1.25 %	0.88 %	0.81 %
S	0.73 %	0.72 %	0.61 %	0.76 %	0.55 %	0.67 %
O[b]	4.82 %	4.54 %	10.19 %	3.62 %	0.02 %	1.11 %
H/C Atomic Ratio	0.67	0.94	1.15	0.78	0.66	0.72

[a] Elemental compositions are not on an ash free basis

[b] Determined by difference

shown in Table 3.2. HCO was a pasty material that needed to be heated in order to process easily. CBB was fluid at ambient temperatures but contained some solid like matter entrained in the fluid. Therefore, it was also heated before processing.

The Antaeus coal liquids were further split into two fractions before use as donor solvents. The raw liquids were vacuum distilled (apparatus shown in Figure 3.1) to approximately 50% by weight. The temperature was kept below 270°C so that pyrolysis reactions do not occur. The light distillate (DACL-L, b.p. < 270 °C, 25-30 in. Hg) and residue (DACL-H, b.p. > 270 °C, 25-30 in. Hg) were collected and stored in the cold room until time for use. DACL-L was fluid at ambient temperature and used without further preparation. DACL-H was a pitch-like solid material that was ground to –8 mesh. This material exhibited a softening point of 120 °C and a coke yield of 46 % by weight. The heavy creosote oil and carbon black base were used without further treatment. The elemental compositions of these reactants are shown in Table 3.2.

3.2 Experimental Procedure for Hydrogenation Reactions

3.2.1 Overview of Hydrogenation Reaction

The effectiveness of five coal-derived liquids as hydrogenation solvents in the direct hydrogenation of a medium-volatile bituminous coal was investigated. Initially, the reaction conditions for each solvent-coal mixture were kept identical. The temperature was 400 ºC, and the initial pressure was 1000 psig of hydrogen in the cold reactor. The solvent-to-coal ratio was 3 to 1 by weight, and the reaction time was one hour. These are standard conditions that have been used before in the literature for reactions of coal and model hydrogen donor solvents, such as tetralin. The products of the hydrogenation reactions were extracted using THF in order to calculate the overall conversion (as THF solubles) for the solvent-coal mixture. Finally, the effects of changing the gas-phase pressure and atmosphere (runs five through ten), and solvent-to-coal ratio (runs four, eleven, and twelve) were investigated. A list of conditions for all

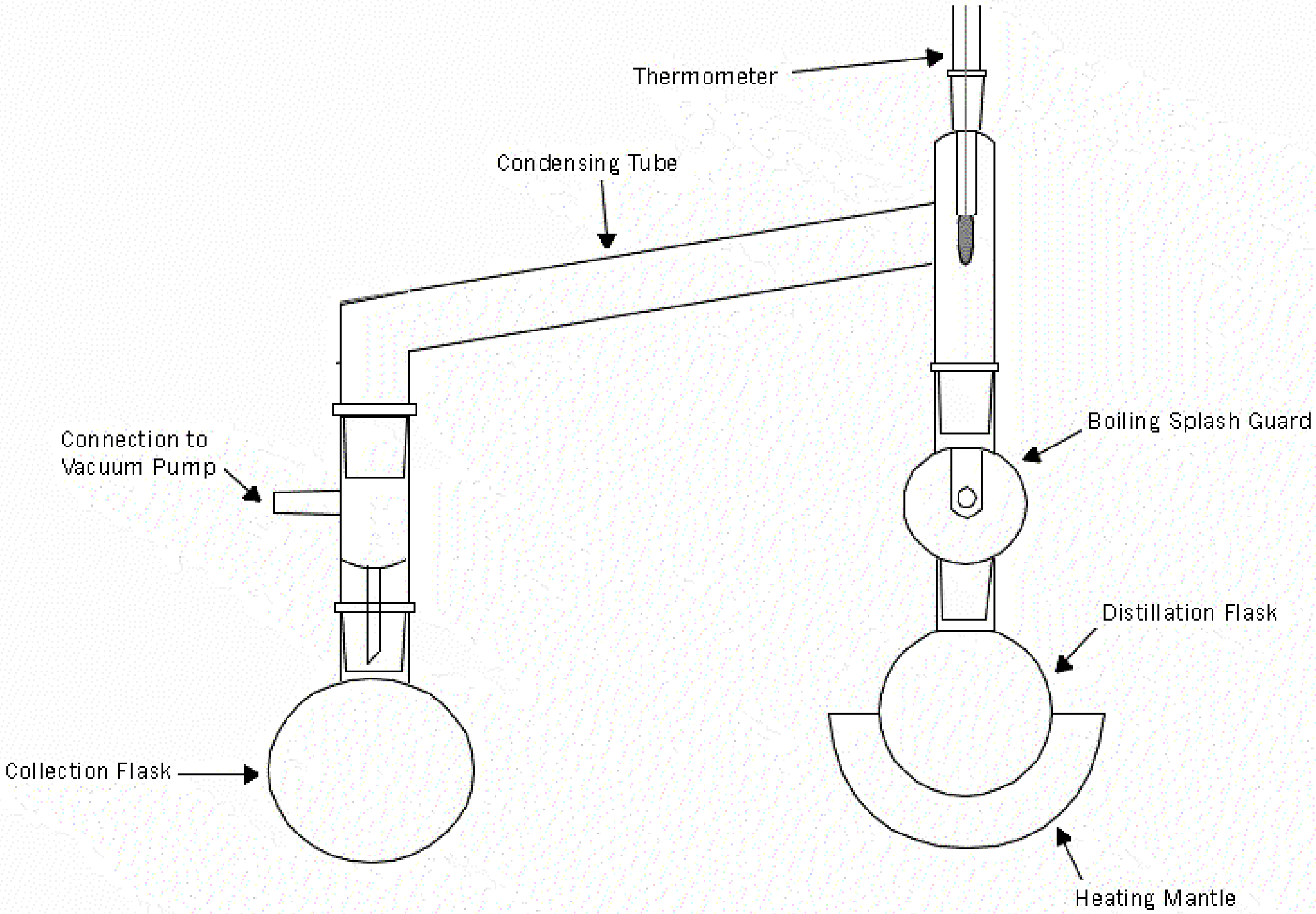


Figure 3.1 Vacuum distillation Apparatus for separating RACL into DACL-L and DACH-H

the reactions is shown in Table 3.3. For each set of reaction conditions given in Table 3.3 (identified by the run number 1 – 12), four repeated trials were performed. These trials are identified by the letters A, B, C, and D. Thus each individual run is identified by a number followed by a letter. The number corresponds to the reaction conditions given in Table 3.3. The letter refers to a specific trial (A, B, C, or D) of the same reaction conditions. A complete list of data from all the reactions is shown in Table A.1 in the appendix.

The extract (THF soluble fraction) was then vacuum distilled to recover a possible recycle solvent and a distillation residue. The heavy distillation residue (termed “pitch” hereafter) was tested as a possible precursor for carbon-products. The effect of the distillation on the pitch characteristics was investigated. Several distillations were performed to remove different amounts of the light fraction (termed “recycle solvent” hereafter). The light distillate is given the name “recycle solvent” because in many similar processes this fraction is recycled to the reactor for further hydrogenation reactions. However, testing the effectiveness of the isolated recycle solvents as subsequent hydrogenation solvents is outside the scope of this research and is not performed. The softening point of the resultant pitch from each distillation was determined. The data from these distillations and softening points allowed the correlation of the amount of recycle solvent removed and the softening point of the resultant pitch. This correlation was used to produce a pitch by vacuum distillation with a target softening point of 120 ºC. A process flow diagram for the overall experimental procedure is shown in Figure 3.2.

Table 3.3 Hydrogenation Reaction Conditions

Run #	Solvent	Temperature (°C)	Atmosphere	Pressure (psig Cold)	Solvent/Coal Ratio	Time (hr)
1	DACL-L	400	H_2	1000	3/1	1
2	DACL-H	400	H_2	1000	3/1	1
3	RACL	400	H_2	1000	3/1	1
4	HCO	400	H_2	1000	3/1	1
5	CBB	400	H_2	1000	3/1	1
6	CBB	400	Argon	1000	3/1	1
7	CBB	400	H_2	500	3/1	1
8	CBB	400	Argon	500	3/1	1
9	CBB	400	H_2	100	3/1	1
10	CBB	400	Argon	100	3/1	1
11	HCO	400	H_2	1000	2/1	1
12	HCO	400	H_2	1000	1/1	1

3.2.2 Fluidized Sand Bath Preparation

A Techne SBL-2 fluidized sand bath was used to heat the reactors during hydrogenation runs. A TECHNE TL-8D temperature controller regulated the sand bath temperature. The sand bath was filled three-quarters full with a –100 mesh aluminum oxide powder (sand). The sand bath was preheated to 25 °C above the desired reaction temperature. The extra temperature accounted for the rapid loss in temperature that occurred when the cold reactors were plunged into the sand bath. The inlet airflow to the bath was adjusted so that light bubbling occurs in the sand. If the airflow was too low, the heat would not be evenly distributed. If the airflow was too high, sand would be propelled out of the overflow tray.

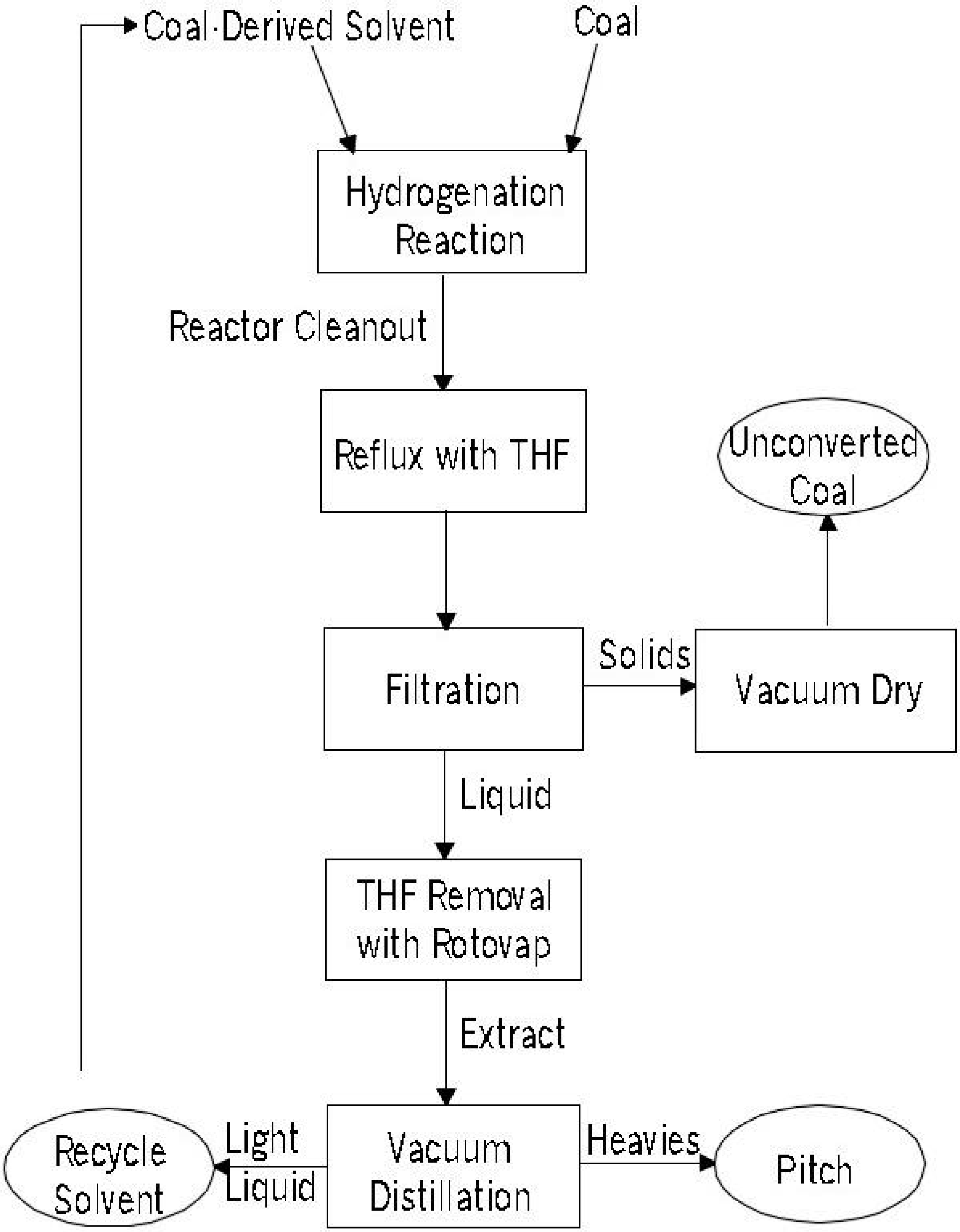


Figure 3.2 Experimental procedure flow sheet for production of carbon product precursors for coal hydrogenation reactions

3.2.3 Reactor Preparation

Two tubing bomb microreactors (TBMR) were prepared for each hydrogenation run (see Figure 3.3). The reactors were cleaned thoroughly before each use. The inside of the reactors was scoured using an appropriately sized cylindrical wire brush. The threads of the end caps were wiped clean using steel wool. Air was then blown down the reactor stem to remove any particulates from the stem.

Once cleaned, one end of the reactor was sealed according to the following procedure. The TBMR was placed in a vise, and a small amount of copper anti-seize lubricant was applied to the threads. The lubricant helped to secure the Swagelok caps and prevented the caps from seizing to the reactor body under the high-temperature reaction conditions. The Swagelok cap was placed on the reactor and tightened until hand tight. An extra quarter turn was added using a wrench to seal the cap fully.

3.2.4 Reactor Charging

Reactants were weighed on an analytical balance (Denver Instruments Model A-200DS) to the nearest 0.1 mg and then added to the reactor. The coal-derived solvent was placed in the reactor first. Since the coal liquids are viscous liquids, their mass was measured by difference. Once their mass was determined, the appropriate amount of coal was added to the reactor. The solvent-to-coal ratio was kept constant at 3 to 1. Finally, some ball bearings (usually five) were weighed and added to the reactor. These were introduced to help stir the contents of the reactor during reaction. Once all the reactants had been charged, the open end of the TBMR was sealed according to step 3.2.3.

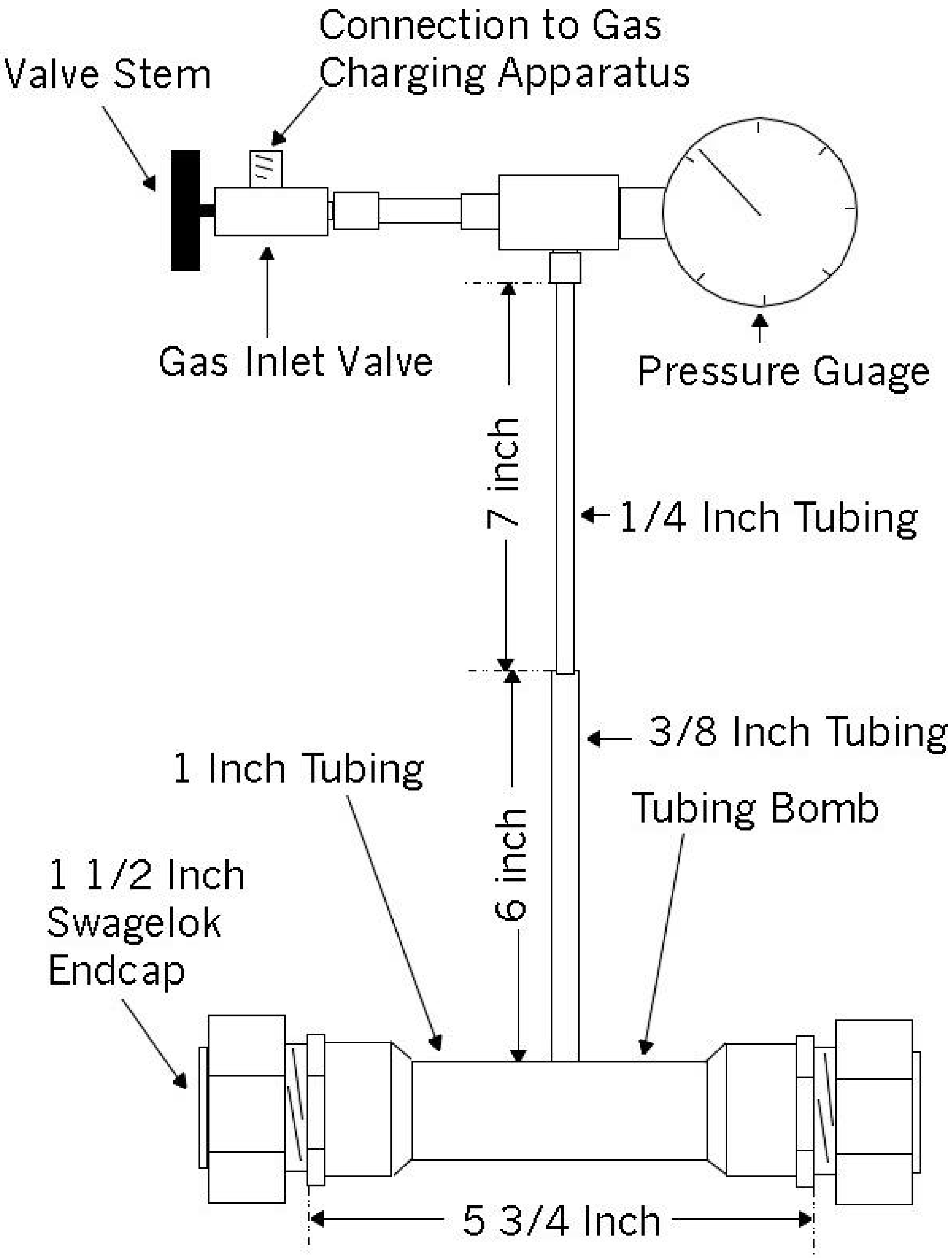


Figure 3.3 Overall view of the 50 mL tubing bomb microreactor

3.2.5 Gas Charging

The hydrogenation reactions were run under either an argon or hydrogen atmosphere. This insured that oxygen would not react with the coal, promoting polymerization and the production of large insoluble coal fragments. Air was removed from the reactors by using a pressure purge cycle. The reactors were pressurized to 1000 psig initially with hydrogen or argon (depending on the specific hydrogenation run, see Table 3.3) and checked for leaks with a soap-water solution. The purge valve was then slowly opened to allow the reactor to reach atmospheric pressure again. Opening the purge valve slowly was essential so that none of the small particulates were lost during depressurization. This pressurization and release process was repeated two more times. Finally, the reactor was pressurized to the desired cold reaction pressure (see Table 3.3). The gas inlet valve of the tubular reactor was then closed, and the port on the gas inlet valve was sealed by screwing on a ¼-inch Swagelok plug.

3.2.6 Reaction Procedure

Once the reactors were charged with reactants and gas, they were placed in the reactor holder above the fluidized sand bath. The reactor holder was attached to a shaking mechanism used during the reaction. Once the reactors were secure in the holder, the shaking mechanism was turned on, and the speed was adjusted so that the reactors were vertically agitated at approximately 400 rpm with a stroke of approximately 1.5 inches.

The reactors were then heated by immersion into the sand bath by raising the sand bath using a winch-and-pulley system. The sand bath was raised until the hot sand completely covered the reactor bodies. The temperature of the bath was then adjusted to the desired reaction temperature. Finally, a stopwatch was started to count down from 58 minutes. The extra two minutes (total reaction time was to be 1 hr) allowed time to remove the reactors from the sand bath and quench the reaction.

Once the reaction time had elapsed (58 minutes), the sand bath was lowered by means of the winch-and-pulley system. The agitator was slowed down and then turned off. The reactors were removed from the holders and placed in a water bath. This served to cool the reactors quickly and quench the hydrogenation reactions.

3.2.7 Product Collection

The products of all the reactions except those using DACL-H or a solvent-to-coal ratio of 1/1 were viscous fluids interlaced with some solid particles. The other two were more solid at ambient temperature and required a separate procedure for collecting the products of the reaction.

For all reactions except those with DACL-H or a solvent-to-coal ratio of 1/1, the reactor was placed in a vise and the Swagelok plug was removed from the gas inlet valve. Then one end cap was slowly removed (so that the pressure could be released). The reactor was not vented through the gas inlet valve in order to keep the hydrogenation products in the main body (not the stem or pressure gauge) for ease of cleaning out the reactor. A small brush was used to clean any sand away from the reactor threads. The end cap was then replaced and only hand tightened. The reactor was flipped in the vice and the same procedure was used to loosen the other end cap.

A 500-mL flat-bottom boiling flask was placed in a clamp in a fume hood and fitted with a glass funnel. One end cap of the reactor was removed and the reactor was clamped over the funnel allowing its contents to drain into the funnel (when creosote oil, carbon black base, or raw antaeus coal liquids were used as the hydrogenation solvent, a heat gun was used to help promote this process). Once the products stop dripping, the reactor was filled with THF. A stainless steel spatula was used to scrape the sides of the reactor while it contained THF. The THF was then drained into the boiling flask. This process was repeated several times until all the reaction mass was washed from the reactor. The transfer of the reaction mass from the reactor must be quantitative since the subsequent mass balance and processing steps depend on this procedure.

The end cap was then placed on the open end of the reactor, and the reactor was turned upside down over the funnel. The opposite end cap was now removed and the reactor was again washed with THF several times. Next, both end caps were removed and the final particulates left in the reactor were washed into the flask. The gas inlet valve was opened and THF was used to flush any matter from the reactor stem. The end caps were then scraped and washed out with THF. Finally, the funnel was washed with THF and removed from the flask.

For reactions using DACL-H or the lowest solvent-to-coal ratio, the reactor was chilled in dry ice for approximately 15 minutes before being opened. The end caps were removed by the procedure described above. The contents of the reactor were then chipped out using a metal spatula into a large metal pan. Once the contents of the reactor were removed to the pan, the products were then poured from the pan into a 500-mL flat-bottom flask through a funnel. The pan, reactor, and funnel were finally washed with THF into the flask.

3.2.8 THF Extraction

The 500-mL round bottom flask containing the coal/solvent/THF solution was filled (if needed) with fresh THF until it was approximately ¾ full. The flask was placed in a heating mantle and fitted with a simple water-cooled condenser. The cooling water was turned on and the heating mantle temperature was adjusted using a variac. The power was set so that a rolling boil (≅75 °C) was obtained. The contents of the flask were allowed to boil overnight (usually 12-16 hours).

The flask was then cooled to room temperature. The contents of the flask were centrifuged for 30 minutes at 2000 rotations-per-minute. The liquid portion of the centrifuged product was poured into a Buchner-type filtering funnel that was under vacuum suction. The filtering funnel was fitted with a pre-weighed piece of filter paper. Following filtration, the solid product (residue) was washed with THF while in the filter funnel. The residues produced by centrifugation and vacuum filtration were finally combined to form the THF insoluble fraction.

The filtrate was poured into a clean, weighed 250-mL flat bottom flask. The THF in the filtrate was removed by rotary evaporation and collected for later use. The soluble product (extract) was set aside for further processing.

The THF insoluble residue was then placed in a vacuum oven (80 °C and 25-30 mm Hg) and allowed to dry overnight (16-20 hours) under a nitrogen purge (100 cc/min). The dried residue was then weighed and the amount of THF insoluble product was calculated. This weight was used to calculate the overall conversion using Equation 3-1. The coal-alone conversion was also calculated using Equation 3-2 [13]. It should be noted that for purposes of calculating the coal-alone conversion, all the THF insoluble matter was assumed to come from the coal only and not from the added solvent.

$$\%\text{ Overall Conversion } = \frac{[(\text{Mass of Reactants}) - (\text{Mass of THF Insolubles})]}{\text{Mass of Reactants}} \qquad 3\text{-}1$$

$$\%\text{ Coal Conversion (daf) } = \frac{[(\text{Mass of Dry Coal}) - (\text{Mass of THF Insolubles})]}{\text{Mass of Coal (daf)}} \qquad 3\text{-}2$$

It is important to note why THF was used in this process rather than NMP, which has been extensively used at West Virginia University as a solvent. Several preliminary reactions were performed using NMP as the extraction solvent, but a large mass loss was observed for the process. The majority of this mass loss occurred during the removal of NMP from the soluble products. Since NMP has a boiling point (202 °C) in the range of many of the light products (particularly those to be collected as the recycle solvent), during the rotoevaporation of NMP, many of the reaction products were lost. Because one of the goals of this research was to isolate a possible recycle solvent, a solvent with a lower boiling point (THF) has been employed.

3.2.9 Product Isolation

Once the THF was removed from the extract, the THF-soluble hydrogenation products were separated using vacuum distillation. This was performed using the same procedure as described for separating the Antaeus coal tar into two fractions with one exception. The distillate was collected in a graduated cylinder in order to quantify the amount collected. The residue from the vacuum distillation was considered to be the soluble coal product (pitch). The distillate was the recycle solvent. The distillation was carried out several times (usually four) for each hydrogenation reaction. Each of these distillations collected a different amount of recycle solvent. The pitch and recycle solvent masses were calculated from each of these fractional distillations to determine the effect that the mass distilled had on the softening point of the pitch.

3.3 Coal Extract Testing

The properties of the coal extract pitches (i.e. high boiling distillate residues) collected from the hydrogenation reactions were evaluated as possible precursors for value-added carbon materials. These evaluation tests included softening point, coke yield, ash content, optical examination, and elemental analysis.

3.3.1 Softening Point

The softening point is required for the characterization of binder pitch, impregnation pitch, and pitch for fiber spinning. The softening point is a measure of the ability of the sample to flow and gives an indication of the rheological consistency of the sample.

The softening point was determined in duplicate using a Mettler FP80HT central processor and a Mettler FP83HT dropping cell following the ASTM D3104 procedure [4]. The sample holder was filled with a sample and heated until melting occurs. The sample was then cooled and allowed to solidify into the sample holder. Additional sample was added and melted into the holder until full. The sample holder was then placed into the dropping cell, where it was heated at a rate of 2 °C/min over a range of about 70 – 200 °C.

The softening point was determined to be the temperature at which the sample, suspended in a cylindrical cup with a ¼ inch hole in the bottom, flowed downward for a distance of 0.8 inches to interfere with a light beam. The softening point was displayed automatically when the beam of light was interrupted.

3.3.2 Coking Value

The coking value provides some insight into the amount of non-volatile matter in the sample. It also gives some indication of the sample's relative coke forming propensity. A desired value for coke yield is between 50 and 60 percent by weight.

The coking value was determined using the West Virginia University (WVU) method. The sample (approximately 0.4 – 0.8 grams) was placed in a pre-weighed porcelain crucible and immersed in coke breeze inside a larger crucible. The coke breeze allowed for the coking process to take place in the absence of oxygen. The sample was

$$\text{Coking Value, \%} = 100\left(\frac{\text{Mass of Residue After Heating}}{\text{Mass of Original Sample}}\right) \qquad 3\text{-}3$$

then heated to 600 °C at a rate of 5 °C/min in a Fisher Scientific Isotemp Programmable Furnace Model 497. The sample was held at 600 °C for two hours and then cooled 10 °C/min until reaching room temperature. The crucible was then removed from the coke breeze and weighed. The coking value was determined using Equation 3-3. This procedure was chosen for obtaining the coke yield so that the resultant coke sample's optical texture could be investigated. The long heating time allowed the characteristic domains of the sample to develop more fully.

3.3.3 Ash Content

After the carbon content of a sample has been burned in air, the ash is the remaining residue. The ash is the inorganic oxides of the mineral matter that were present in the original coal. For most carbon products, the ash or inorganic portion of the sample is considered an impurity.

The ash content determination was carried out in a Fisher Scientific Isotemp Programmable Furnace Model 497. The ash content was determined according to the procedure specified by ASTM D2415 [3]. The sample was placed in a pre-weighed, partially covered crucible, set in the furnace, and heated at a rate of 8 °C/min until the furnace reaches 500 °C in air. The heating rate was then changed to 4 °C/min until the temperature reaches 750 °C. The sample was held here for three hours in air and then cooled at a rate of 10 °C/min to ambient temperature. The final weight of the crucible and sample was determined, and the ash content was calculated from Equation 3-4.

$$\text{Ash Content, \%} = 100\left(\frac{\text{Mass of Residual Ash}}{\text{Mass of Original Sample}}\right) \qquad 3\text{-}4$$

3.3.4 Optical Texture

Once the pitch sample has been converted to coke, the optical texture can be determined. The texture of a coke can be isotropic, anisotropic, or in between. The degree of optical texture can give some insight into the possible end uses for the carbon sample. It also indicates the surface and graphitization properties of each of the samples.

The optical texture of the sample was determined under a polarized-light optical microscope (Zeiss Axiostop, West Germany). The coke sample from the WVU method of coking was used to determine optical texture. The sample was embedded in epoxy resin and its cross section was polished on a Buchler Ltd. Metallurgical Apparatus with different textured abrasives. The sample was then observed under the Zeiss polarized-light microscope and optical texture (isotropic or anisotropic) was determined. A camera was mounted on the polarized-light microscope to photograph the optical textures.

3.3.5 Elemental Analysis

An elemental analysis was performed on several representative pitches, residues, and recycle solvents. By combining this information with the elemental composition of the original hydrogenation reactants, an elemental balance could be performed for several different reaction conditions.

A Flash EA 1112 series elemental analyzer from ThermoQuest was used for this analysis. A small amount of sample (1-3 mg) was weighed and placed in a small tin container. Vanadium pentoxide (3-5 mg) was added to the tin container for use as an oxidizing agent to insure complete combustion of the sample. The tin container was closed and crushed to evacuate all the air in the sample container. The sample was placed in the autosampler and the mass and sample name were recorded. The instrument then dropped the sample container into combustion reactor were the sample was converted into carbon dioxide, water, nitrogen oxides, and sulfur trioxide. The nitrogen oxides and sulfur trioxide were converted to elemental nitrogen and sulfur dioxide, respectively by reduction. These gases then passed into a gas chromatographic column, where they were separated. The eluted gases were detected by a thermal conductivity detector and processed to give the percentages of nitrogen, carbon, hydrogen, and sulfur in the sample with oxygen being determined by difference.

Several parameters could be adjusted to give the best results, such as carrier gas flow, oxygen flow rate, oxygen injection duration, cycle time, and sampling delay. The carrier gas was helium and was set at a flow rate of 130 ml/min. Oxygen was used in the combustion reactor and was set at a flow rate of 240 ml/min for an injection time of 7 seconds. The cycle time for each sample was set at 600 seconds and the sample delay was 12 seconds. Each sample was analyzed in triplicate, and any erroneous values were discarded before averaging the results.

3.4 Error Calculation

In order to determine the accuracy and consistency of the experimental procedures presented herein, a percent relative error was calculated for the different quantitative characterization techniques. Unless otherwise noted in this report, all error is reported as a relative error. The relative error is a percent deviation from the average value of the number reported. For example, an error of ±2 % in a value of 90.00 means that the range of error of 88.2 to 91.8 %. The relative error was used to determine the error in two different values evaluated at the same conditions according to Equation 3-5.

$$\%\,\text{Relative Error} = \left(\frac{\left|\text{Value 1} - \text{Value 2}\right|}{\left(\frac{\text{Value 1} + \text{Value 2}}{2} \right)} \right) \times 100 \qquad 3\text{-}5$$

CHAPTER 4
RESULTS AND DISCUSSION

In this chapter, the results of the production of carbon product precursors from the direct hydrogenation of coal are presented. Hydrogenation reactions were performed with various coal-derived solvents under similar conditions in order to determine the most effective solvent. Several of the reaction conditions (pressure, gas-phase composition, and solvent-to-coal ratio) were then varied so that their role in producing carbon-product precursors could be assessed. The results focus on the effect of gas pressure, gas-phase composition, solvent, and solvent-to-coal ratio on the conversion of coal to pitch-like materials and the properties of the pitch. The resultant materials were characterized by softening point, ash content, coking value, and optical texture. Products from several of the hydrogenation runs were also characterized by elemental analysis. Overall mass and ash balances were also performed for each run and are presented here. By evaluating the results, an optimum set of reaction conditions for the production of carbon-product precursors from coal can be established.

4.1 Mass Balances

A mass balance was performed for each hydrogenation reaction trial. The components of the mass balance were the amount of coal and solvent charged into the reactor and the amount of pitch, THF insolubles (residue), and recycle solvent collected after processing the hydrogenation products. The results of the mass balances can be seen in Table 4.1. The conditions for each hydrogenation run are given in Table 3.3.

For every reaction, a negative mass balance was observed, indicating a net loss of mass during the reaction and product separation steps. There are several different explanations for the negative mass balances. First, any product gas that may have formed during the reactions was not collected and quantified and thus is absent from the mass balance calculation. Typically the mass loss due to gas production could be between 2 - 5 % by weight. Second, any light material that was produced during the hydrogenation

Table 4.1 Overall Mass Balances of the Coal Hydrogenation Reactions

Run	Trial	In Coal (g)	In Solvent (g)	Total In (g)	Out Pitch (g)	Out THF Ins. (g)	Out Rec. Solv. (g)	Total Out (g)	Out - In (g)	(Out-In)/In (%)
1	A	8.3812	25.1046	33.4858	8.5037	4.6171	16.6769	29.7977	-3.6881	-11.0
1	B	8.4897	25.4679	33.9576	12.3280	4.7903	14.4829	31.6012	-2.3564	-6.9
1	C	8.3809	25.1423	33.5232	9.6637	4.8612	15.3188	29.8437	-3.6795	-11.0
1	D	8.4776	25.4351	33.9127	6.9489	4.8407	17.4629	29.2525	-4.6602	-13.7
2	A	5.9996	17.9994	23.999	17.2400	6.6085	0.0000	23.8485	-0.1505	-0.6
2	B	5.9988	17.9999	23.9987	16.2053	6.6643	0.0000	22.8696	-1.1291	-4.7
2	C	6.0008	18.0008	24.0016	12.7595	6.8085	1.9900	21.558	-2.4436	-10.2
2	D	6.0009	17.9990	23.9999	9.5452	7.2738	3.9600	20.779	-3.2209	-13.4
3	A	7.6118	22.8324	30.4442	9.9431	6.9708	10.2900	27.2039	-3.2403	-10.6
3	B	7.6541	22.9600	30.6141	11.5130	7.1990	9.7100	28.422	-2.1921	-7.2
3	C	7.6744	23.0200	30.6944	8.8603	7.2135	11.2000	27.2738	-3.4206	-11.1
3	D	8.2833	24.8500	33.1333	12.2342	8.6765	9.0800	29.9907	-3.1426	-9.5
4	A	8.7873	26.3643	35.1516	11.0642	6.0297	14.6300	31.7239	-3.4277	-9.8
4	B	8.8595	26.5785	35.438	5.4141	6.4669	21.2400	33.121	-2.317	-6.5
4	C	8.8076	26.4215	35.2291	7.5975	6.2503	17.1900	31.0378	-4.1913	-11.9
4	D	8.9488	26.8472	35.796	6.4161	6.5263	17.4800	30.4224	-5.3736	-15.0
4	E	8.7055	26.1183	34.8238	7.1096	6.9566	20.2183	34.2845	-0.5393	-1.5
5	A	9.0940	27.2847	36.3787	8.6773	6.9411	19.1700	34.7884	-1.5903	-4.4
5	B	8.9570	26.8698	35.8268	7.1536	7.0941	20.6700	34.9177	-0.9091	-2.5
5	C	8.8303	26.4937	35.324	5.6086	6.9512	21.2800	33.8398	-1.4842	-4.2
5	D	8.8314	26.4938	35.3252	8.5937	7.0349	19.2400	34.8686	-0.4566	-1.3
6	A	8.6048	25.8137	34.4185	6.0769	7.2494	16.9400	30.2663	-4.1522	-12.1
6	B	9.0270	27.0806	36.1076	4.7830	8.1360	20.5800	33.499	-2.6086	-7.2
6	C	8.5940	25.7836	34.3776	3.4138	7.9002	21.8700	33.184	-1.1936	-3.5
6	D	8.9388	26.8162	35.755	6.5164	7.8078	19.1700	33.4942	-2.2608	-6.3
7	A	8.5583	25.6744	34.2327	6.4744	7.0102	17.7300	31.2146	-3.0181	-8.8
7	B	8.9103	26.7293	35.6396	5.3671	7.2512	21.4800	34.0983	-1.5413	-4.3
7	C	8.6285	25.8895	34.518	5.4428	7.7470	18.8400	32.0298	-2.4882	-7.2
7	D	8.8169	26.4519	35.2688	7.7059	7.7566	17.9700	33.4325	-1.8363	-5.2

Table 4.1 (Continued) Overall Mass Balances of the Coal Hydrogenation Reactions

Run	Trial	In Coal (g)	In Solvent (g)	Total In (g)	Out Pitch (g)	Out THF Ins. (g)	Out Rec. Solv. (g)	Total Out (g)	Out - In (g)	(Out-In)/In (%)
8	A	8.9144	26.7416	35.656	7.3802	8.0749	17.6100	33.0651	-2.5909	-7.3
8	B	8.5729	25.7200	34.2929	3.9747	7.6985	20.1200	31.7932	-2.4997	-7.3
8	C	8.8134	26.4439	35.2573	6.1858	8.3588	18.5200	33.0646	-2.1927	-6.2
8	D	8.6033	25.8076	34.4109	4.9405	7.8483	19.6000	32.3888	-2.0221	-5.9
9	A	8.9656	26.8936	35.8592	8.7617	8.2419	17.1200	34.1236	-1.7356	-4.8
9	B	8.6900	26.0717	34.7617	5.4339	8.1171	19.1000	32.651	-2.1107	-6.1
9	C	9.1626	27.4904	36.653	5.6319	8.4754	18.9100	33.0173	-3.6357	-9.9
10	A	8.5836	25.7540	34.3376	7.3670	8.5019	15.8400	31.7089	-2.6287	-7.7
10	B	9.0234	27.0691	36.0925	4.7132	8.9974	18.9400	32.6506	-3.4419	-9.5
10	C	8.6621	25.9863	34.6484	6.4714	7.9306	17.1300	31.532	-3.1164	-9.0
10	D	8.8383	26.5110	35.3493	6.1156	7.9726	17.4600	31.5482	-3.8011	-10.8
11	A	11.7463	23.4898	35.2361	7.2230	8.5762	14.3000	30.0992	-5.1369	-14.6
11	B	11.5104	23.0186	34.529	8.0716	8.7815	15.2900	32.1431	-2.3859	-6.9
11	C	11.6680	23.3358	35.0038	6.8942	9.1683	15.8000	31.8625	-3.1413	-9.0
11	D	11.5366	23.0717	34.6083	6.9836	8.6664	17.2200	32.87	-1.7383	-5.0
12	A	14.9673	14.9673	29.9346	8.1438	10.7303	8.5800	27.4541	-2.4805	-8.3
12	B	15.1486	15.1480	30.2966	7.5261	11.1392	9.5600	28.2253	-2.0713	-6.8
12	C	15.7095	15.7103	31.4198	6.2607	11.1933	9.7100	27.164	-4.2558	-13.5
12	D	15.4615	15.4618	30.9233	8.1711	11.1289	9.2400	28.54	-2.3833	-7.7

reaction that condensed upon quenching of the reaction could have been lost during the THF extraction process. During THF removal by rotary evaporation, some of this lighter material could have become volatile and collected with the removed THF causing a negative mass balance. These types of materials would also be lost during the initial period of vacuum distillation. Any very light material would not condense in the graduated cylinder with the other recycle solvent but would rather be collected in the cold trap of the vacuum pump. This was confirmed by periodically checking the cold trap of the vacuum pump for the presence of collected liquid (small amounts of liquid were usually present). Finally, the process of separating the hydrogenation products into different fractions (pitch, residue, and recycle solvent) required a significant amount of experimental transfers and procedures. Each of these procedures resulted in some amount of mass loss.

For the majority of the reaction runs listed in Table 4.1, the amount of mass loss was around 10 % by weight or less. This is a reasonable result considering the procedures that were used in obtaining the product fractions. Several of the runs did, however, have a mass loss of greater than 10 %. This is most likely due to mass loss that occurred during the vacuum distillation step of product separation. The majority of the distillate (recycle solvent) needed to be heated in the condensing tube in order to make it flow into the graduated cylinder for collection. During these runs of greater lost mass, some recycle solvent could have been left in the condensing tube and therefore, not accounted for in the mass balance calculation. An example of this effect can be seen by evaluating the product distribution of the different trials of run twelve (12). Since, the only difference in processing from trial to trial was the amount of recycle solvent removed during vacuum distillation (as seen in the column labeled “Out Rec. Solv.”), the percent of THF solubles (the sum of the pitch and recycle solvent fractions) of the feed should be equivalent for each run. Also, since the hydrogenation reaction and product isolation procedures are the same, the amount of mass loss from gas production and experimental error should be equivalent for each trial. Figure 4.1 shows that this assumption was accurate for three of the four trials. Trial C had a dip in the amount of THF solubles recovered, which explains the spike in the loss of mass data. This dip in

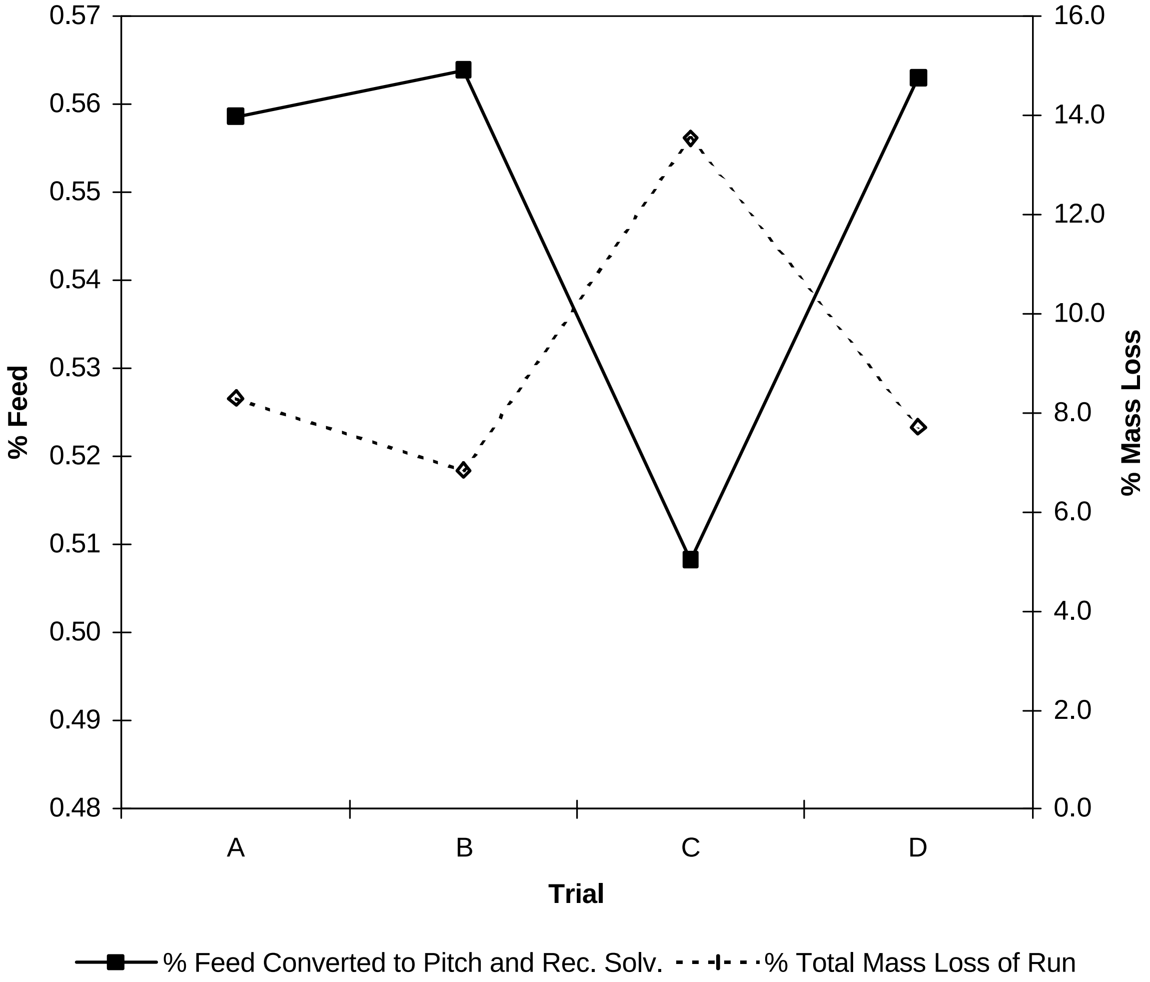


Figure 4.1 Comparison of the percent of the reaction feed recovered as THF solubles and the total mass lost during each trial of hydrogenation run twelve (12)

the THF solubles recovered corresponds to mass lost by some distillate accumulating in the condensation tube of the distillation apparatus.

The presence of a negative mass balance will have some effects on further calculations and results below. The error from the mass balance is carried over into any calculation that depends on the data from the mass balance such as an ash balance or elemental balance. However, the accuracy of the mass balance (within 10%) is good for this type of reaction system.

4.2 Ash Balance

An ash balance was performed on the products for all hydrogenation reactions and is presented in Table 4.2 with the various run conditions presented in Table 3.3. The ash content for each sample was determined according to the procedure outlined in Section 3.3.3 and on average had a relative error of less than ±2%. The ash content was determined for the reactants (coal and solvent) and for the pitch and THF insoluble portion of the products. Several samples of the recovered recycle solvent (the distillate) were tested for ash, but as expected the values were negligible. Therefore, the recycle solvent portion of the products was eliminated from the ash balance calculations. The weight of ash in each fraction was determined by multiplying the amount of each fraction (from the mass balance) by the ash percentage of that particular sample.

The results of the ash balance in Table 4.2 show a relatively random distribution of gain and loss of ash during the pitch production process. Since the ash balance depends on the mass of each fraction for calculation, any error in the mass balance will effect the ash balance results. Two figures, the ash present in the coal and the ash present in the THF insoluble residue, dominate the ash balance. The positive ash balance corresponds to the negative values of the mass balance calculations. If organic material is lost, the percentage of ash is elevated in the products, thus producing a positive ash balance. A negative ash balance could be attributed to incomplete separation of THF solubles and insolubles. A small amount of THF solubles mixed with insolubles would cause a

Table 4.2 Ash Balance of Hydrogenation Reactants and Products for All Runs

Run	Trial	Ash In Coal (g)	Ash In Solv. (g)	Total Ash In (g)	Ash Out Pitch (g)	Ash Out THF Ins. (g)	Total Ash Out (g)	Out - In (g)	(Out-In)/In (%)
1	A	0.6030	0.0000	0.6030	0.0094	0.5333	0.5426	-0.0604	-10.0
1	B	0.6108	0.0000	0.6108	0.0100	0.5207	0.5308	-0.0801	-13.1
1	C	0.6030	0.0000	0.6030	0.0100	0.5882	0.5982	-0.0048	-0.8
1	D	0.6100	0.0000	0.6100	0.0025	0.5228	0.5253	-0.0846	-13.9
2	A	0.4317	0.0243	0.4560	0.0000	0.4011	0.4011	-0.0548	-12.0
2	B	0.4316	0.0243	0.4559	0.0045	0.4538	0.4584	0.0025	0.5
2	C	0.4318	0.0243	0.4561	0.0031	0.4837	0.4869	0.0308	6.8
2	D	0.4318	0.0243	0.4561	0.0029	0.5110	0.5139	0.0578	12.7
3	A	0.5477	0.0215	0.5691	0.0026	0.6012	0.6039	0.0347	6.1
3	B	0.5507	0.0216	0.5723	0.1036	0.5604	0.6641	0.0918	16.0
3	C	0.5522	0.0216	0.5738	0.0020	0.5558	0.5578	-0.0160	-2.8
3	D	0.5960	0.0234	0.6193	0.0032	0.5809	0.5841	-0.0353	-5.7
4	A	0.6322	0.0000	0.6322	0.0023	0.7169	0.7193	0.0870	13.8
4	B	0.6374	0.0000	0.6374	0.0004	0.7146	0.7150	0.0776	12.2
4	C	0.6337	0.0000	0.6337	0.0014	0.6644	0.6658	0.0321	5.1
4	D	0.6439	0.0000	0.6439	0.0015	0.8452	0.8467	0.2028	31.5
4	E	0.6264	0.0000	0.6264	0.0036	0.8035	0.8071	0.1807	28.9
5	A	0.6543	0.0132	0.6675	0.0039	0.7101	0.7140	0.0465	7.0
5	B	0.6445	0.0130	0.6575	0.0066	0.7874	0.7941	0.1366	20.8
5	C	0.6353	0.0128	0.6482	0.0018	0.7229	0.7247	0.0766	11.8
5	D	0.6354	0.0128	0.6483	0.0020	0.6979	0.6998	0.0516	8.0
6	A	0.6191	0.0125	0.6316	0.0042	0.5919	0.5961	-0.0355	-5.6
6	B	0.6495	0.0131	0.6626	0.0093	0.6379	0.6472	-0.0154	-2.3
6	C	0.6183	0.0125	0.6308	0.0000	0.0000	0.0000	-0.6308	-100.0
6	D	0.6431	0.0130	0.6562	0.0027	0.6207	0.6234	-0.0328	-5.0
7	A	0.6158	0.0125	0.6282	0.0024	0.7115	0.7139	0.0857	13.6
7	B	0.6411	0.0130	0.6541	0.0027	0.6910	0.6937	0.0396	6.1
7	C	0.6208	0.0126	0.6334	0.0009	0.7402	0.7411	0.1077	17.0
7	D	0.6344	0.0128	0.6472	0.0014	0.8044	0.8057	0.1585	24.5

Table 4.2 (Continued) Ash Balance of Hydrogenation Reactants and Products for All Runs

Run	Trial	Ash In Coal (g)	Ash In Solv. (g)	Total Ash In (g)	Ash Out Pitch (g)	Ash Out THF Ins. (g)	Total Ash Out (g)	Out - In (g)	(Out-In)/In (%)
8	A	0.6414	0.0130	0.6544	0.0020	0.6952	0.6973	0.0429	6.6
8	B	0.6168	0.0125	0.6293	0.0028	0.6671	0.6699	0.0406	6.4
8	C	0.6341	0.0128	0.6469	0.0010	0.6503	0.6513	0.0043	0.7
8	D	0.6190	0.0125	0.6315	0.0008	0.6169	0.6177	-0.0138	-2.2
9	A	0.6451	0.0130	0.6581	0.0032	0.7030	0.7062	0.0481	7.3
9	B	0.6252	0.0126	0.6379	0.0019	0.6871	0.6890	0.0511	8.0
9	C	0.6592	0.0133	0.6726	0.0058	0.6539	0.6596	-0.0129	-1.9
10	A	0.6176	0.0125	0.6301	0.0056	0.6780	0.6836	0.0535	8.5
10	B	0.6492	0.0131	0.6624	0.0101	0.7355	0.7456	0.0833	12.6
10	C	0.6232	0.0126	0.6358	0.0055	0.6491	0.6546	0.0188	3.0
10	D	0.6359	0.0129	0.6488	0.0066	0.6306	0.6372	-0.0115	-1.8
11	A	0.8451	0.0000	0.8451	0.0077	0.9177	0.9254	0.0802	9.5
11	B	0.8282	0.0000	0.8282	0.0068	0.9484	0.9552	0.1270	15.3
11	C	0.8395	0.0000	0.8395	0.0022	0.9627	0.9649	0.1254	14.9
11	D	0.8301	0.0000	0.8301	0.0171	0.8926	0.9097	0.0797	9.6
12	A	1.0769	0.0000	1.0769	0.0016	1.0999	1.1015	0.0246	2.3
12	B	1.0899	0.0000	1.0899	0.0047	1.0359	1.0406	-0.0493	-4.5
12	C	1.1303	0.0000	1.1303	0.0015	1.1361	1.1376	0.0073	0.6
12	D	1.1125	0.0000	1.1125	0.0033	1.1079	1.1112	-0.0013	-0.1

negative deviation in the ash content of the THF insolubles. Incomplete separation of the THF fractions could be attributed to the swelling of the filter paper and a large filter cake being formed during vacuum filtration. When the filtration slowed for these reasons, THF was removed by evaporation into the fume hood, depositing some THF solubles on the residue fraction, thus decreasing the ash content in the THF insoluble fraction and causing a negative ash balance.

4.3 Solvent Evaluation

The first goal of this research was to determine the effectiveness of five coal-derived liquids as hydrogen-donor solvents for coal. Each of the five coal liquids was used as a hydrogenation solvent under the same conditions. These reactions are run numbers one (1) through five (5) from Table 3.3. Initially, these liquids were characterized according to their ability to convert coal to THF soluble material. Two different methods of measuring their effectiveness were used: (1) the overall conversion based on the total feed (i.e. coal plus solvent) and (2) the coal-alone conversion based on the weight of coal only. The definition of these conversions is given by Equations 3-1 and 3-2, respectively in Section 3.2.8.

The overall conversion for each of the solvents is given in Figure 4.2. These results show that the most effective solvent for conversion to THF solubles was DACL-L at 85.8 ± 0.3 %. The least effective solvent was DACL-H at 71.5 ± 1.3 % overall conversion. As expected, the overall conversion achieved using RACL falls between the above two values at 76.0 ± 1.5 %. The two liquids from Koppers Industries, Inc., HCO and CBB were also very effective according to Figure 4.2 with overall conversion values of 82.2 ± 1.1 % and 80.4 ± 0.4 %, respectively.

The conversion results are quite different, however, when the coal-alone conversion is used. Figure 4.3 illustrates the effectiveness of the coal liquids as hydrogenation solvents on a coal-only basis. The order of conversion for each solvent

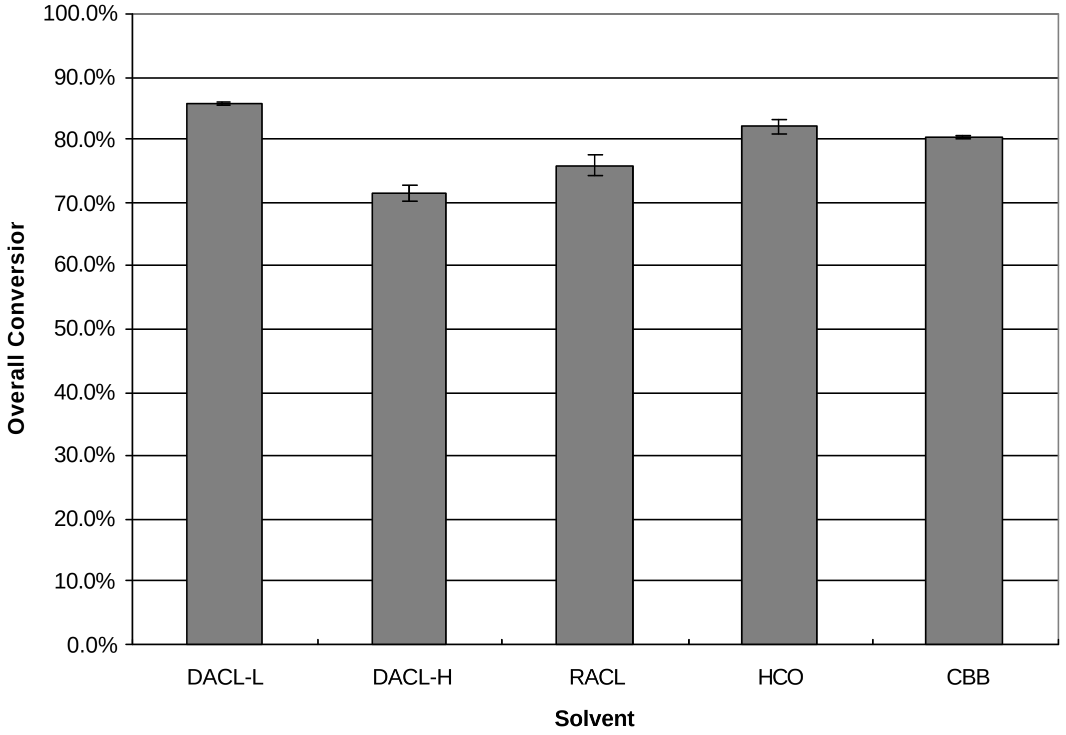


Figure 4.2 The effect of the hydrogenation solvent on the overall conversion to THF solubles at the reaction conditions of 400 °C, 1000 psig H_2 (cold), 3/1 solvent-to-coal ratio, and 1 hour

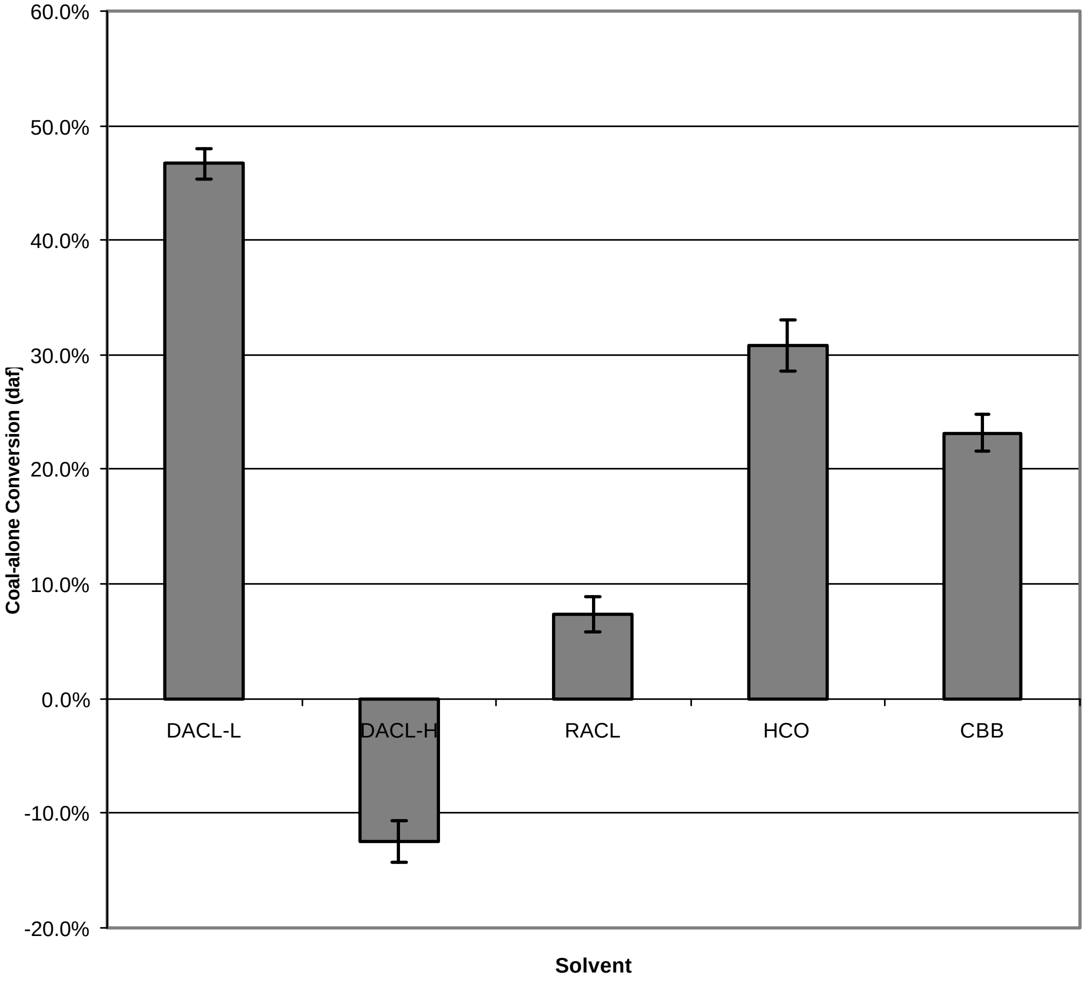


Figure 4.3 The effect of the hydrogenation solvent on the coal-alone conversion (daf basis) of coal to THF solubles at the reaction conditions of 400 °C, 1000 psig H_2 (cold), 3/1 solvent-to-coal ratio, and 1 hour

when compared to the other solvents did not change by going to a coal-only basis. However, the absolute value of the conversion changed drastically for each solvent. The coal-alone conversion for reactions using DACL-L was 46.7 ± 1.3 % while a conversion of -12.5 ± 1.8 % was calculated for DACL-H reactions. The negative conversion signified that not only was very little of the coal converted to THF solubles, but also some of the hydrogenation solvent (DACL-H) was insoluble in THF due to possible coking reactions. The coal-alone conversion for the hydrogenation reactions using RACL, HCO, and CBB were 7.3 ± 1.5 %, 30.8 ± 2.2 %, and 23.2 ± 1.6 %, respectively.

The reason for the large difference between the values of the two methods of calculating the conversions is that the overall conversion includes the solvent in its calculation, while the coal-alone conversion does not. Because the coal liquids (solvents) exhibited a high solubility in THF to begin with and the use of high solvent-to-coal ratio (3/1 by weight), the majority of the THF soluble fraction of the hydrogenation products was derived from the solvent itself. Therefore, the effect of changing solvents on coal conversion was masked by the large amount of solvent that was being included in the overall conversion calculation. But nonetheless, the DACL-L did a reasonable job by converting about 47 % of the coal to THF-soluble products.

4.4 Reaction Pressure

The reactor pressures were recorded throughout all hydrogenation reactions in order to gain some insight into the role that the hydrogen atmosphere might play in the coal conversion. An empty reactor charged with hydrogen gas (1000 psig cold) only was also heated to the reaction temperature, and the pressure was recorded throughout the time scale of other hydrogenation reactions. The average reaction pressure recorded over time for each solvent is illustrated in Figure 4.4. The most glaring observation from Figure 4.4 is that after the pressure reached a maximum (between 1950 and 2150 psig depending on the solvent) due to the rapid heating, the pressure decreased with time for each run except for the empty reactor. There are two possible reasons for the observed

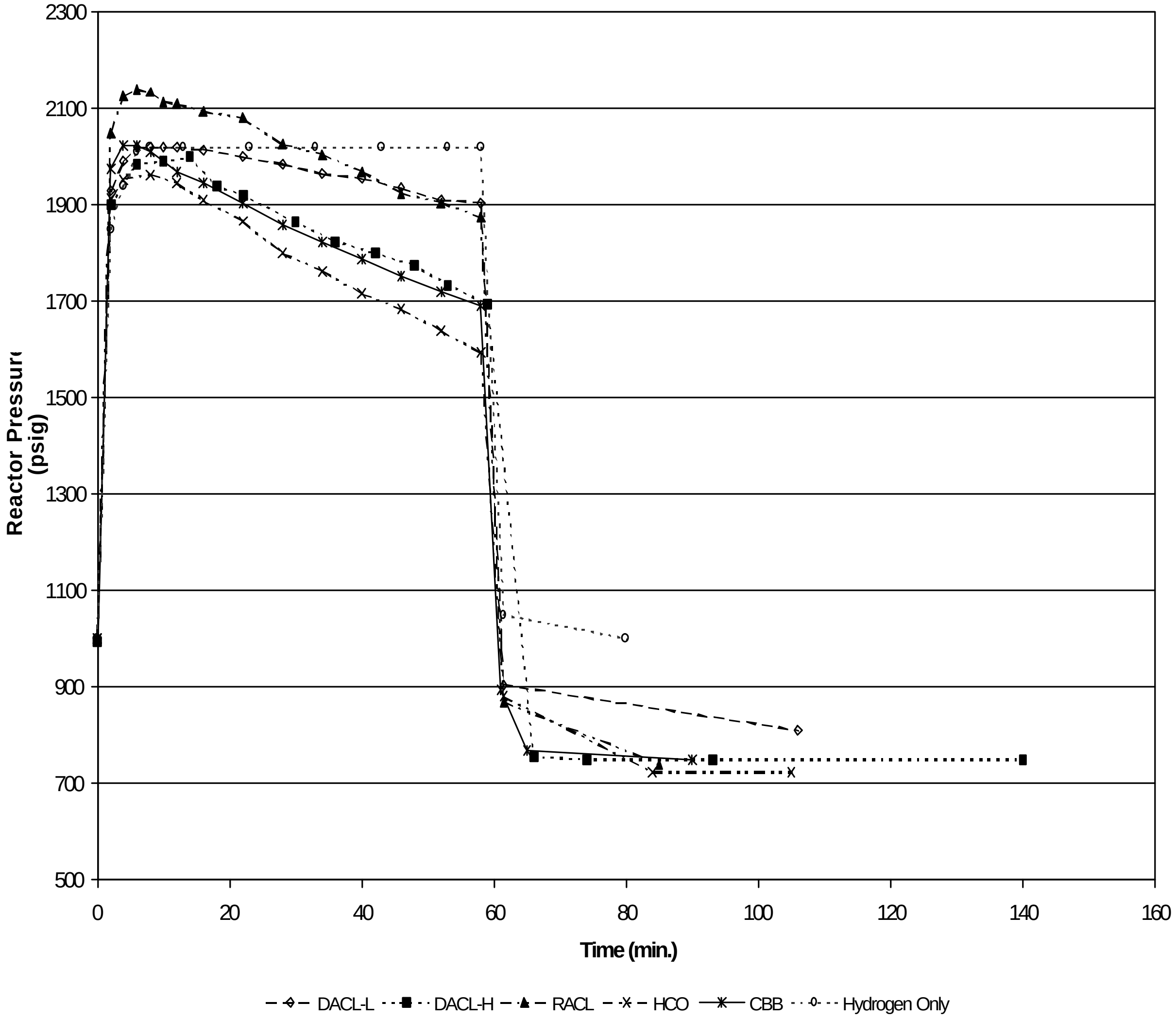


Figure 4.4 Reactor pressures during coal hydrogenation reactions with coal-derived solvents at reaction conditions of 400 °C, 1000 psig H_2 (cold), 3/1 solvent-to-coal ratio, and 1 hour

effect. First, the reactors could have been leaking. However, the reactors were thoroughly checked and sealed before immersion in the sand bath. The reactors were also allowed to sit overnight following each reaction in order to insure that no slow leaks could be detected. If any reactors showed a decline in pressure after this period, the sample was discarded and thus not presented here. Therefore, leaks in the reactors were not the cause for such an effect. The second possible explanation was that the hydrogen gas was being consumed by the reactants. This being the most likely interpretation, the hydrogen could be transferred to two different components of the reaction. The hydrogen could have been consumed by hydrogenation of the solvent or by adding hydrogen to the coal such as described by the free radical mechanism of hydrogenation. At this time the exact mechanism of hydrogen consumption for these conditions cannot be determined. The decrease in pressure during the hydrogenation reaction also indicates that the hydrogen gas is being consumed faster than gaseous products are being evolved.

The second important observation from Figure 4.4 is the relative maximum pressure that each solvent achieved during the reactions. With the exception of RACL solvent, the relative height of the pressure curves decreases as the carbon content of the solvent increases. This was expected since as the carbon content of the solvent increases so does the concentration of higher molecular weight species in the solvent. These higher molecular weight species would not be as volatile under the present reaction conditions, thus corresponding to lower reactor pressures.

Finally, it is important to notice the pressure of the reactor system once the reaction has been quenched by immersion in a water bath. The sharp decrease in pressure that occurred at sixty minutes is due to this quenching process. Once the pressure drop ceased (usually by the 90 minute mark) the reactor could be considered at room temperature. It is significant to note that for each reaction system illustrated in Figure 4.4, the final pressure of the system (720 to 850 psig depending on the solvent) was less than that of the initial pressure (1000 psig H_2 cold). This again may indicate the consumption of hydrogen during the hydrogenation reaction.

4.5 Product Distillation

Once the hydrogenation reaction products were separated into THF soluble and insoluble fractions and the THF was removed from the soluble fraction, the soluble fraction was further split into two fractions, the light distillate (or recycle solvent) and the heavy distillation residue (or pitch). This separation was achieved by the vacuum distillation described in Section 3.2.9. Each trial of every run was distilled to a different extent in order to collect a different amount of recycle solvent. This was done to gain some insight into the effect that the distillation process would have on the resultant pitch softening point and other characteristics such as coking value, ash content, and optical texture.

Figure 4.5 shows the effect that the extent of distillation has on the softening point of the pitch resulting from the hydrogenation reactions. This figure shows a linear relationship between the amount of feed recovered as pitch and the softening point of the resultant pitch. Using this relationship, a pitch can be tailored to a specific softening point by controlling the distillation step of production. The relative amounts of pitch recovered for the products made from the three Antaeus coal liquids show a predictable relationship. The light material (DACL-L) required the most distillation to achieve a softening point of 120 ° C or higher. The heavy fraction (DACL-H) required the least amount of distillation while the original coal liquid (RACL) fell in between and nearly in the middle of these two lines. This was not unexpected since the split of DACL-L and DACL-H from RACL was approximately 50 % by weight.

The two interesting trends shown in Figure 4.5 are those for HCO and CBB. According to the trends shown by the Antaeus coal liquids, the heavier materials should be shifted to the right of this graph. The starting materials for these two sets of reactions were clearly higher in heavy material than that of DACL-L. However, both of the Koppers Industries, Inc. liquids fell to the left (required more distillation) than that of DACL-L. This phenomenon can be explained by examining the coal-alone conversion exhibited when each of these solvents was employed. DACL-L had a significantly higher

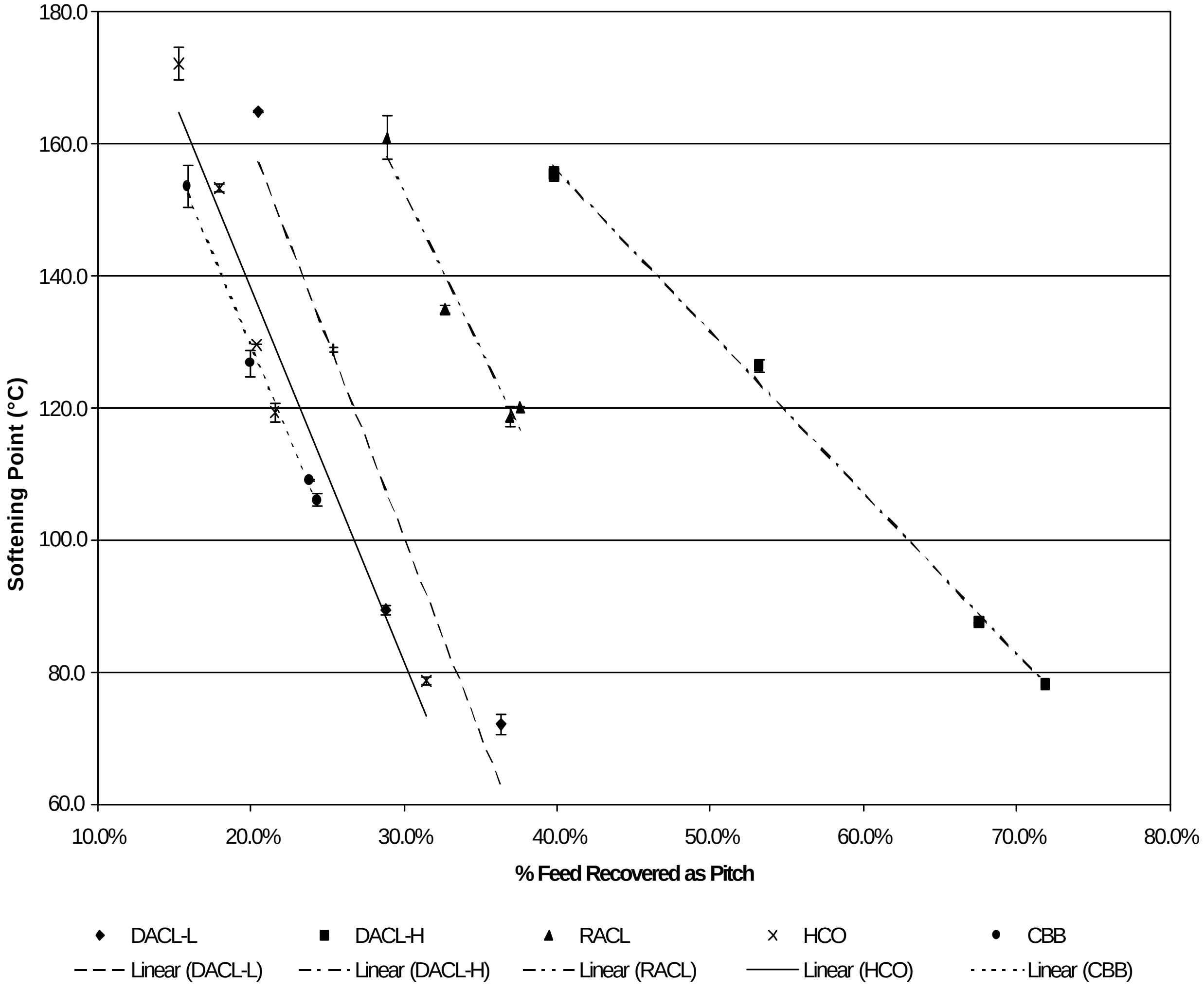


Figure 4.5 Effect of distillation on the softening point of the pitch resulting from hydrogenation reactions with coal-derived solvents at reaction conditions of 400 °C, 1000 psig H_2 (cold), 3/1 solvent-to-coal ratio, and 1 hour

coal-alone conversion (approximately 47 %) than that of HCO and CBB (approximately 31 % and 23 % respectively). Therefore, the products recovered from reactions performed with DACL-L should have more heavy components (converted from coal) than those reactions using HCO and CBB. This would lead to the phenomenon of the HCO and CBB distillation trends shown in Figure 4.5 being to the left of the DACL-L linear representation.

4.6 Hydrogenation Products

Once the distillation step has occurred, the hydrogenation products have now been partitioned into three different fractions: (1) THF insolubles, (2) pitch, and (3) recycle solvent. The THF insolubles and recycle solvents were considered to be by-products of pitch production and, hence, were not thoroughly characterized. The ash content of the THF insolubles was determined so that an ash balance (Section 4.2) could be calculated, and an elemental analysis was performed on several of the insoluble and recycle solvent fractions. The remainder of this section is focused on characterizing and comparing the pitch produced by hydrogenation with the different coal-derived solvents. In order to compare the pitches produced from the separate solvents, pitches of approximately the same softening point ($T_{sp} \approx 120$ °C) were derived and characterized.

The product distribution of the hydrogenation products with a softening point of about 120 °C depends on the particular solvent. Figure 4.6 illustrates the product distribution for the hydrogenation reactions using the five coal-derived solvents. The product distribution from the reactions using DACL-L, HCO, and CBB all appear rather similar. The dominant fraction for each reaction was the recycle solvent, with the pitch fraction being the next highest. DACL-H reactions exhibit a very different profile in Figure 4.6. The majority of the product was converted to pitch, however, the coal conversion for these reactions was the lowest (even negative for the coal only conversion). This phenomenon is created by the physical properties of the original solvent. DACL-H at room temperature is solid pitch-like material with a softening point greater than 100 °C. Therefore, after reaction, only the light material created during

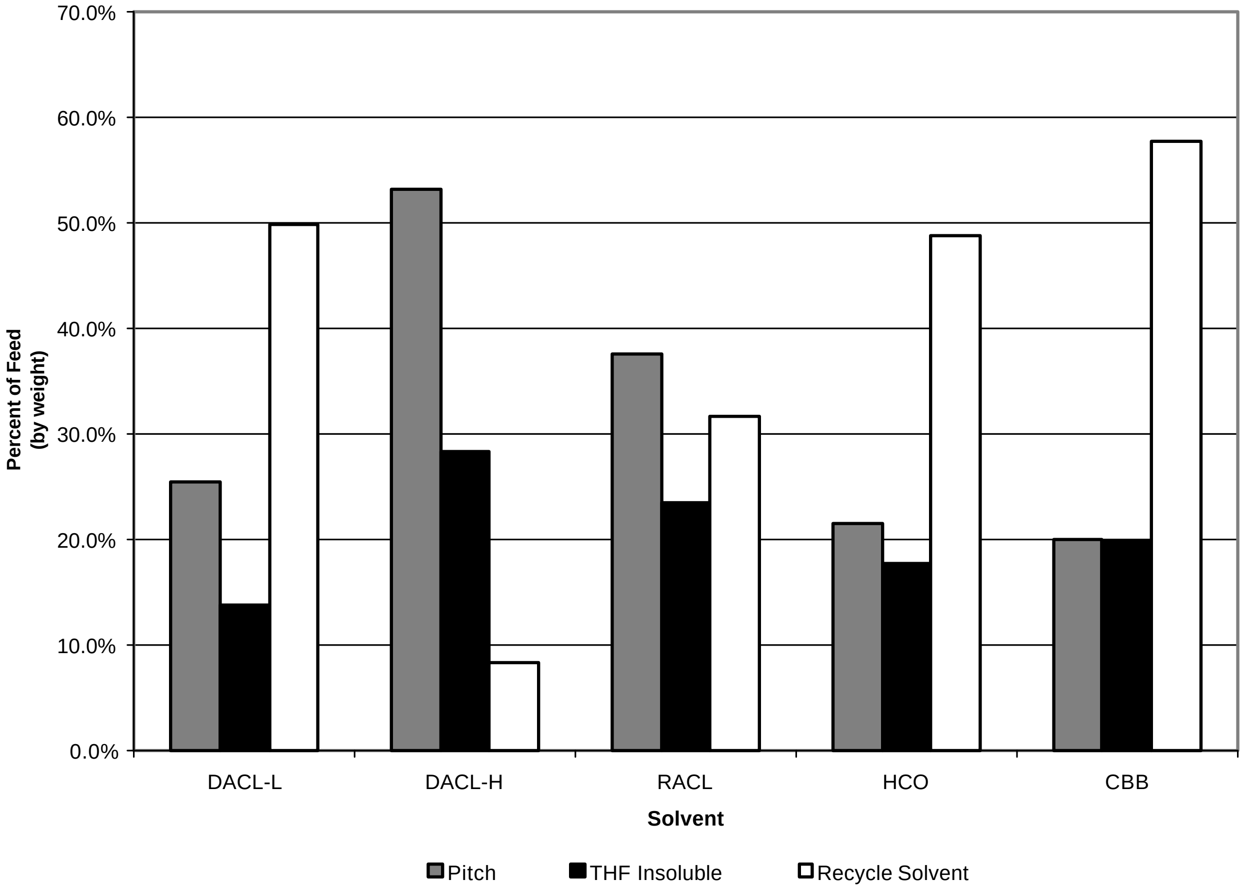


Figure 4.6 Effect of solvent choice on the hydrogenation product distribution with reaction conditions of 400 °C, 1000 psig H_2 (cold), 3/1 solvent-to-coal ratio, and 1 hour for a pitch with approximately 120 °C softening point

hydrogenation needs to be removed to get the softening point to 120 °C, and since the conversion is so low, very little light material was produced causing the high pitch production with low recycle solvent production.

It is also interesting to note that according to the above discussion and Figure 4.6 it is apparent that there is a trade-off between the amount of pitch produced and the amount of recycle solvent recovered depending on the solvent employed for hydrogenation. A large amount of pitch means more final pitch product, however, a low amount of recycle solvent means that the process may not be able to sustain itself. Therefore, a balance between the amount of pitch and recycle solvent produced needs to be struck. However, this balance may not be an equal one depending on the amount of recycle solvent required to perform subsequent reactions. This would depend on the optimum solvent-to-coal ratio which is discussed in a later section.

4.6.1 Ash Content

The ash content of the pitch and THF insoluble fractions was determined according to the ASTM method outlined in Section 3.3.3. For most carbon-product precursors, ash is considered to be an impurity and as such low values are required for the product pitches. The amount of relative error in determining the ash content for the insoluble fractions, which contain most of the ash, is small, ± 2 %. However, the pitch fractions contain a very small amount of ash (usually less than 0.1 % by weight) leading to a much higher relative error of ± 18 % for the ash determinations. Several of the recycle solvents were tested for ash, and each was found to contain no ash. This is expected since the recycle solvent is the distillate portion of the hydrogenation products. Therefore, any ash that may have been transferred into the THF soluble portion of the hydrogenation products would be concentrated in the pitch sample.

The ash contents of the pitch and insoluble fractions of the hydrogenation products are presented in Table 4.3 for each different solvent. The percent ash in all of the pitch products is at or less than 0.1 % signifying that they are all very pure products.

The ash content of the insoluble fraction has a wide range depending on the type of solvent that was used. This can be related to the solvent's ability to convert the organic material of the coal into soluble material. The solvents showing the higher coal conversions (Figure 4.3) also have the highest ash contents for the THF insolubles. As more coal is converted to soluble material the percentage of ash in the unconverted material (THF insoluble) would rise since it is based on the total organic material in the residue and not the coal. Reactions performed with DACL-L also produced the pitch with the highest ash content, but this could be due to the error in the ash analysis.

Table 4.3 Softening Point of Pitch and Ash Content of Pitch and THF Insoluble Fractions of Hydrogenation Products

Solvent	Pitch Softening Point (^oC)	% Ash in Pitch	% Ash in THF Insol.
DACL-L	129.0	0.110%	11.55%
DACL-H	126.5	0.025%	7.11%
RACL	120.2	0.009%	7.79%
HCO	119.4	0.019%	10.63%
CBB	126.9	0.093%	11.10%

4.6.2 Coke Yield

The coking value gives an indication of the amount of non-volatile matter in the pitch sample. The coke yield was determined according to the procedure described in Section 3.3.2. This characterization technique typically has a relative error of ± 2% so it is an accurate measurement. The coke yields of the pitches with a softening point of approximately 120 °C for each solvent-coal reaction are detailed in Figure 4.7. Each of these coke yields are in the range of 43.5 to 48 % by weight, which is slightly below the

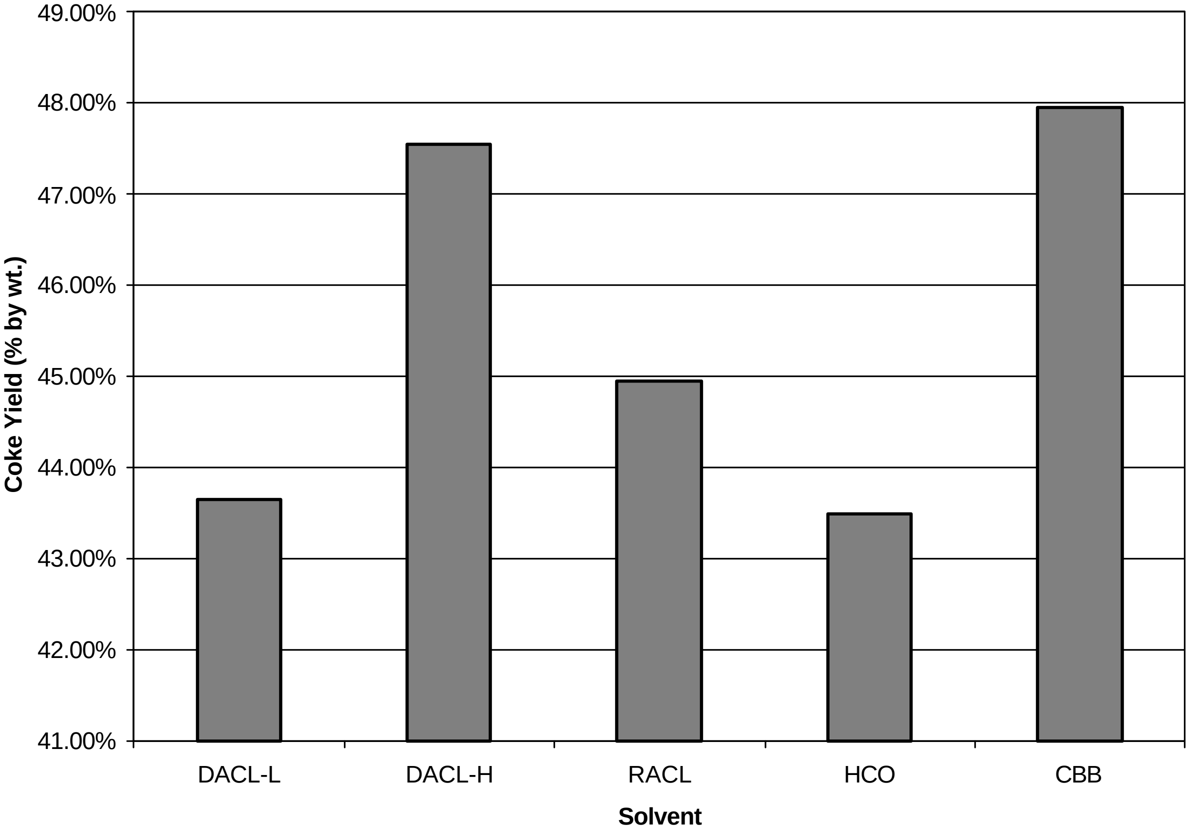


Figure 4.7 Effect of hydrogenation solvent on the coke yield of the pitches resulting from hydrogenation reactions with the conditions of 400 °C, 1000 psig H_2 (cold), 3/1 solvent-to-coal ratio, and 1 hour. Pitch softening point is around 120 °C.

desired value of commercial pitches (50 – 60 %). However, the difference in coke yields when compared by the various solvents is insignificant when factoring in the relative error of the test.

There are two possible ways of increasing the coke yield of the hydrogenation pitches. First, the desired softening point of the pitch could be increased. This would eliminate more of the light volatile compounds that are relinquished during the coking. The second possible way of increasing the coke yield of the pitch is to lower the solvent-to-coal ratio of the hydrogenation reactions assuming the coal conversion is the same at a lower solvent-to-coal ratio. This would reduce the amount of solvent in the final pitch product, thus increasing the coking value. The results of lowering the solvent-to-coal ratio are discussed in a later section. The effect of raising the softening point on the coke yield of the resultant pitch is illustrated by Figure 4.8. For all of the pitches shown, there is a linear dependence of coke yield on the pitch softening point. Furthermore, all of the pitches are in the same basic range on the graph except DACL-L derived pitches, which are shifted slightly to the right. This suggests that the pitch made from coal and DACL-L contains on average more volatile components, thus requiring greater distillation (leading to an increase in softening point) to increase the coke yield. In order to achieve a pitch with a coke yield of greater than 50 % by weight, Figure 4.8 shows that the softening point of the pitch needs to be at or above approximately 140 ºC.

4.6.3 Optical Texture

Once the coke samples were weighed and the coke yield was calculated, the coke sample was embedded in epoxy and polished for observation under the polarized-light microscope. This technique allowed for determination of the optical texture of the coke, which is extremely important in determining the end use of the carbon product precursor. The optical texture was determined according the procedure described in Section 3.3.4, and photographs were taken of all coke samples. A comprehensive collection of these pictures is given in Appendix B. Figure 4.9 shows cokes produced from the various pitches; the softening point of the pitches was approximately 120 ºC. All reaction conditions for these pitches were the same except for the choice of solvent.

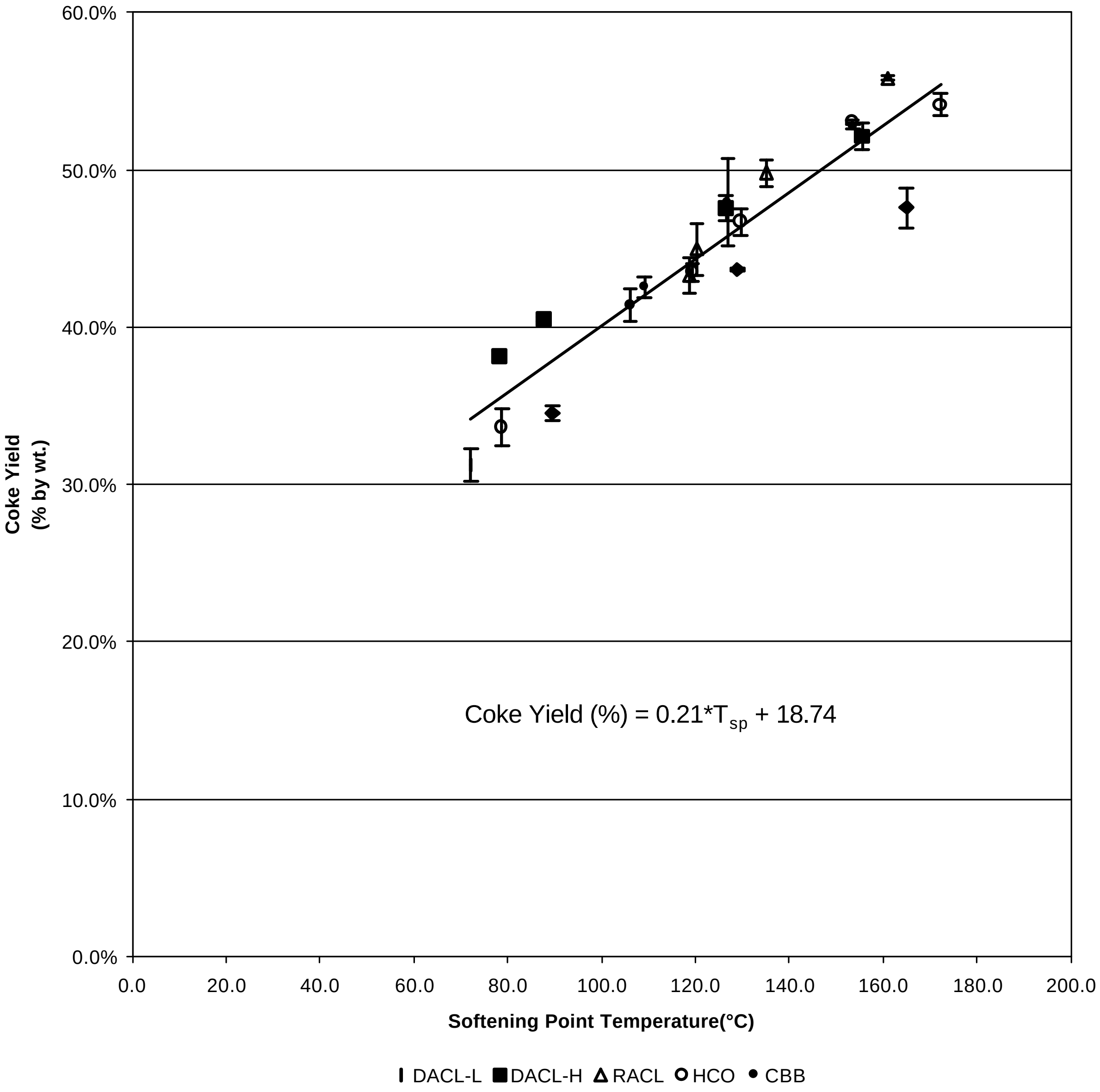
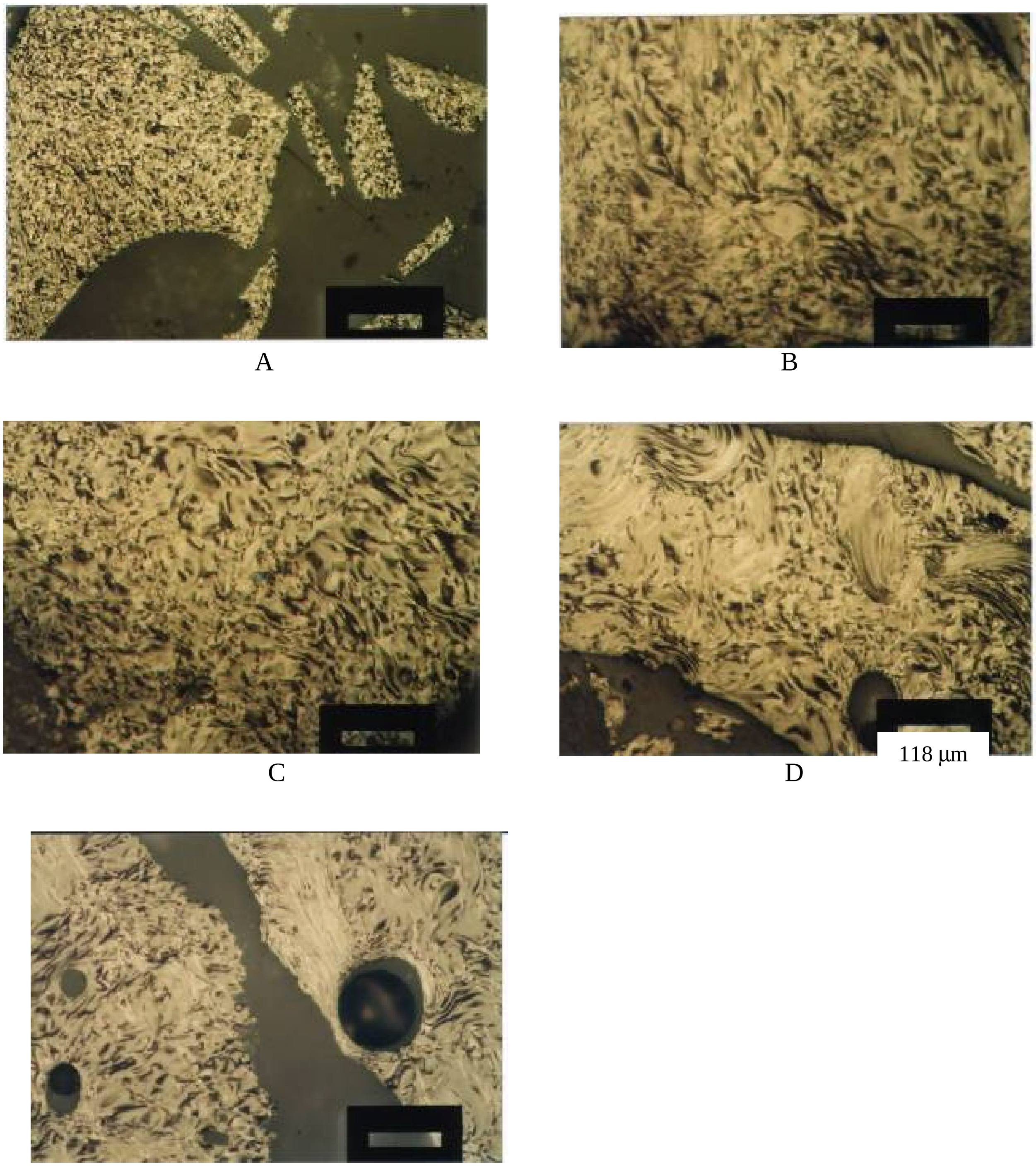


Figure 4.8 Effect of softening point on the coke yield of pitches made from hydrogenation reactions using the five different coal-derived solvents under reaction conditions of 400 °C, 1000 psig H_2 (cold), 3/1 solvent-to-coal ratio, and 1 hour



A

B

C

D

E

Figure 4.9 Optical micrographs of cokes produced from pitches (with softening points around 120 °C) using different solvents during hydrogenation reactions with conditions of 400 °C, 1000 psig H_2 (cold), 3/1 solvent-to-coal ratio, and 1 hour and solvents A) DACL-L, B) DACL-H, C) RACL, D) HCO, and E) CBB

Figure 4.9 shows that the optical texture for each of the cokes produced from hydrogenation reactions of coal and a coal-derived solvent were anisotropic. The major difference observed when comparing the solvents is in the domain size of the anisotropic cokes. The domains produced by using DACL-H and RACL (Figure 4.9 B and C, respectively) seem to be similar in size and are also fairly uniform throughout the sample. The cokes produced from HCO and CBB solvents (Figure 4.9 D and E, respectively) have areas of very large domains interspersed with areas of slightly smaller domains, similar to that of the cokes produced with DACL-H and RACL. The type of texture determines the possible end uses for the carbon product precursors. As mentioned previously in Section 2.3, the anisotropic coke is good for the production of graphite electrodes, while the isotropic coke is more suited to the production of nuclear graphite which requires a high purity and uniform dimensional stability.

4.6.4 Elemental Analysis

An elemental analysis was performed on a select group of pitches and their corresponding THF insoluble and recycle solvent fractions. The select pitches were again ones with a softening point of approximately 120 °C and from each different solvent. The elemental analysis was used to determine the amount of carbon, hydrogen, nitrogen, and sulfur in the sample according to the procedure outline in Section 3.3.5. The results of the elemental analysis for the carbon and hydrogen percentage in the samples are very accurate with relative errors of ± 2% for carbon and ± 5% for the hydrogen content. The error involved in determining the nitrogen and sulfur content in the samples is significantly larger due to the fact that the samples contain smaller amounts of these two elements compared to the carbon content. The relative error involved in determining the nitrogen and sulfur content is on the order of ± 20%. Therefore, further discussion on the elemental content of the hydrogenation reactants and products will only concern the carbon and hydrogen content.

The elemental composition and hydrogen-to-carbon atomic ratios of the selected hydrogenation products are shown in Table 4.4. The reaction conditions for each run can be seen in Table 3.3. For each set of hydrogenation products, some general trends can be observed. The hydrogen-to-carbon ratio increases for each hydrogenation run from the THF insolubles to the pitch fraction up to the recycle solvent. This is the expected result since the recycle solvent is the lightest component of the hydrogenation products corresponding to the highest hydrogen-to-carbon ratio. Also, the hydrogen-to-carbon atomic ratios for the recycle solvents have a higher value than that of the original solvent employed in the reaction. This indicates that some lighter material was being produced during the hydrogenation reaction. The carbon content of the product pitches are similar at a value of about 90% by weight. The THF insoluble fraction also does not show a significant difference in carbon (≈ 81%) and hydrogen (≈ 4%) content when comparing the different solvents used. However, the recovered recycle solvent does show a significant difference from one sample to another. The carbon content of the recycle solvents recovered from the reactions using HCO and CBB (93.9% and 90.7%, respectively) are higher than those produced using the other solvents (less than 85%). This can be attributed to the fact that the original solvents, HCO and CBB, have a higher carbon content than the other hydrogenation solvents.

The elemental analysis was also used to perform a carbon and hydrogen balance for each of the selected hydrogenation reactions. The results of the elemental balances can be seen in Table 4.5 and Table 4.6 for carbon and hydrogen, respectively. The carbon balance shows a negative balance for all of the selected runs. This is consistent with the negative mass balance that was observed during each of these runs. Since carbon is by far the most abundant element in all of the reaction species, any loss of mass would correspond to a significant loss in elemental carbon causing the observed negative carbon balances. The hydrogen balances shown in Table 4.6 also show a negative hydrogen balance for each of the selected runs. This also corresponds to a negative mass balance. However, a positive hydrogen balance could have been expected from examining the transient reactor pressure for each reaction (see Figure 4.4). It showed that hydrogen was being consumed by the hydrogenation reactants throughout the thermal

Table 4.4 Elemental Composition of Select Hydrogenation Products

Run	Element	Original Solvent	Product Fraction		
			Pitch	THF Insoluble	Recycle Solvent
1A	C	80.51 %	86.80%	82.52%	82.62%
	H	7.74 %	6.16%	4.18%	8.21%
	N	0.94 %	1.22%	1.53%	0.87%
	S	0.61 %	0.67%	0.91%	0.19%
	H/C Atomic Ratio	1.15	0.85	0.61	1.19
2C	C	88.51 %	89.70%	83.08%	85.60%
	H	5.72 %	5.62%	4.15%	7.25%
	N	1.25 %	1.68%	2.02%	1.48%
	S	0.76 %	0.66%	0.85%	0.57%
	H/C Atomic Ratio	0.78	0.75	0.60	1.02
3B	C	86.67 %	90.53%	80.72%	81.86%
	H	6.76 %	5.83%	4.55%	8.44%
	N	1.22 %	1.29%	2.19%	1.87%
	S	0.72 %	0.73%	0.92%	0.67%
	H/C Atomic Ratio	0.94	0.77	0.68	1.24
4C	C	93.41 %	91.16%	79.02%	93.90%
	H	5.14 %	5.31%	3.96%	5.23%
	N	0.88 %	1.45%	1.42%	0.93%
	S	0.55 %	0.71%	0.96%	0.48%
	H/C Atomic Ratio	0.66	0.70	0.60	0.67
5B	C	91.85 %	89.75%	79.17%	90.73%
	H	5.51 %	5.14%	3.97%	5.79%
	N	0.81 %	1.15%	0.86%	0.89%
	S	0.67 %	0.63%	0.94%	0.69%
	H/C Atomic Ratio	0.72	0.69	0.60	0.77

Table 4.5 Elemental Carbon Balance for Hydrogenation Reactants and Products for Selected Runs

Run	Trial	Carbon In Coal (g)	Carbon In Solv. (g)	Total Carbon In (g)	Carbon Out Pitch (g)	Carbon Out THF Ins. (g)	Carbon Out Rec. Solv. (g)	Total Carbon Out (g)	Out - In (g)	(Out-In)/In (%)
1	A	6.8381	20.2105	27.0486	7.3812	3.8101	13.7776	24.9690	-2.0796	-7.7
2	C	4.8960	15.9325	20.8285	11.4446	5.6568	1.7034	18.8048	-2.0237	-9.7
3	B	6.2449	19.8992	26.1441	10.4227	5.8113	7.9482	24.1822	-1.9619	-7.5
4	C	7.1860	24.7083	31.8944	6.9261	4.9389	16.1406	28.0056	-3.8888	-12.2
5	B	7.3079	24.6799	31.9878	6.4201	5.6164	18.7533	30.7898	-1.1980	-3.7

Table 4.6 Elemental Hydrogen Balance for Hydrogenation Reactants and Products for Selected Runs

Run	Trial	Hydrogen in Coal (g)	Hydrogen in Solv. (g)	Total Hydrogen In (g)	Hydrogen Out Pitch (g)	Hydrogen Out THF Ins. (g)	Hydrogen Out Rec. Solv. (g)	Total Hydrogen Out (g)	Out - In (g)	(Out-In)In (%)
1	A	0.3825	1.9426	2.3251	0.5236	0.1928	1.3695	2.0859	-0.2391	-10.3
2	C	0.2739	1.0299	1.3038	0.7168	0.2826	0.1442	1.1436	-0.1602	-12.3
3	B	0.3493	1.5525	1.9019	0.6717	0.3274	0.8198	1.8190	-0.0829	-4.4
4	C	0.4020	1.3614	1.7633	0.4031	0.2477	0.9109	1.5617	-0.2017	-11.4
5	B	0.4088	1.4804	1.8892	0.3676	0.2817	1.1972	1.8464	-0.0428	-2.3

treatment process. Since hydrogen was being consumed, one might expect an increase in the total hydrogen out of the hydrogenation reactions. However, by examining the different causes for error in the mass balance calculation, the explanation of a negative hydrogen balance becomes apparent. The two major causes for loss of mass throughout these reactions were the fact that the product gas was not quantified and the loss of light material during THF removal and vacuum distillation. Both of these mass losses involve the loss of the lightest products which are produced by the hydrogenation reactions. These light materials would have been the significantly more hydrogen-rich products of the reactions. Because these materials are the ones that are unaccounted for in the mass balance calculation and elemental analysis, a negative hydrogen balance unfortunately occurs.

4.7 Variation of Hydrogenation Parameters

In order to understand further how the hydrogenation conditions would affect the final products, three of the reaction conditions were altered. The pressure, gaseous atmosphere, and solvent-to-coal ratio were all varied in reactions six (6) through twelve (12). The initial hydrogen pressure was lowered from 1000 psig to 500 psig and finally to 100 psig in runs five (5), seven (7), nine (9). Hydrogenation reactions with these same pressures but under an argon atmosphere were performed in runs six (6), eight (8), and ten (10). Finally, the solvent-to-coal ratio was lowered from 3/1 to 2/1 down to 1/1 by weight in reactions four (4), eleven (11), and twelve (12). All other conditions for these reactions were kept constant and can be seen in Table 3.3.

4.7.1 Effect of Pressure and Atmosphere

Reactions five (5) through ten (10) were performed to determine the effect of lowering the initial pressure and employing an inert atmosphere instead of hydrogen on the conversion, product distribution, and pitch characteristics. Each reaction was performed with the CBB solvent, at a temperature of 400 °C, a solvent-to-coal ratio of 3/1, and run for one hour. The CBB solvent was used for these experiments rather than

DACL-L, which showed a higher conversion (both types), because it is a commercially-available material and could be used as is. The Antaeus liquid is not currently available commercially. Each set of reaction conditions was run four times and separated into different softening point pitches by vacuum distillation. Again, a target softening point of 120 °C was desired though not always achieved.

Figure 4.10 shows the effect of increasing the reaction pressure and changing the atmosphere on the overall conversion, while Figure 4.11 depicts the same effect on the coal-alone conversion of the hydrogenation reactions. As the pressure is increased, regardless of the gaseous atmosphere, both the overall and coal-alone conversions increase. However, the overall conversion actually only increases 3% from pressures of 100 psig to 1000 psig hydrogen and only 2% for the same increase in argon pressure. This is an insignificant increase when considering a ten fold increase in pressure was required. The effect of increasing the gas pressure on the overall conversion is masked due to the low amount of coal compared to solvent charged to the reactors. This becomes evident when the effect of gas pressure on the coal-alone conversion is investigated in Figure 4.11. When hydrogen gas is employed the coal-alone conversion increases from 7% to 23% when the pressure is raised from 100 psig to 1000 psig. This is a much more significant increase than that shown in Figure 4.10 for the overall conversion. The coal-alone conversion also increases (6% to 12%) when argon pressure is raised from 100 to 1000 psig, however, not as significantly. This shows that when hydrogen gas is being used in the hydrogenation reaction, it is beneficial to the reaction of coal to soluble products.

Another way of illustrating the use of gaseous hydrogen in the hydrogenation reactions is to compare the reactor pressures during the thermal treatment when the same initial pressures are employed with hydrogen and argon atmospheres. These results are depicted in Figures 4.12, 4.13 and 4.14 for the initial reaction pressures of 1000, 500, and 100 psig, respectively. It is interesting to note that when the initial pressures were either 1000 or 500 psig (Figures 4.12 and 4.13), the hydrogen charged reactors decreased in

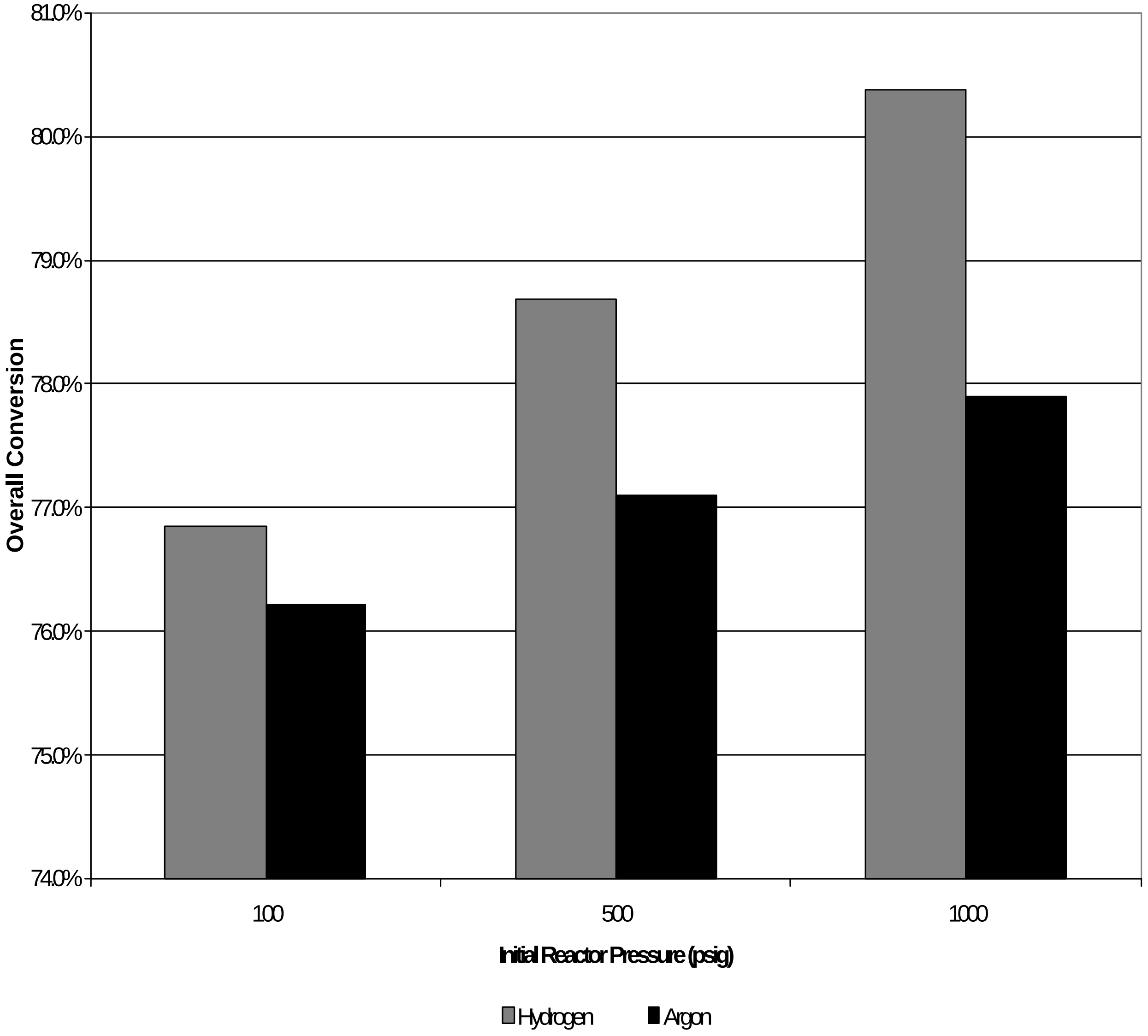


Figure 4.10 Effect of initial reactor pressure and gaseous atmosphere on the overall conversion of hydrogenation reactions with CBB and reaction conditions of 400 °C, 3/1 solvent-to-coal ratio, and 1 hour

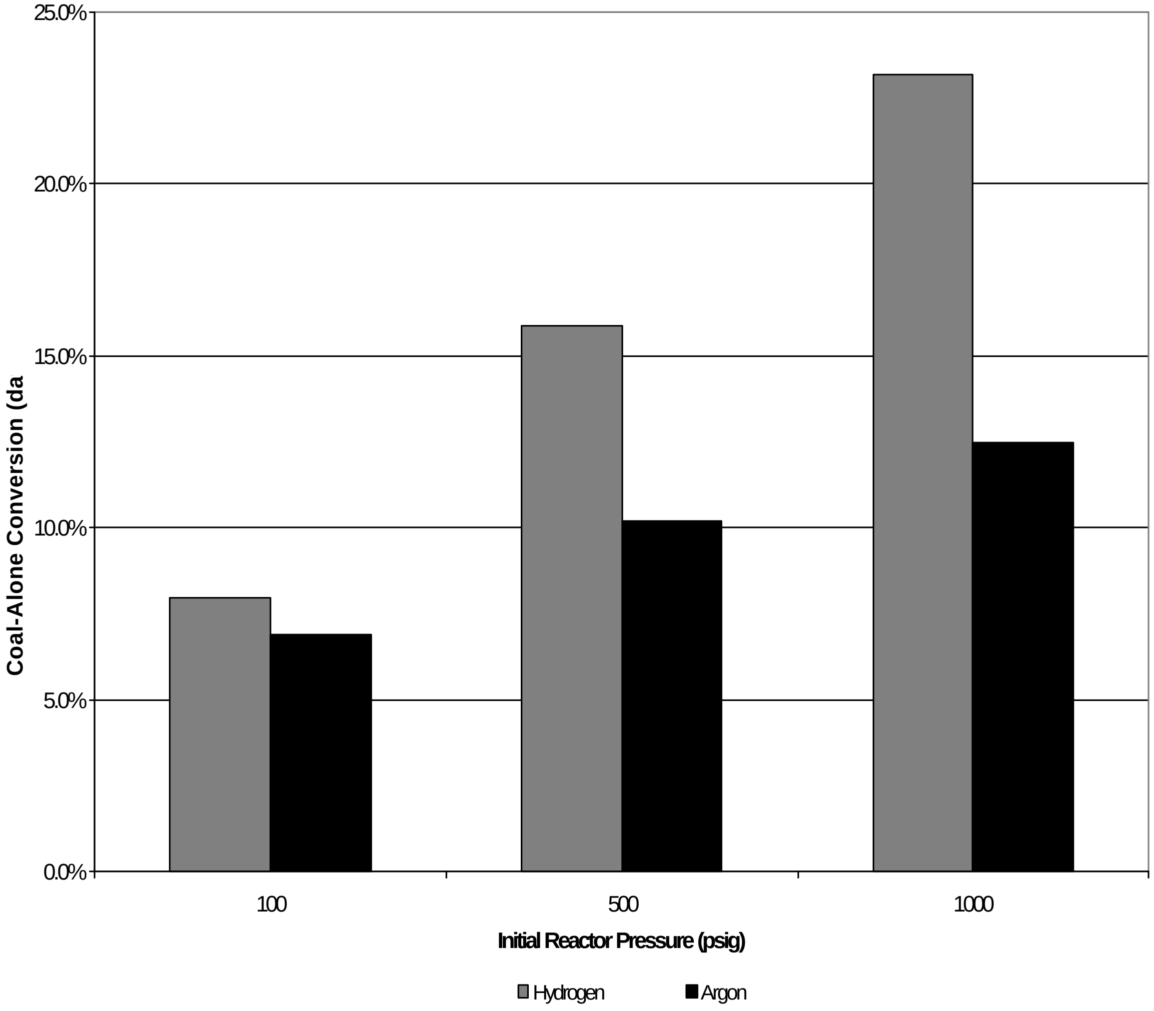


Figure 4.11 Effect of initial reactor pressure and gaseous atmosphere on the coal-alone conversion of hydrogenation reactions with CBB and reaction conditions of 400 °C, 3/1 solvent-to-coal ratio, and 1 hour

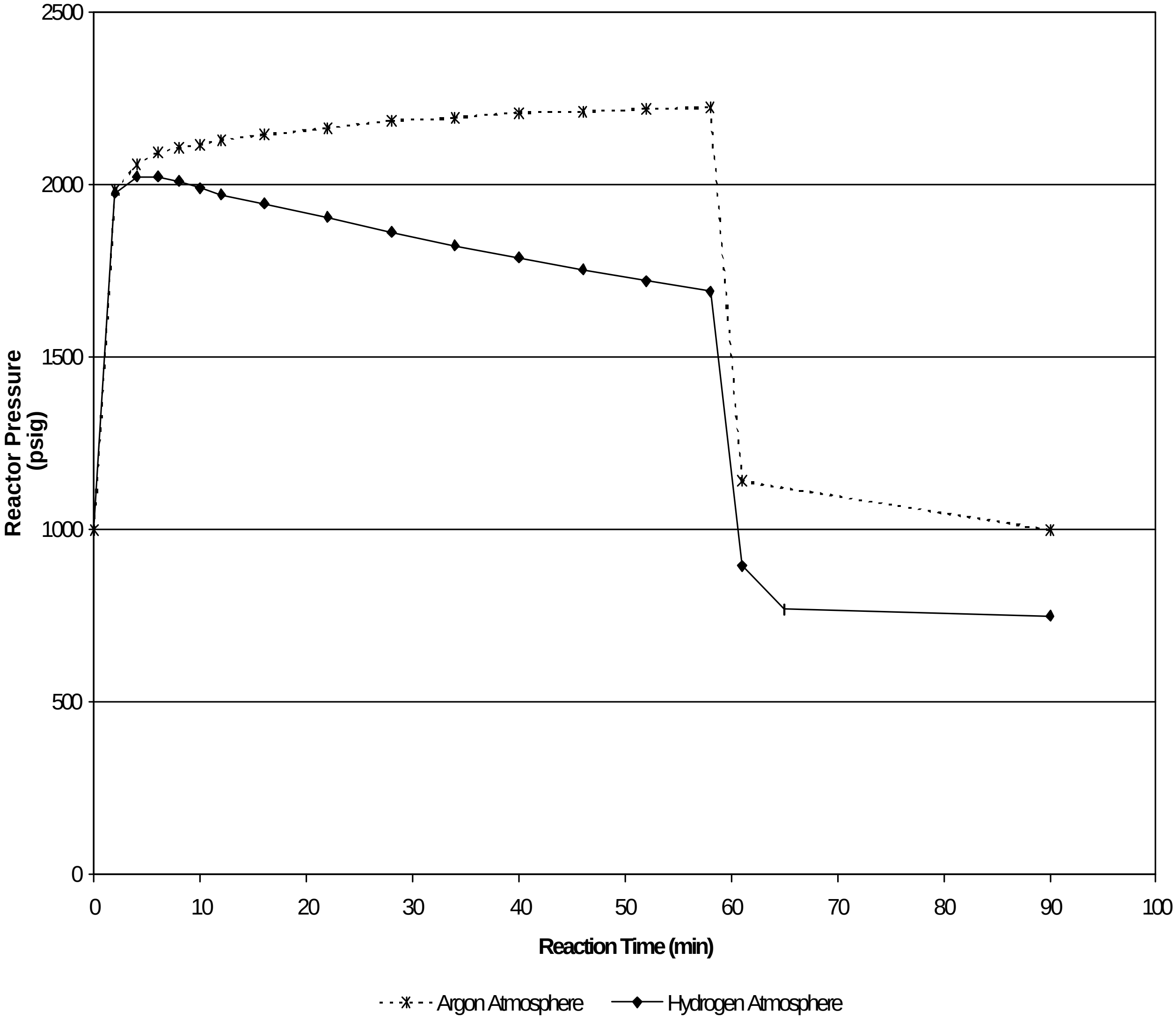


Figure 4.12 Average reactor pressures over time of hydrogenation reactions using CBB, 1000 psig initial hydrogen or argon pressure, 400 °C, 3/1 solvent-to-coal ratio, and 1 hour

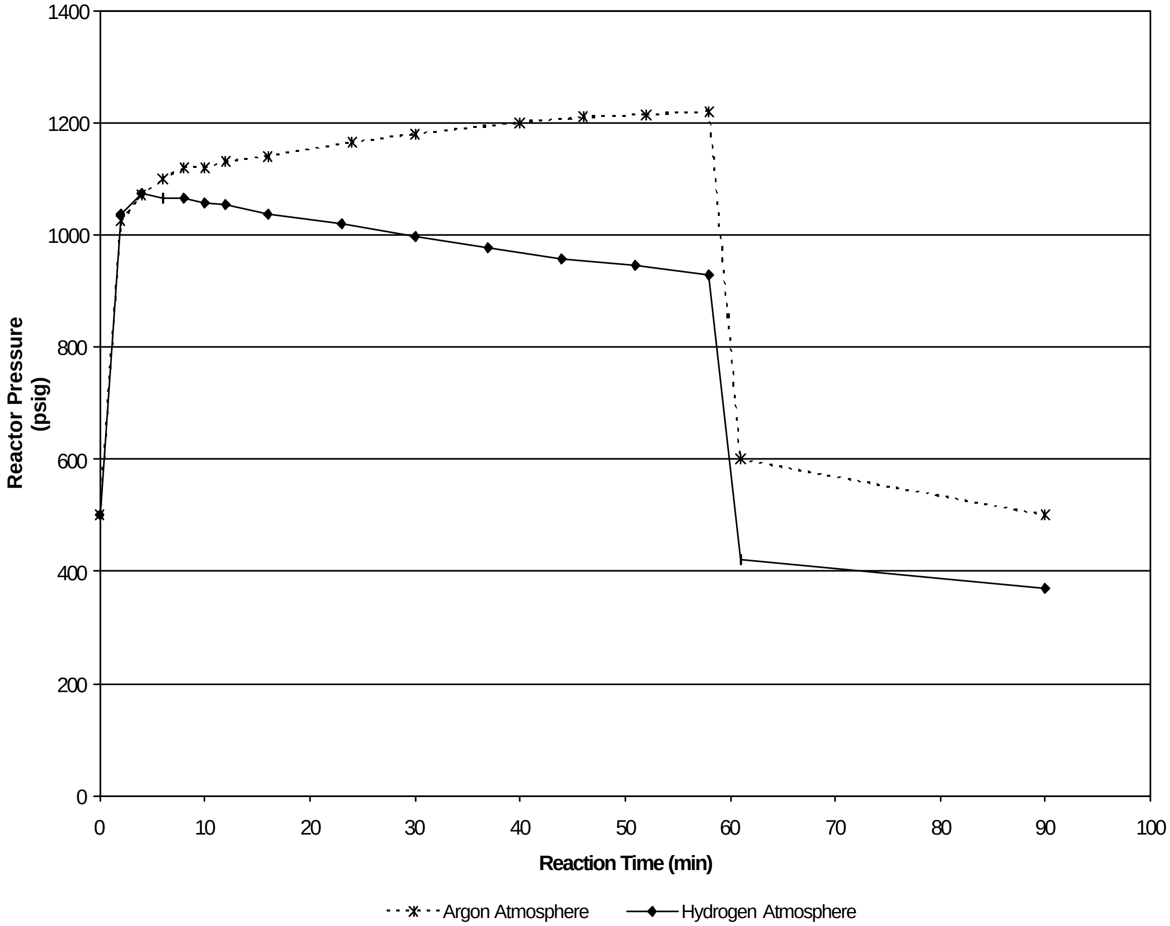


Figure 4.13 Average reactor pressures over time of hydrogenation reactions using CBB, 500 psig initial hydrogen or argon pressure, 400 °C, 3/1 solvent-to-coal ratio, and 1 hour

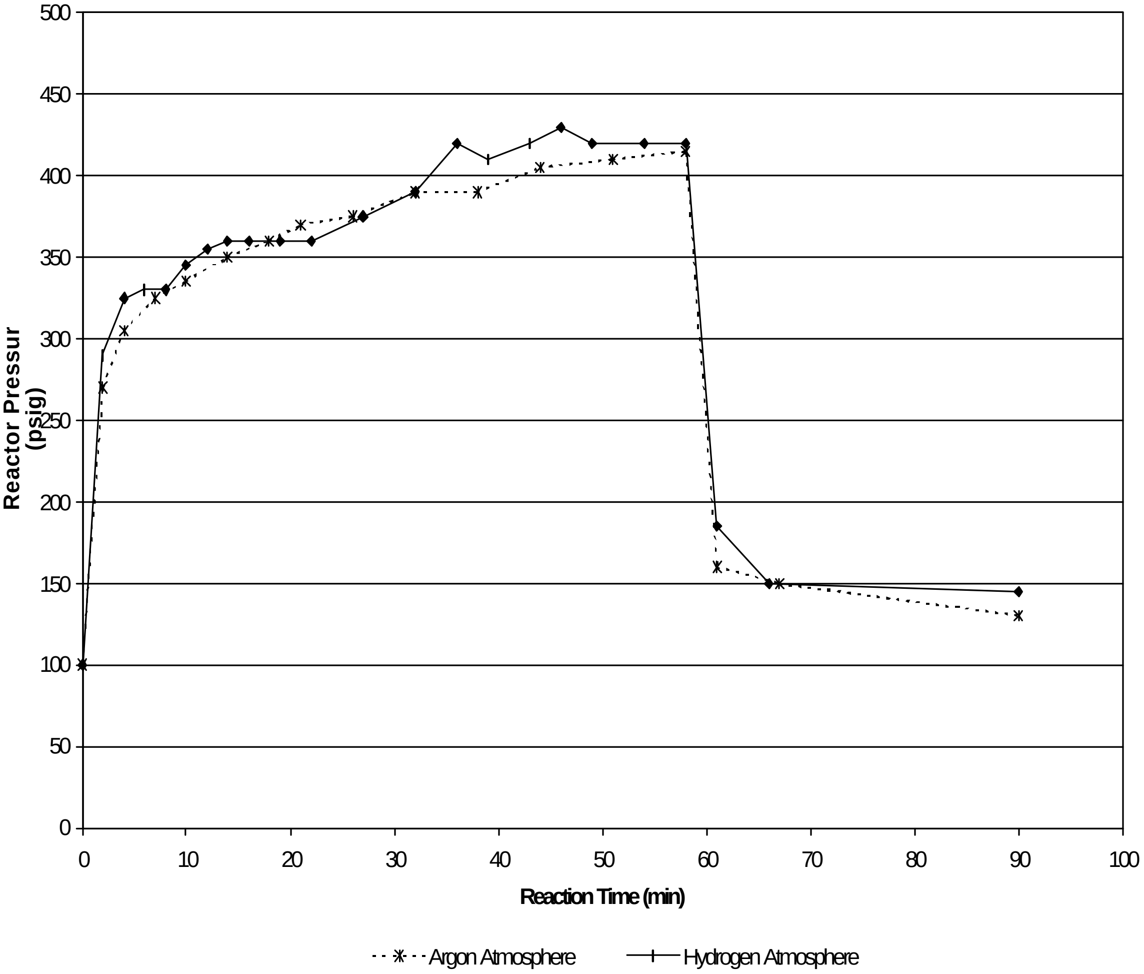


Figure 4.14 Average reactor pressures over time of hydrogenation reactions using CBB, 100 psig initial hydrogen or argon pressure, 400 °C, 3/1 solvent-to-coal ratio, and 1 hour

pressure over time, while the argon charged reactors continued to increase in pressure throughout the reaction time. The decrease in pressure in the hydrogen charged reactions was again due to the fact that the hydrogen was consumed by hydrogenating either transient coal radicals and/or the solvent. By comparing the initial and final pressures of the reactions performed under a hydrogen atmosphere, an estimation of the amount of hydrogen consumed can be made. The hydrogen consumed for the reactions with 1000 psig initial hydrogen pressure was approximately 0.04 moles of hydrogen or 0.2 % of the reaction feed mass. The hydrogen consumed for the reactions with 500 psig initial hydrogen pressure was approximately 0.02 moles of hydrogen or 0.1 % of the reaction feed mass. The increase in pressure during the argon charged reactions is from the production of gas. However, this gas most likely condensed when the reaction was quenched and cooled, as evidenced by the fact that the final reactor pressure was equal to the initial reactor pressure. This does not mean, however, that no product gases were formed during the hydrogen charged reactions -- only that the amount of gas production inside the reactor was less than the amount of hydrogen consumption. This would lead to the net decrease in reactor pressure observed when hydrogen was used in both Figures 4.12 and 4.13.

Figure 4.14 shows a different trend with the lower initial pressure of 100 psig. Both the hydrogen and argon charged reactors increase in pressure over time. Therefore, gas was being produced throughout both sets of reactions. This time in the hydrogen charged reactor, however, the rate of gas production was greater than the rate of hydrogen gas consumption. This explanation is further justified by comparing the initial and final pressures in the reactors. For both systems, the final pressure is greater than the initial pressure, signifying a net production in gas and less hydrogen reacted at 100 psig.

The effect of changing the initial reactor pressure and atmosphere on the product distribution is illustrated in Figure 4.15. The distributions shown represent the products thus formed when a pitch with a softening point in the proximity of 120 ºC was obtained. For both the argon and hydrogen charged reactions, as the pressure is increased the amount of THF insolubles decreased slightly from 23% to 21% for argon reactions and

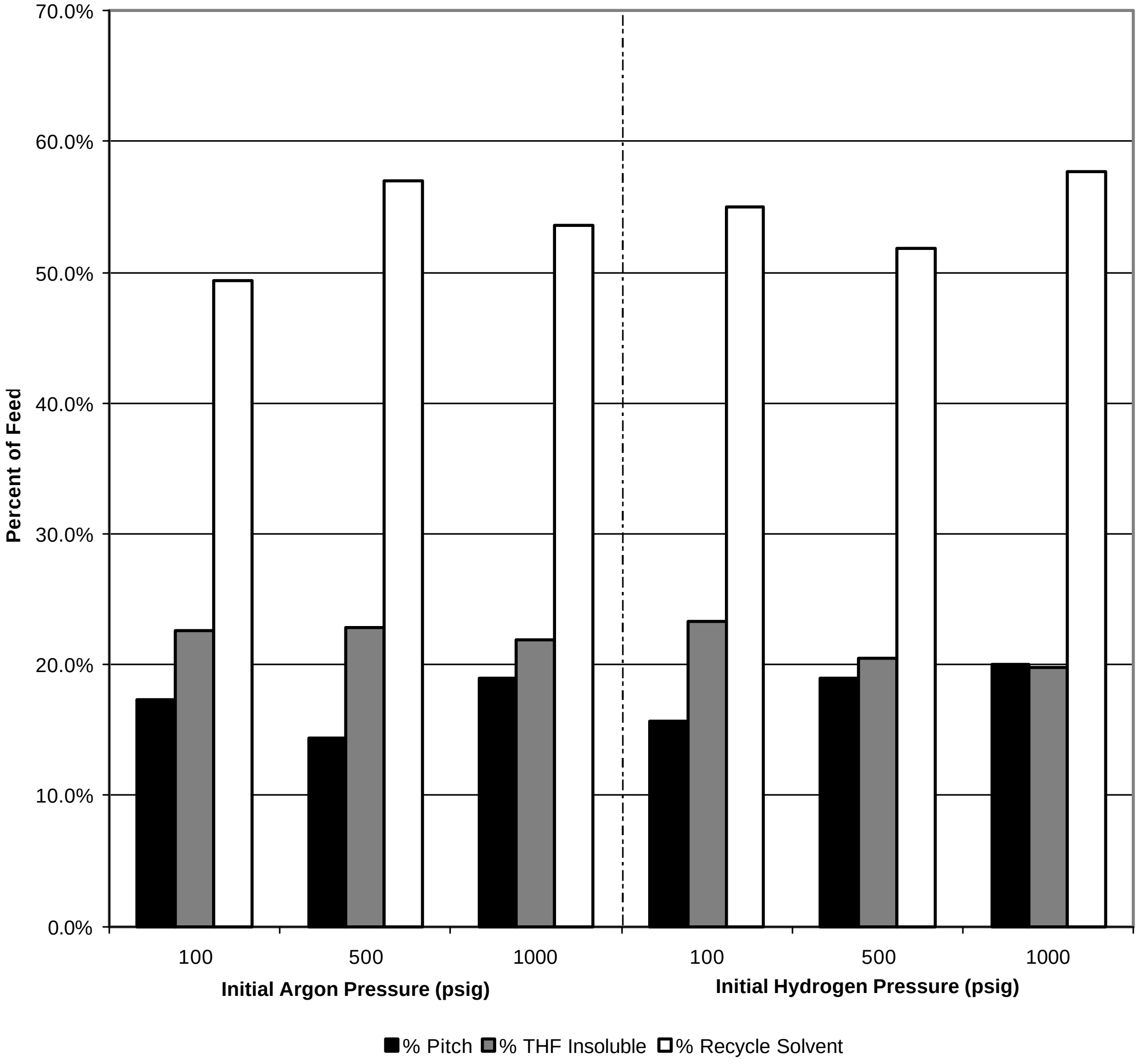


Figure 4.15 Effect of initial reactor pressure and atmosphere on the product distribution of reactions run to produce a pitch with a softening point of 120 ºC under reaction conditions of CBB solvent, 400 ºC, 3/1 solvent-to-coal ratio, and 1 hour

23.5 to 20% for hydrogen reactions. This is directly responsible for the increase in both the overall and coal-alone conversions as more coal is reacted. The percent of pitch and recycle solvent recovered from the feed seems to be fairly constant when experimental error is considered. The percent of pitch obtained with a hydrogen atmosphere increased slightly (from 16% to 20%) as the initial reactor pressure increased. This could be attributed to the increase of coal conversion when the hydrogen pressure was increased. The percent of pitch obtained from the feed when using an argon atmosphere does not show such a trend. The percent of feed going to pitch did increase from 100 psig initial argon pressure to 1000 psig initial argon pressure, but a dip was observed when 500 psig initial argon pressure was employed. This dip can be attributed to overshooting the desired softening point of 120 ºC. The pitches obtained when using 100 and 1000 psig initial argon pressure had average softening points of 120.3 and 119.3 ºC, respectively. The pitch obtained from the reaction charged with 500 psig initial argon pressure was distilled to an average softening point of 132.5 ºC (due to an error in distillation). This increase in softening point corresponds to a smaller amount of pitch produced due to more recycle solvent being removed during distillation. This could explain the dip in the pitch production shown at 500 psig initial argon pressure in Figure 4.15.

After separating the hydrogenation products into the fractions shown in Figure 4.15, the effect of the pressure and atmosphere on the pitch characteristics was studied. The selected pitches with a softening point in the area of 120 ºC (from 119.3 to 132.5 ºC) were characterized by ash content, coke yield, optical microscopy, and elemental analysis (the corresponding insoluble and recycle solvent fractions were also characterized by elemental analysis). The results of the ash test for the selected pitches and THF insoluble fraction are shown in Table 4.7. As described previously in Section 4.6.1, the ash content of the THF insoluble fraction varies with the conversion of hydrogenation reactants to soluble products. The highest ash content corresponds to the highest conversion (1000 psig Hydrogen initially) due to the decreased amount of organic material left in the THF insoluble fraction. The ash varies randomly from pitch to pitch but is always at a very low value (below 0.1%). This is important because the ash content is considered an impurity in the development of carbon products.

Table 4.7 Ash content of pitch and THF insoluble fractions of pitch produced while varying the initial reactor pressure and gaseous atmosphere

Run	Trial	Initial Reactor Pressure (psig)	Gas	Pitch Average Softening Point (^{o}C)	% Ash in Pitch	% Ash in THF Insoluble	% Pitch Recovered
5	B	1000	Hydrogen	126.9	0.093%	11.10%	20.0 %
6	D	1000	Argon	119.3	0.041%	7.95%	18.9 %
7	A	500	Hydrogen	113.2	0.037%	10.15%	18.9 %
8	D	500	Argon	132.5	0.017%	7.86%	14.4 %
9	B	100	Hydrogen	123.6	0.035%	8.47%	15.6 %
10	D	100	Argon	120.3	0.108%	7.91%	17.3 %

The coke yield of the selected pitches was also determined. However, because the coke yield is very dependent on the softening point of the pitch (as shown earlier by Figure 4.8) and some of the selected pitches (7A and 8D) have softening points that deviate greatly from the target of 120 ºC, a plot of coke yield versus softening point is used to evaluate the effect of pressure and atmosphere on the pitches' coke yield. This plot is shown in Figure 4.16. The coke yield shows little dependence on the hydrogenation reaction conditions of gas composition and pressure. However, it does depend significantly on the softening point of the pitch. From this plot, it can be determined that a pitch with a softening point of 120 ºC would have a coke yield of approximately 45% by weight. In order to achieve a coke yield of 50% by weight, the softening point would have to be increased to approximately 145 ºC, and to reach a coke yield of 60% by weight, a softening point of greater than 180 ºC would be required.

Once the coke samples have been formed, the optical texture can be investigated by optical microscopy. Photographs were taken of every coke that was formed to produce the data shown in Figure 4.16 and can be seen in Appendix B. The micrographs

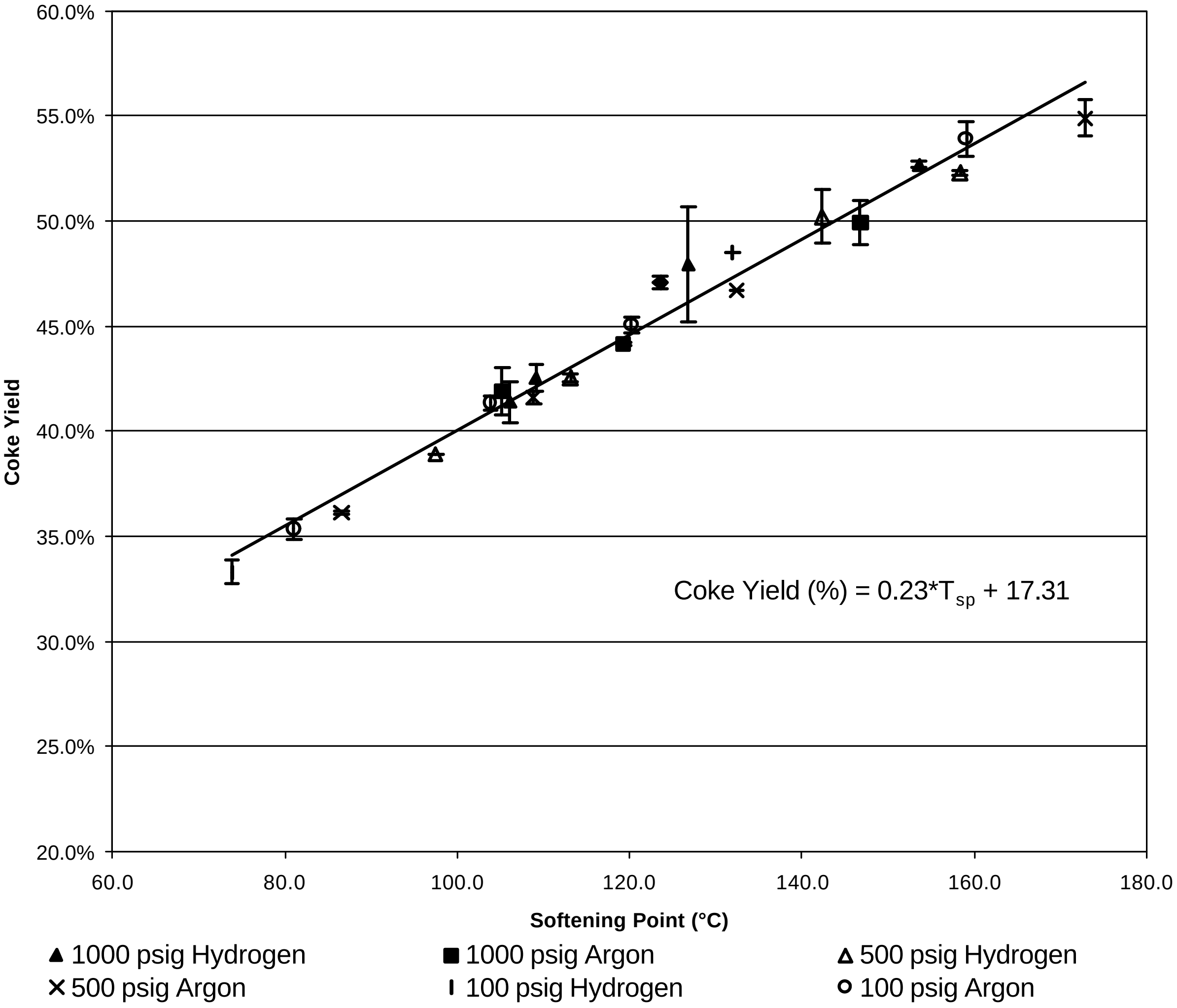


Figure 4.16 Effect of raising the softening point of pitches produced under different atmospheres and initial reaction pressures on the coke yield with reaction conditions of CBB solvent, 400 ºC, 3/1 solvent-to-coal ratio, 1 hour

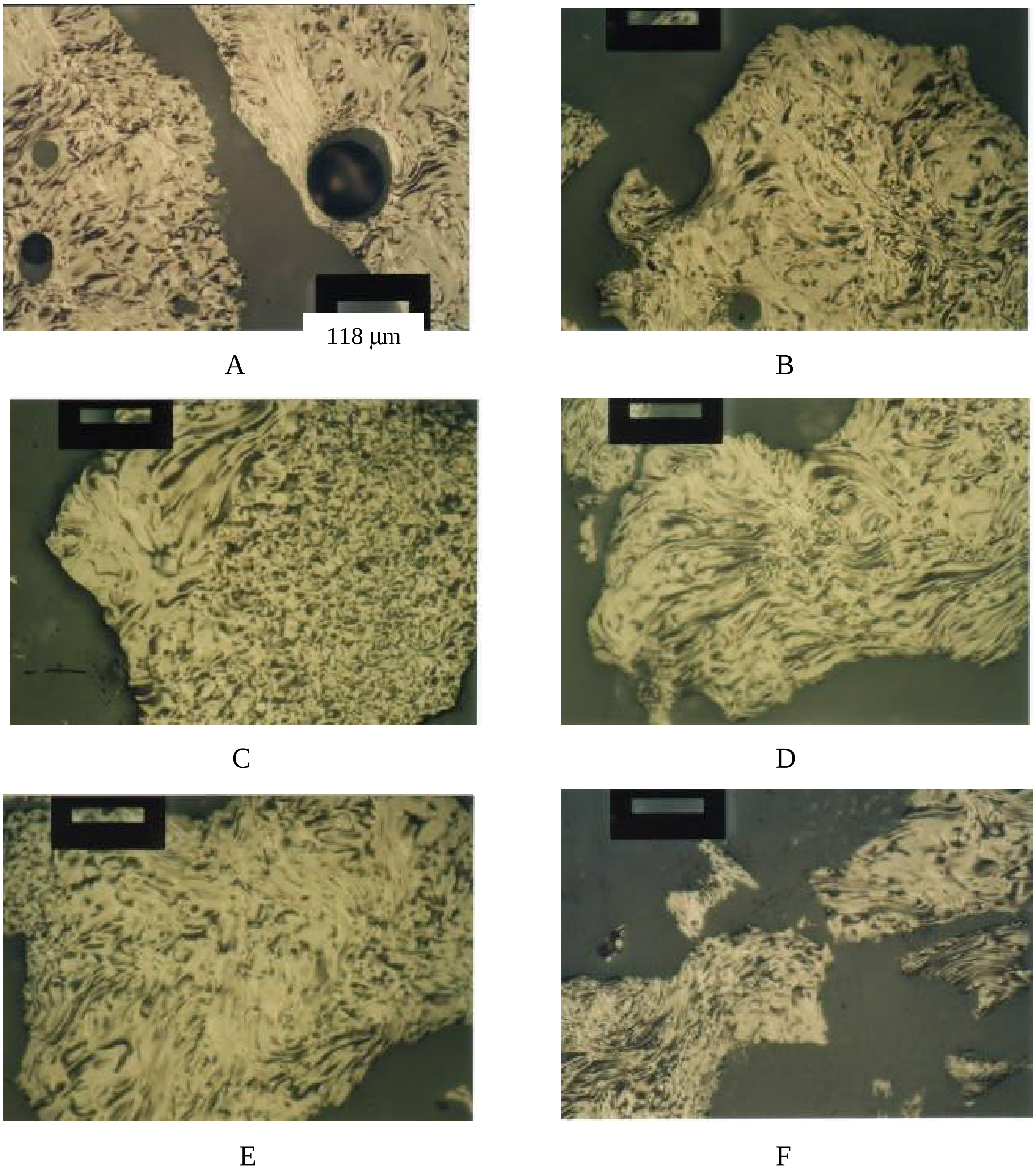


Figure 4.17 Optical micrographs of cokes produced from select pitches derived from hydrogenation products from reactions (CBB solvent, 400 ºC, 3/1 solvent-to-coal ratio, 1 hour) with varying initial pressures and atmospheres, A) 1000 psig Hydrogen, B) 1000 psig Argon, C) 500 psig Hydrogen, D) 500 psig Argon, E) 100 psig Hydrogen, and F) 100 psig Argon

of cokes produced from the pitches with a softening point close to 120 ºC (the same ones shown in Table 4.7) are shown in Figure 4.17. Each of these represents a different hydrogenation pressure and atmosphere. Each coke sample has an anisotropic texture with the domain sizes differing depending on the reaction condition used. However, there does not seem to be a direct correlation between the domain sizes in the cokes and the hydrogenation pressure or atmosphere. Therefore, high hydrogen pressures are not required to make anisotropic coke. This is an important result since high pressures and hydrogen incur higher operational costs and hazards.

The final characterization that was carried out on these hydrogenation products was an elemental analysis. This was done according to the procedure described in Section 3.3.5. The results of the elemental analysis for the three product fractions are shown in Table 4.8 and were also used to calculate a carbon and hydrogen balance (shown in Tables 4.9 and 4.10, respectively). Table 4.8 shows that the elemental composition of each product fraction is approximately equal (within experimental error) for each hydrogenation run, regardless of the initial pressure and atmosphere. This could be due to the low conversions achieved which lead to a significant amount of original solvent left in the pitch fraction. Table 4.9 and Table 4.10 reveal a negative carbon and hydrogen balance for the selected hydrogenation reactions. This deviation can be attributed to depending on the mass balance to calculate the carbon and hydrogen balances. The reason for these errors is similar to that described for the previous carbon and hydrogen balances in Section 4.6.4. However, it is important to note that the hydrogen balance is more accurate for the runs with added hydrogen pressure than those with argon. This indicates that more hydrogen was being added when hydrogen was employed as the gas phase.

4.7.2 Effect of Solvent-to-Coal Ratio

Thus far, the carbon product precursors (pitches) have had a very desirable ash content and optical texture, but the coke yield for the pitches with a softening point in an acceptable range of the target has been below desired levels. The effect of raising the

Table 4.8 Elemental composition of select pitches produced from hydrogenation reactions (CBB solvent, 400 ºC, 3/1 solvent-to-coal ratio, 1 hour) with different initial pressures and atmospheres: 5B) 1000 psig Hydrogen, 6D) 1000 psig Argon, 7A) 500 psig Hydrogen, 8D) 500 psig Argon, 9B) 100 psig Hydrogen, and 10D) 100 psig Argon

Run (Initial Pressure psig)	Element	Original Solvent CBB	Product Fraction		
			Pitch	THF Insoluble	Recycle Solvent
5B (1000 H_2)	C	91.85 %	89.75%	79.17%	90.73%
	H	5.14 %	5.14%	3.97%	5.79%
	N	0.88 %	1.15%	0.86%	0.89%
	S	0.55 %	0.63%	0.94%	0.69%
	H/C Atomic Ratio	0.66	0.69	0.60	0.77
6D (1000 Ar)	C	91.85 %	91.42%	82.60%	92.89%
	H	5.14 %	5.31%	3.91%	5.51%
	N	0.88 %	1.29%	1.08%	0.45%
	S	0.55 %	0.84%	0.78%	0.78%
	H/C Atomic Ratio	0.66	0.70	0.57	0.71
7A (500 H_2)	C	91.85 %	91.51%	82.49%	91.26%
	H	5.14 %	5.27%	4.09%	5.75%
	N	0.88 %	1.68%	1.24%	0.01%
	S	0.55 %	0.77%	0.88%	0.63%
	H/C Atomic Ratio	0.66	0.69	0.59	0.76
8D (500 Ar)	C	91.85 %	92.50%	81.41%	89.59%
	H	5.14 %	5.04%	4.21%	5.27%
	N	0.88 %	1.73%	1.92%	0.59%
	S	0.55 %	0.79%	0.81%	0.76%
	H/C Atomic Ratio	0.66	0.65	0.62	0.71
9B (100 H_2)	C	91.85 %	91.55%	82.22%	92.09%
	H	5.14 %	5.19%	4.08%	5.80%
	N	0.88 %	1.12%	1.30%	0.87%
	S	0.55 %	0.69%	0.84%	0.61%
	H/C Atomic Ratio	0.66	0.68	0.60	0.76
10D (100 Ar)	C	91.85 %	89.04%	82.02%	89.58%
	H	5.14 %	5.07%	4.19%	5.47%
	N	0.88 %	1.51%	1.20%	0.77%
	S	0.55 %	0.80%	0.64%	0.46%
	H/C Atomic Ratio	0.66	0.68	0.61	0.73

Table 4.9 Carbon balance of select pitches produced from hydrogenation reactions with different initial pressures and atmospheres: 5B) 1000 psig Hydrogen, 6D) 1000 psig Argon, 7A) 500 psig Hydrogen, 8D) 500 psig Argon, 9B) 100 psig Hydrogen, and 10D) 100 psig Argon

Run	Trial	Carbon In Coal (g)	Carbon In Solv. (g)	Total Carbon In (g)	Carbon Out Pitch (g)	Carbon Out THF Ins. (g)	Carbon Out Rec. Solv. (g)	Total Carbon Out (g)	Out - In (g)	(Out-In)/In (%)
5	B	7.3079	24.6799	31.9878	6.4201	5.6164	18.7533	30.7898	-1.1980	-3.7
6	D	7.2931	24.6307	31.9238	5.9574	6.4492	17.8073	30.2139	-1.7099	-5.4
7	A	6.9826	23.5819	30.5646	5.9244	5.7824	16.1809	27.8877	-2.6768	-8.8
8	D	7.0193	23.7043	30.7236	4.5702	6.3890	17.5604	28.5195	-2.2041	-7.2
9	B	7.0901	23.9469	31.0369	4.9749	6.6739	17.5893	29.2381	-1.7989	-5.8
10	D	7.2111	24.3504	31.5614	5.4455	6.5388	15.6412	27.6255	-3.9359	-12.5

Table 4.10 Hydrogen balance of select pitches produced from hydrogenation reactions with different initial pressures and atmospheres: 5B) 1000 psig Hydrogen, 6D) 1000 psig Argon, 7A) 500 psig Hydrogen, 8D) 500 psig Argon, 9B) 100 psig Hydrogen, and 10D) 100 psig Argon

Run	Trial	Hydrogen in Coal (g)	Hydrogen in Solv. (g)	Total Hydrogen In (g)	Hydrogen Out Pitch (g)	Hydrogen Out THF Ins. (g)	Hydrogen Out Rec. Solv. (g)	Total Hydrogen Out (g)	Out - In (g)	(Out-In)In (%)
5	B	0.4088	1.4804	1.8892	0.3676	0.2817	1.1972	1.8464	-0.0428	-2.3
6	D	0.4080	1.4775	1.8854	0.3461	0.3056	1.0562	1.7080	-0.1775	-9.4
7	A	0.3906	1.4146	1.8052	0.3415	0.2866	1.0201	1.6482	-0.1570	-8.7
8	D	0.3927	1.4219	1.8146	0.2691	0.3302	1.0323	1.6317	-0.1829	-10.1
9	B	0.3966	1.4364	1.8331	0.2822	0.3310	1.1074	1.7206	-0.1124	-6.1
10	D	0.4034	1.4607	1.8640	0.3099	0.3341	0.9551	1.5991	-0.2650	-14.2

softening point in order to achieve a higher coke yield has been thoroughly discussed in Section 4.6.2 and the middle of Section 4.7.1. However, there could be another alternative to raising the softening point to increase the coke yield. By lowering the solvent-to-coal ratio, less solvent would be retained by the produced pitch. Since the retained solvent would generally be volatilized during the coking process, decreasing the amount of solvent retained by the pitch could increase the coke yield by increasing the proportion of heavier coal-derived species, again assuming lowering the solvent-to-coal ratio does not affect the coal conversion. Hydrogenation runs four (4), eleven (11) and twelve (12) explore this option. For the three sets of reactions, HCO was employed as the solvent (again because it is more commercially available than DACL-L, however because of limited quantities of HCO, it was only used for this test and not in the previous section), and the reactions were carried out at 400 ºC, 1000 psig initial hydrogen pressure, 1 hour, and a decreasing solvent-to-coal ratio (by weight) of 3/1 for run four (4), 2/1 for run eleven (11), and 1/1 for run twelve (12). The effect of lowering the solvent-to-coal ratio on the overall and coal-alone conversions, ash content, coking value, and elemental analysis is discussed below.

The overall and coal-alone conversions for runs four (4), eleven (11), and twelve (12) are depicted in Figure 4.18. It is interesting to note that the overall conversion decreases as the solvent-to-coal ratio decreases, but the coal-alone conversion remains relatively constant (within experimental error). This shows that the coal-alone conversion does not depend significantly on the amount of solvent, only on the reaction conditions. The loss in overall conversion depicted in Figure 4.18 can be attributed to less solvent being carried into the THF soluble fraction. This is expected since there is less solvent in the original reaction feed as the solvent-to-coal ratio is decreased. The result of the coal-alone conversion section of Figure 4.18 is that the coal conversion is independent of the solvent-to-coal ratio. Therefore, the least amount of solvent that allows adequate processing of the reactants and products could be employed. From a coal-alone conversion standpoint, the optimum solvent-to-coal ratio is 2/1 because the 1/1 ratio would not flow when heated, leading to significant processing problems.

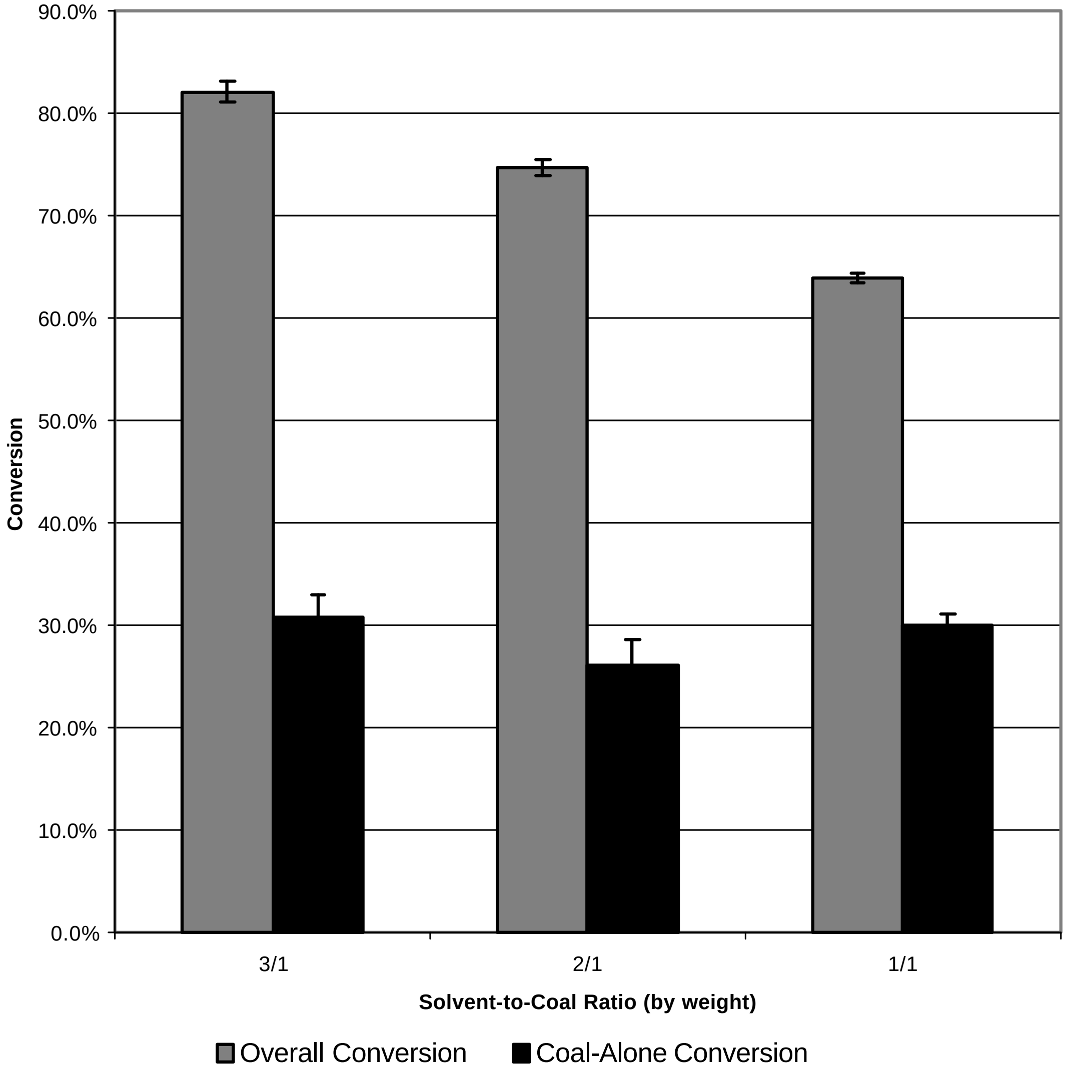


Figure 4.18 Effect of solvent-to-coal ratio on the overall and coal-alone conversions of hydrogenation reactions performed with the HCO solvent under conditions of 400 ºC, 1000 psig Hydrogen, and 1 hour

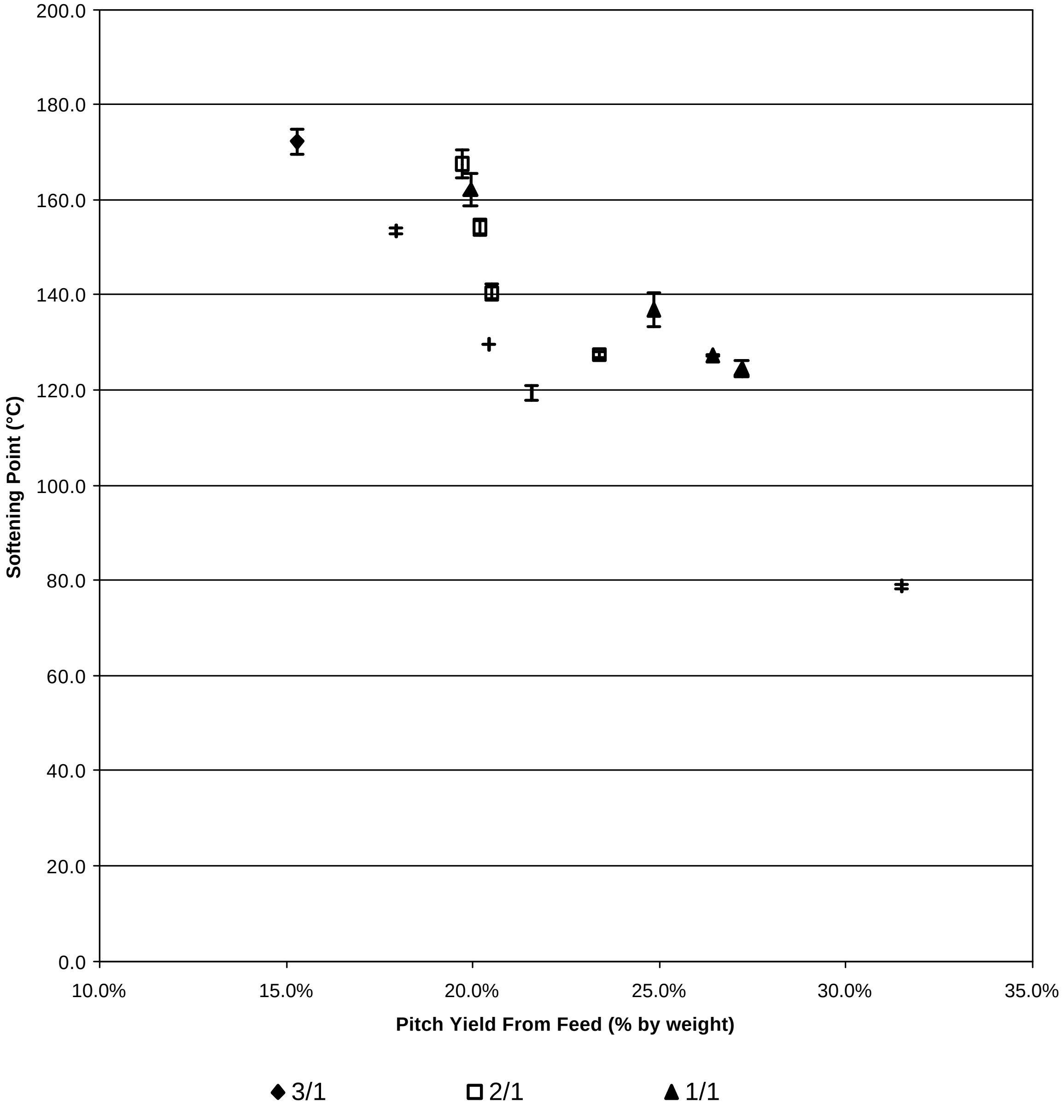


Figure 4.19 Effect of solvent-to-coal ratio on the amount of distillation required to achieve a specific softening point from hydrogenation reactions with conditions of HCO solvent, 400 ºC, 1000 psig hydrogen, and 1 hour

Once the THF extraction was completed, the THF soluble fraction was separated by vacuum distillation into the pitch and recycle solvent fractions. This was done in such a way that pitches of several different softening points were obtained, including a sample from each run close to the target value of 120 ºC. Figure 4.19 shows a nearly linear dependence of the final softening point of the pitch with the percentage of pitch recovered from the original reaction feed. It is interesting to note that as the solvent-to-coal ratio is decreased, the linear representation of softening point versus percent pitch yield shifts to the right in Figure 4.19. This shift corresponds to less distillation required to achieve a similar softening point as the solvent-to-coal ratio is decreased. This phenomenon is expected since a lower solvent content in the feed suggests that less recycle solvent will be recovered and less solvent needs to be distilled from the pitch to achieve the same softening point. This has some advantages and disadvantages. The advantages are that it produces a higher pitch yield and good coal conversion, but the disadvantages are that the products will be harder to process and less recycle solvent will be generated.

After the distillation was performed, three pitches were isolated (one from each run) with a softening point at or near the 120 ºC. These runs were 4C, 11B and 12A and had a softening point of 119.4, 127.5 and 124.6 ºC, respectively. These three samples were used to evaluate the ash and elemental content of the resultant products.

The ash content of the pitch and THF insoluble fraction of these three trials are shown in Table 4.11. For each of the selected samples, the ash content of the pitch and insoluble fractions are very similar. This is consistent with the fact that the coal-alone conversion remains constant as the solvent-to-coal ratio is lowered.

As with the previous experiments, an elemental analysis was conducted on the hydrogenation products for the selected trials as the solvent-to-coal ratio was lowered and the results of these analyses are shown in Table 4.12. These results indicate that in general the carbon content of each of the pitch fractions decreases (from 91.16% to 87.29%) as the solvent-to-coal ratio decreases. However, the hydrogen content remains constant at approximately 5.3%. The carbon and hydrogen contents of the THF insoluble and recycle solvent fractions are all within experimental error of each other, thus showing no dependence on the solvent-to-coal ratio of the hydrogenation reactions. The elemental compositions of the pitch fractions in Table 4.12 are also similar to those of the pitch fractions shown in Tables 4.4 and 4.8. Each pitch fraction has a carbon content of approximately 90 % and a hydrogen content between 5 and 6 % regardless of reaction conditions or the solvent employed.

Table 4.11 Ash content of pitch and THF insoluble fractions of selected hydrogenation runs with decreasing solvent-to-coal ratio with reaction conditions of HCO solvent, 400 ºC, 1000 psig hydrogen, and 1 hour

Run	Trial	Solvent-to-Coal Ratio	Average Softening Point (°C)	% Ash in Pitch	% Ash in THF Insoluble
4	C	3/1	119.4	0.019%	10.63%
11	B	2/1	127.5	0.084%	10.80%
12	A	1/1	124.6	0.024%	10.15%

Finally, the effect of lowering the solvent-to-coal ratio on the coke yield of the resultant pitch was investigated. It was hypothesized that by lowering the solvent-to-coal ratio, the amount of solvent remaining in the pitch fraction after distillation would decrease. This decrease in solvent content would cause an increase in the coke yield. Again, because of the dependence of the coke yield on the softening point, a plot of coke yield versus softening point was produced as Figure 4.20 in order to illustrate this effect. However, as Figure 4.20 illustrates, lowering the solvent-to-coal ratio has little or no effect on the coke yield thus proving the previous hypothesis invalid. All three solvent-to-coal ratios seem to fall along a similar linear representation of coke yield versus softening point. It is interesting to note that in order to achieve a coke yield of 50 percent by weight, according to Figure 4.20, a softening point of approximately 145 ºC would be required.

This linear representation is also similar to that shown in both Figure 4.8 and Figure 4.16. The equations of the linear representations for each graph are very similar. The slopes of the lines for Figures 4.8, 4.16, and 4.20 are 0.21, 0.23, and 0.24, respectively. The y-intercept for each figure is 19, 17, and 15 for Figures 4.8, 4.16, and 4.20. This similarity in equations leads to producing a plot (Figure 4.21) of coke yield versus softening point for all pitches produced. Figure 4.21 shows that the linear trends from the three previous figures (4.8, 4,16, and 4.20) are virtually all on the same line. This illustrates that once the pitch is formed, the relationship between coke yield and softening point is the same regardless of the reaction conditions. It is important to note that for these solvents and this type of coal, a coke yield can be predicted from the pitch softening point and is not changed by the reaction conditions of gas composition, gas pressure, solvent-to-coal ratio, and solvent choice. It is not known from this study if the particular linear relationship is dependent on the characteristics of the coal. Further study is warranted in this area.

Table 4.12 Elemental analysis of selected hydrogenation trials as the solvent-to-coal ratio was lowered but all other reaction conditions were kept constant at HCO solvent, 400 ºC, 1000 psig hydrogen, and 1 hour

Run (Solvent-to-Coal Ratio)	Element	Product Fraction		
		Pitch	THF Insoluble	Recycle Solvent
4C (3/1)	C	91.16%	79.02%	93.90%
	H	5.31%	3.96%	5.53%
	N	1.45%	1.42%	0.93%
	S	0.71%	0.96%	0.48%
	H/C Atomic Ratio	0.70	0.60	0.71
11B (2/1)	C	89.59%	77.53%	90.32%
	H	5.18%	3.95%	5.44%
	N	1.47%	1.70%	0.85%
	S	0.64%	0.71%	0.39%
	H/C Atomic Ratio	0.69	0.61	0.72
12A (1/1)	C	87.29%	76.81%	90.46%
	H	5.34%	4.11%	5.74%
	N	1.09%	1.36%	0.66%
	S	0.64%	0.72%	0.42%
	H/C Atomic Ratio	0.73	0.64	0.76

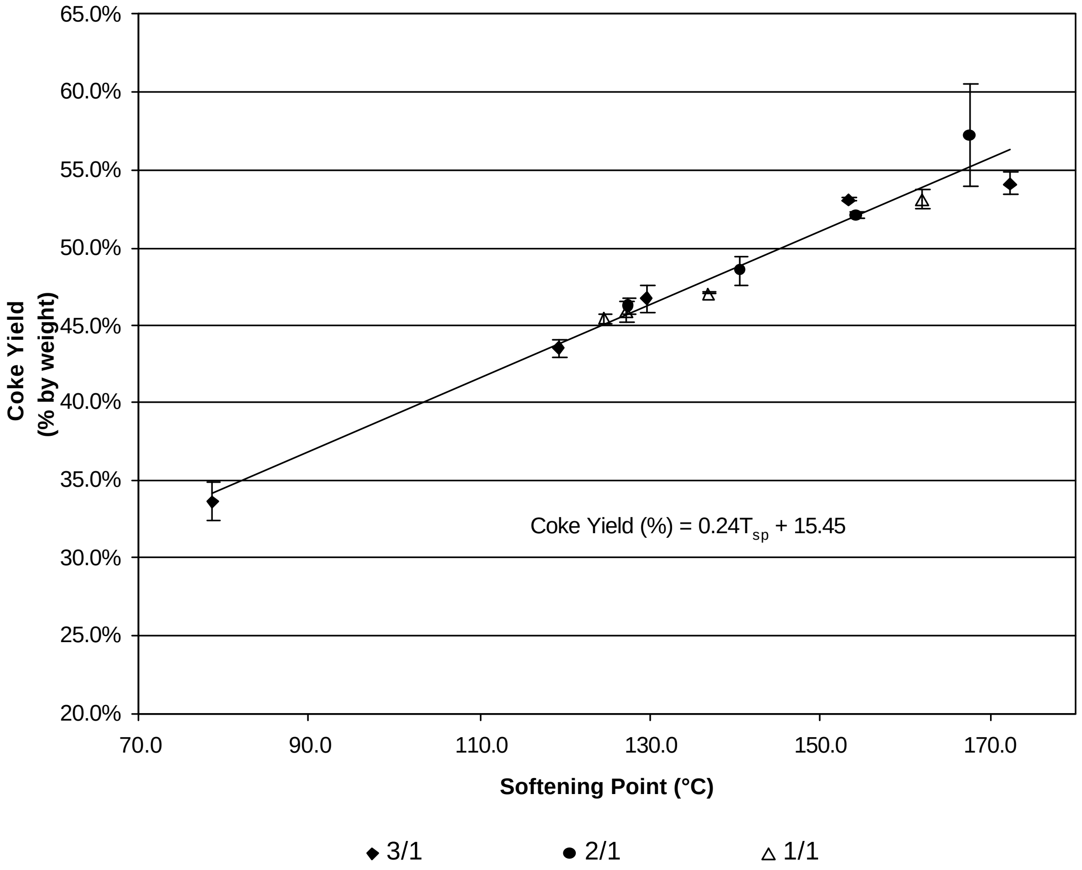


Figure 4.20 Effect of lowering the solvent-to-coal ratio on the pitch coke yield and various softening points from hydrogenation reactions with conditions of HCO solvent, 400 ºC, 1000 psig hydrogen, and 1 hour

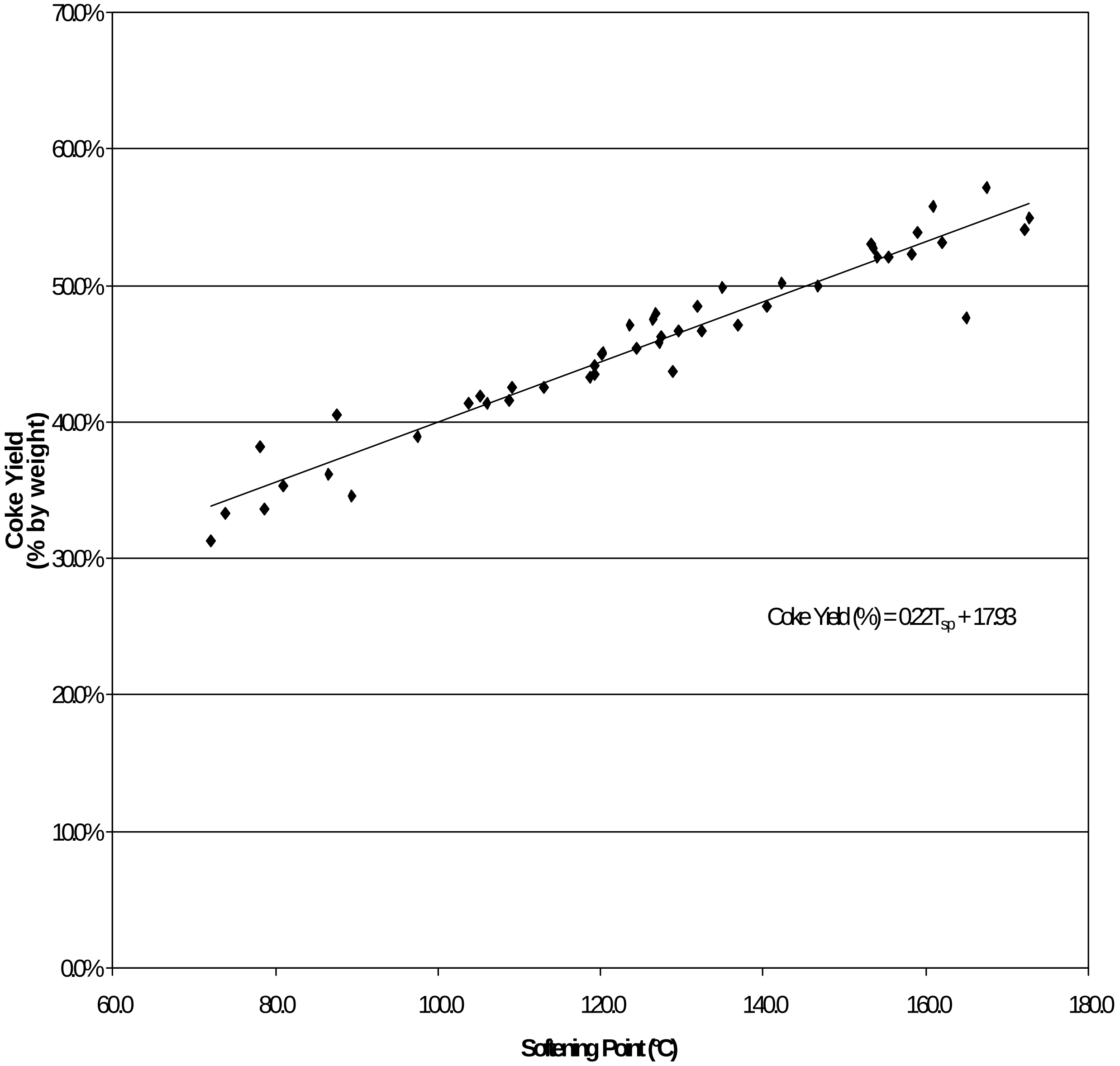


Figure 4.21 Effect of pitch softening point on the coke yield for all pitch fractions produced under varying reaction conditions

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this thesis project was to evaluate the effectiveness of five coal-derived liquids as possible hydrogenation solvents for the production of carbon-product precursors from coal. Each of these solvents was employed as a hydrogen donor under constant reaction conditions. The hydrogenation products were then separated into three fractions, pitch, THF insolubles, and recycle solvent. The pitch fraction was then characterized by standard methods to compare its properties to those of commercially available pitches. Finally, some of the reaction conditions were varied (pressure, gas composition, and solvent-to-coal ratio) in order to understand their effect on the products of the hydrogenation reactions. From these experiments several conclusions can be drawn.

1) The overall conversion seems to mask the effect of changing reaction conditions on coal reactivity because of the high amounts of solvent compared to the amount of coal included in the calculation. The coal-alone conversion, on the other hand, gives a relatively clear picture of the effect of changing the reaction conditions.

2) By using the coal-alone conversion, the most effective solvent for creating soluble species from coal was DACL-L (46.7%) followed by HCO (30.8%) and CBB (23.2%).

3) The coal-alone conversion was also dependent on the initial reaction pressure and gas composition. As the pressure increased, the coal-alone conversion increased for both hydrogen and argon atmospheres but not as significantly for the argon. This leads to the conclusion that the gaseous hydrogen does play an active role in converting the coal to soluble species.

4) The coal-alone conversion did not show a dependence on the solvent-to-coal ratio in the hydrogenation reactions. This is a valuable result in that the least amount

of solvent can be employed that physically allows for practical processing. It was found that a solvent-to-coal ratio of 1/1 was too low for adequate processing in these experiments because of the resistance to flow of the reaction products. Therefore, a 2/1 solvent-to-coal ratio is recommended for any subsequent reactions.

5) Once the hydrogenation reactions took place, the products were separated into the THF insolubles, recycle solvent, and the primary product of pitch. This pitch fraction was tested as a possible precursor for carbon products by standard characterization techniques, such as softening point, ash content, coke yield, optical texture, and elemental analysis. The softening point of each pitch could be tailored to a specific need by changing the extent of distillation. Pitches were produced with a softening point as low as 70 ºC up to 180 ºC regardless of the reaction conditions utilized.

6) The ash content of all of the product pitches was at an acceptably low value of less than 0.1%. This ash value is lower than that for pitches currently used as binders and is approaching the ash value of impregnation pitches.

7) The effect of the processing conditions on the coke yield of the product pitches was also investigated. The coke yield was nearly linearly dependent on the softening point of the pitch (controlled by extent of distillation) for all reaction conditions. The coke yield of pitches with a softening point near the commercial target value of 120 ºC, however, was somewhat lower than that desired for commercial applications (45% compared to 50 – 60%). Although the coke yield was dependent on the extent of distillation, it showed no other dependence on the reaction conditions. Changing the reaction pressure, gas composition, solvent-to-coal ratio, and even solvent did not have a significant effect on the coking value.

8) Anisotropic pitch was produced regardless of the solvent choice. Anisotropic pitch could also be produced at low pressures (100 psig) and without hydrogen. This discovery could significantly reduce the operational costs of pitch production.

9) Two important observations were derived from the elemental analysis of the pitch and recycle solvent fractions. First, the pitch fraction showed a carbon content (≅90%) similar to that of commercial binder pitches. Also, the elemental composition of the recycle solvent is similar to that of the original solvent. This could lead to a process that generates its own process solvent, thus alleviating the need for adding more solvent.

The above conclusions lead to the recommendation of an optimum process for the production of pitch from coal and coal-derived liquids. The solvent of choice would be HCO since it exhibited the highest coal-alone conversion while being commercially-available and produced a pitch which yielded an anisotropic carbon. The solvent-to-coal ratio would be 2/1 for ease of processing, and the pressure and gas composition would be 1000 psig hydrogen to maximize conversion. However, the pressure and gas composition could be changed if the processing costs outweigh that of maximizing the conversion.

5.1 Recommendations for Future Work

The outcome of this thesis research leads to several recommendations for future work. First, the hydrogenation reaction and process of pitch production should be scaled up somewhat. This would allow for more pitch and recycle solvent to be made. With a greater supply of pitch, a more thorough analysis of the pitch characteristics could be instituted to include measurements of viscosity, aromaticity, density, and solubility in characterization solvents such as toluene and quinoline. By increasing the amount of recycle solvent produced, there would be enough to test it as hydrogenation solvent.

Also, the solvent-to-coal ratio could be varied between 1/1 and 2/1 to establish the minimum amount needed for adequate processing.

A second study could be performed aiming to increase the conversion of coal to soluble species by the selected solvents. The effect of changing the reaction temperature, time, or addition of a catalyst could be quantified. It would be beneficial to perform a gas-phase analysis on the product gas produced from the hydrogenation reactions. The reaction temperature inside the reactor should be recorded by adding a thermocouple. Finally, the effect of using a different coal sample for the hydrogenation reactions on a similar representation of Figure 4.21 should be investigated.

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APPENDIX A

Experimental Raw Data

Table A.1 Hydrogenation Reactants and Subsequent Product Masses

Run	Trial	In Coal (g)	In Solvent (g)	Out Pitch (g)	Out THF Ins. (g)	Out Rec. Solv. (g)
1	A	8.3812	25.1046	8.5037	4.6171	16.6769
1	B	8.4897	25.4679	12.3280	4.7903	14.4829
1	C	8.3809	25.1423	9.6637	4.8612	15.3188
1	D	8.4776	25.4351	6.9489	4.8407	17.4629
2	A	5.9996	17.9994	17.2400	6.6085	0.0000
2	B	5.9988	17.9999	16.2053	6.6643	0.0000
2	C	6.0008	18.0008	12.7595	6.8085	1.9900
2	D	6.0009	17.9990	9.5452	7.2738	3.9600
3	A	7.6118	22.8324	9.9431	6.9708	10.2900
3	B	7.6541	22.9600	11.5130	7.1990	9.7100
3	C	7.6744	23.0200	8.8603	7.2135	11.2000
3	D	8.2833	24.8500	12.2342	8.6765	9.0800
4	A	8.7873	26.3643	11.0642	6.0297	14.6300
4	B	8.8595	26.5785	5.4141	6.4669	21.2400
4	C	8.8076	26.4215	7.5975	6.2503	17.1900
4	D	8.9488	26.8472	6.4161	6.5263	17.4800
4	E	8.7055	26.1183	7.1096	6.9566	20.2183
5	A	9.0940	27.2847	8.6773	6.9411	19.1700
5	B	8.9570	26.8698	7.1536	7.0941	20.6700
5	C	8.8303	26.4937	5.6086	6.9512	21.2800
5	D	8.8314	26.4938	8.5937	7.0349	19.2400
6	A	8.6048	25.8137	6.0769	7.2494	16.9400
6	B	9.0270	27.0806	4.7830	8.1360	20.5800
6	C	8.5940	25.7836	3.4138	7.9002	21.8700
6	D	8.9388	26.8162	6.5164	7.8078	19.1700
7	A	8.5583	25.6744	6.4744	7.0102	17.7300
7	B	8.9103	26.7293	5.3671	7.2512	21.4800
7	C	8.6285	25.8895	5.4428	7.7470	18.8400
7	D	8.8169	26.4519	7.7059	7.7566	17.9700

Table A.1(Continued) Hydrogenation Reactants and Subsequent Product Masses

Run	Trial	In Coal (g)	In Solvent (g)	Out Pitch (g)	Out THF Ins. (g)	Out Rec. Solv. (g)
8	A	8.9144	26.7416	7.3802	8.0749	17.6100
8	B	8.5729	25.7200	3.9747	7.6985	20.1200
8	C	8.8134	26.4439	6.1858	8.3588	18.5200
8	D	8.6033	25.8076	4.9405	7.8483	19.6000
9	A	8.9656	26.8936	8.7617	8.2419	17.1200
9	B	8.6900	26.0717	5.4339	8.1171	19.1000
9	C	9.1626	27.4904	5.6319	8.4754	18.9100
10	A	8.5836	25.7540	7.3670	8.5019	15.8400
10	B	9.0234	27.0691	4.7132	8.9974	18.9400
10	C	8.6621	25.9863	6.4714	7.9306	17.1300
10	D	8.8383	26.5110	6.1156	7.9726	17.4600
11	A	11.7463	23.4898	7.2230	8.5762	14.3000
11	B	11.5104	23.0186	8.0716	8.7815	15.2900
11	C	11.6680	23.3358	6.8942	9.1683	15.8000
11	D	11.5366	23.0717	6.9836	8.6664	17.2200
12	A	14.9673	14.9673	8.1438	10.7303	8.5800
12	B	15.1486	15.1480	7.5261	11.1392	9.5600
12	C	15.7095	15.7103	6.2607	11.1933	9.7100
12	D	15.4615	15.4618	8.1711	11.1289	9.2400

Table A.2 Hydrogenation Pitch Softening Point (Tsp ºC) and Coke Yield and Ash Content of Pitch and Insoluble Fraction

		Pitch		Pitch		THF Insolubles		Pitch	
Run	Trial	Tsp	Tsp	% Ash	% Ash	% Ash	% Ash	% Coke	% Coke
1	A	129.2	128.7	0.100%	0.120%	10.44%	12.66%	43.6%	43.7%
1	B	71.0	73.3	0.088%	0.075%	10.75%	10.99%	30.5%	32.0%
1	C	90.0	89.0	0.106%	0.101%	12.50%	11.70%	34.2%	34.9%
1	D	165.1	164.9	0.036%	0.037%	10.50%	11.10%	46.7%	48.5%
2	A	78.1	78.4	0.000%	0.000%	6.11%	6.03%	37.9%	38.4%
2	B	87.6	87.6	0.019%	0.037%	6.84%	6.78%	40.4%	40.6%
2	C	125.8	127.1	0.030%	0.019%	7.18%	7.03%	47.0%	48.1%
2	D	154.8	156.2	0.042%	0.019%	6.94%	7.11%	51.5%	52.7%
3	A	134.6	135.5	0.016%	0.037%	8.63%	8.62%	50.4%	49.2%
3	B	120.1	120.3	0.018%	0.000%	7.79%	7.78%	43.8%	46.1%
3	C	163.3	158.6	0.022%	0.024%	7.80%	7.61%	55.9%	55.7%
3	D	119.7	117.6	0.028%	0.024%	6.61%	6.78%	44.1%	42.5%
4	A	79.1	78.4	0.018%	0.024%	11.83%	11.95%	34.5%	32.8%
4	B	174.0	170.4	0.000%	0.015%	11.00%	11.10%	54.6%	53.6%
4	C	118.3	120.4	0.019%	0.018%	10.63%	10.63%	43.1%	43.9%
4	D	152.9	153.8	0.023%	0.024%	12.90%	13.00%	53.0%	53.1%
4	E	129.7	129.6	0.023%	0.078%	11.50%	11.60%	46.1%	47.3%
5	A	109.2	109.1	0.048%	0.043%	9.96%	10.50%	42.1%	43.0%
5	B	128.3	125.4	0.062%	0.123%	11.10%	11.10%	49.9%	46.0%
5	C	151.4	155.8	0.026%	0.039%	10.40%	10.40%	52.6%	52.8%
5	D	105.4	106.8	0.024%	0.022%	9.86%	9.98%	40.7%	42.1%
6	A	105.5	104.9	0.068%	0.071%	8.13%	8.20%	41.1%	42.7%
6	B	147.8	145.8	0.230%	0.160%	7.86%	7.82%	49.2%	50.7%
6	C	> 200	> 200	Sample coked during distillation -- discarded.					
6	D	117.5	121.1	0.041%	0.041%	7.93%	7.97%	44.2%	44.1%
7	A	114.1	112.2	0.036%	0.037%	10.10%	10.20%	42.4%	42.7%
7	B	158.6	158.1	0.037%	0.062%	9.49%	9.57%	52.4%	52.2%
7	C	141.8	143.0	0.016%	0.017%	9.55%	9.56%	51.1%	49.3%
7	D	97.3	97.7	0.017%	0.019%	10.40%	10.34%	38.9%	38.9%

Table A.2 (Continued) Hydrogenation Pitch Softening Point (Tsp ºC) and Coke Yield and Ash Content of Pitch and Insoluble Fraction

		Pitch		Pitch		THF Insolubles		Pitch	
Run	Trial	Tsp	Tsp	% Ash	% Ash	% Ash	% Ash	% Coke	% Coke
8	A	87.3	85.9	0.035%	0.020%	8.72%	8.50%	36.2%	36.1%
8	B	172.4	173.3	0.048%	0.093%	8.58%	8.75%	54.3%	55.5%
8	C	108.1	109.6	0.018%	0.013%	7.70%	7.86%	41.4%	41.8%
8	D	131.5	133.4	0.016%	0.018%	7.70%	8.02%	46.7%	46.7%
9	A	73.9	73.9	0.041%	0.032%	8.59%	8.47%	33.7%	32.9%
9	B	124.0	123.2	0.039%	0.030%	8.39%	8.54%	47.3%	46.9%
9	C	132.1	131.8	0.130%	0.075%	7.61%	7.82%	48.5%	48.5%
10	A	80.5	81.6	0.028%	0.123%	8.03%	7.92%	35.7%	35.0%
10	B	157.0	161.2	0.202%	0.227%	8.19%	8.16%	53.3%	54.5%
10	C	103.5	104.2	0.101%	0.069%	8.26%	8.11%	41.6%	41.1%
10	D	119.4	121.1	0.102%	0.114%	8.03%	7.79%	45.3%	44.8%
11	A	139.3	141.8	0.044%	0.170%	10.90%	10.50%	49.2%	47.8%
11	B	127.1	127.8	0.120%	0.048%	10.70%	10.90%	45.9%	46.6%
11	C	165.4	169.6	0.023%	0.042%	10.30%	10.70%	54.9%	59.5%
11	D	153.0	155.3	0.240%	0.250%	10.30%	10.30%	51.9%	52.2%
12	A	123.4	125.7	0.048%	0.000%	10.20%	10.10%	45.6%	45.2%
12	B	134.4	139.3	0.026%	0.054%	9.91%	10.00%	47.0%	47.1%
12	C	159.6	164.5	0.019%	0.021%	10.30%	10.20%	53.5%	52.7%
12	D	127.2	127.4	0.043%	0.082%	9.30%	9.30%	46.3%	45.4%

Table A.3 Reactor Pressures of Hydrogenation Reactions with DACL-L under conditions of 400 ºC, 1000 psig Hydrogen, 3/1 Solvent-to-Coal Ratio and 1 hour

Time	Pressure	
(min)	Run 1	Run 2
0	1000	1000
2	1960	1900
4	2010	1970
6	2040	2000
8	2040	2000
10	2040	2000
12	2040	2000
16	2040	1990
22	2020	1980
28	2010	1960
34	1990	1940
40	1980	1930
46	1960	1910
52	1930	1890
58	1920	1890
61.5	910	900
106	800	820
1230	800	820

Table A.4 Reactor Pressures of Hydrogenation Reactions with DACL-H under conditions of 400 ºC, 1000 psig Hydrogen, 3/1 Solvent-to-Coal Ratio and 1 hour

Time	Pressure	
(min)	Run 1	Run 2
0	1000	990
2	1900	1900
6	2020	1950
10	2020	1960
14	2020	1980
18	1980	1900
22	1960	1880
30	1880	1850
36	1840	1810
42	1820	1780
48	1780	1770
53	1740	1730
59	1700	1690
66	750	760
74	750	750
93	750	750
140	750	750
600	750	750

Table A.5 Reactor Pressures of Hydrogenation Reactions with RACL under conditions of 400 ºC, 1000 psig Hydrogen, 3/1 Solvent-to-Coal Ratio and 1 hour

Time (min)	Pressure Run 1	Run 2
0	1000	1000
2	2060	2040
4	2130	2120
6	2150	2130
8	2140	2130
10	2120	2110
12	2120	2100
16	2100	2090
22	2090	2070
28	2040	2010
34	2020	1990
40	1980	1960
46	1930	1920
52	1910	1900
58	1890	1860
61.5	880	860
85	750	730
1140	750	730

Table A.6 Reactor Pressures of Hydrogenation Reactions with HCO under conditions of 400 ºC, 1000 psig Hydrogen, 3/1 Solvent-to-Coal Ratio and 1 hour

Time (min)	Pressure Run 1	Run 2	Run 3
0	1000	1000	1000
2	1980	1880	1880
4	2030	1920	1910
8	2060	1920	1910
12	2060	1920	1860
16	2030	1880	1820
22	1980	1840	1780
28	1920	1800	1680
34	1880	1740	1670
40	1830	1700	1620
46	1790	1660	1600
52	1740	1620	1560
58	1700	1590	1490
61.5	980	860	800
84	800	710	660
105	800	710	660
490	800	710	660

Table A.7 Reactor Pressures of Hydrogenation Reactions with CBB under conditions of 400 ºC, 1000 psig Hydrogen, 3/1 Solvent-to-Coal Ratio and 1 hour

Time	Pressure			
(min)	Run 1	Run2	Run 3	Run 4
0	1000	1000	1000	1000
2	1970	1960	1980	1990
4	2020	2010	2020	2040
6	2020	2020	2020	2030
8	2010	2010	2000	2020
10	1980	1980	1990	2010
12	1960	1970	1970	1980
16	1940	1940	1940	1960
22	1900	1900	1900	1920
28	1850	1860	1860	1870
34	1820	1820	1820	1830
40	1780	1790	1780	1800
46	1750	1760	1750	1750
52	1720	1730	1710	1720
58	1690	1700	1680	1690
61	900	900	910	870
65	760	800	760	760
90	740	780	750	730

Table A.8 Reactor Pressures of Hydrogenation Reactions with CBB under conditions of 400 ºC, 1000 psig Argon, 3/1 Solvent-to-Coal Ratio and 1 hour

Time	Pressure			
(min)	Run 1	Run2	Run 3	run 4
0	1000	1000	1000	1000
2	2000	1900	2030	2000
4	2060	1980	2120	2070
6	2100	2020	2140	2110
8	2120	2040	2150	2120
10	2130	2040	2160	2130
12	2140	2060	2170	2140
16	2170	2070	2180	2160
22	2190	2100	2190	2170
28	2210	2110	2220	2200
34	2220	2120	2220	2210
40	2230	2140	2240	2220
46	2240	2140	2240	2220
52	2240	2140	2260	2230
58	2250	2150	2260	2230
61	1150	1140	1140	1130
90	1000	1000	1000	1000

Table A.9 Reactor Pressures of Hydrogenation Reactions with CBB under conditions of 400 ºC, 500 psig Hydrogen, 3/1 Solvent-to-Coal Ratio and 1 hour

Time	Pressure			
(min)	Run 1	Run2	Run 3	Run 4
0	500	500	500	500
2	1020	1020	1040	1070
4	1060	1060	1070	1100
6	1060	1060	1050	1090
8	1060	1060	1050	1090
10	1060	1050	1040	1080
12	1050	1050	1040	1080
16	1040	1030	1020	1060
23	1020	1020	1000	1040
30	1000	1000	980	1010
37	980	980	960	990
44	960	970	940	960
51	950	950	930	950
58	940	940	910	920
61	430	420	420	410
90	380	380	360	360

Table A.10 Reactor Pressures of Hydrogenation Reactions with CBB under conditions of 400 ºC, 500 psig Argon, 3/1 Solvent-to-Coal Ratio and 1 hour

Time	Pressure	
(min)	Run 1	Run2
0	500	500
2	1020	1030
4	1070	1070
6	1100	1100
8	1120	1120
10	1120	1120
12	1130	1130
16	1140	1140
24	1160	1170
30	1180	1180
40	1200	1200
46	1210	1210
52	1220	1210
58	1220	1220
61	600	600
90	500	500

Table A.11 Reactor Pressures of Hydrogenation Reactions with CBB under conditions of 400 ºC, 100 psig Hydrogen, 3/1 Solvent-to-Coal Ratio and 1 hour

Time	Pressure	
(min)	Run 1	Run2
0	100	100
2	300	280
4	330	320
6	340	320
8	340	320
10	350	340
12	360	350
14	360	360
16	360	360
19	360	360
22	360	360
27	380	370
32	390	390
36	440	400
39	440	380
43	440	400
46	450	410
49	440	400
54	440	400
58	440	400
61	200	170
66	170	130
90	160	130

Table A.12 Reactor Pressures of Hydrogenation Reactions with CBB under conditions of 400 ºC, 100 psig Argon, 3/1 Solvent-to-Coal Ratio and 1 hour

Time	Pressure	
(min)	Run 1	Run2
0	100	100
2	240	300
4	280	330
7	300	350
10	310	360
14	320	380
18	330	390
21	340	400
26	350	400
32	360	420
38	360	420
44	380	430
51	380	440
58	390	440
61	160	160
67	150	150
90	130	130

APPENDIX B

Micrographs of Cokes

(All scale factors are 118 μm)

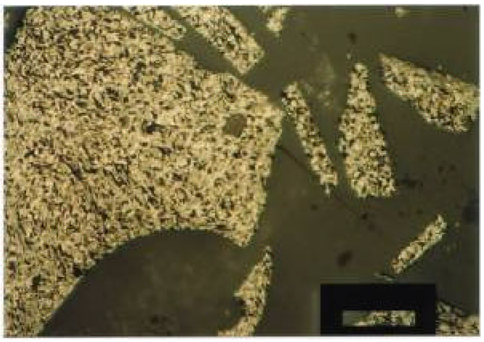

Figure B.1 Photograph of coke produced from hydrogenation reaction 1A with DACL-L, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 129 °C.

Figure B.2 Photograph of coke produced from hydrogenation reaction 1D with DACL-L, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 165 °C.

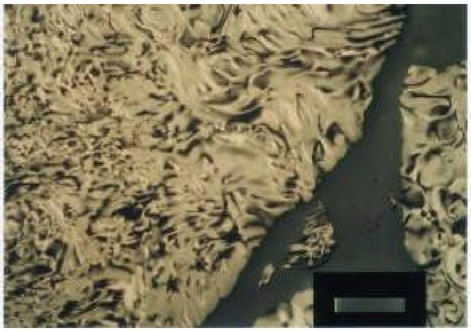

Figure B.3 Photograph of coke produced from hydrogenation reaction 2A with DACL-H, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 78.3 °C.

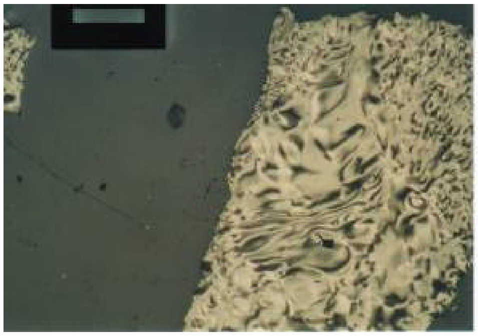

Figure B.4 Photograph of coke produced from hydrogenation reaction 2B with DACL-H, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 87.6 °C.

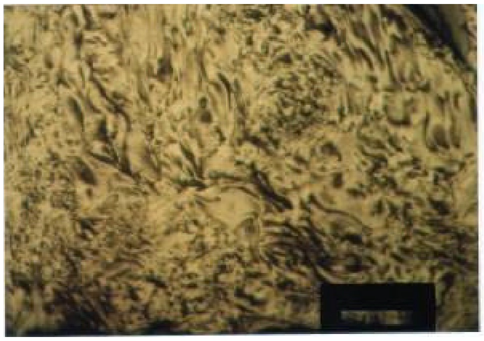

Figure B.5 Photograph of coke produced from hydrogenation reaction 2C with DACL-H, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 126.5 °C.

Figure B.6 Photograph of coke produced from hydrogenation reaction 3A with RACL, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 135.1 °C.

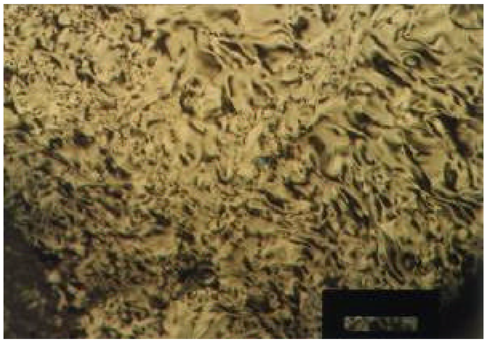

Figure B.7 Photograph of coke produced from hydrogenation reaction 3B with RACL, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 120.2 °C.

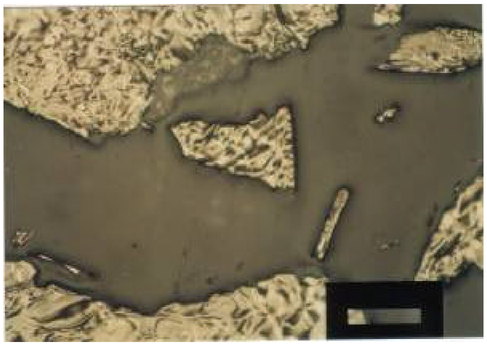

Figure B.8 Photograph of coke produced from hydrogenation reaction 3C with RACL, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 161.0 °C.

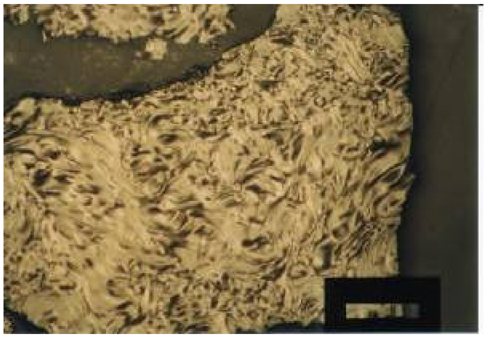

Figure B.9 Photograph of coke produced from hydrogenation reaction 3D with RACL, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 118.7 °C.

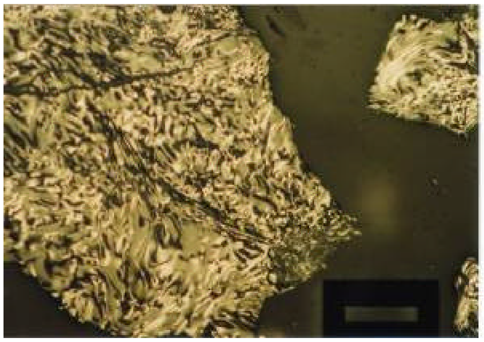

Figure B.10 Photograph of coke produced from hydrogenation reaction 4B with HCO, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 172.2 °C.

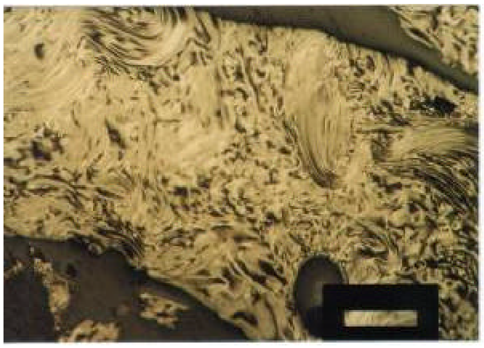

Figure B.11 Photograph of coke produced from hydrogenation reaction 4C with HCO, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 119.4 °C.

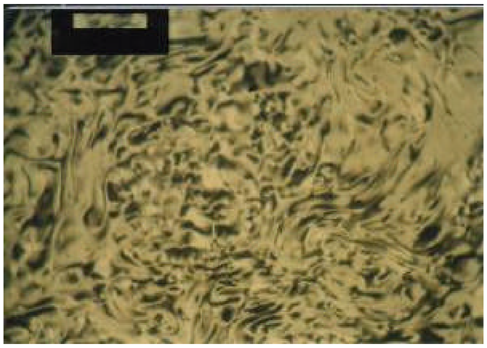

Figure B.12 Photograph of coke produced from hydrogenation reaction 4D with HCO, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 153.4 °C.

Figure B.13 Photograph of coke produced from hydrogenation reaction 4E with HCO, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 129.7 °C.

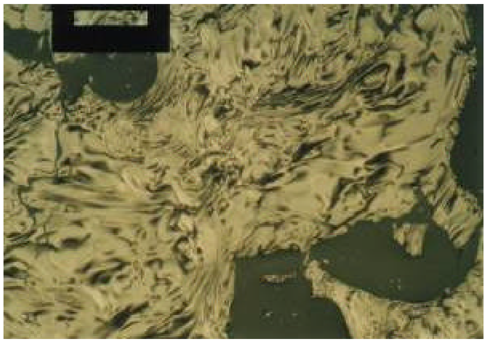

Figure B.14 Photograph of coke produced from hydrogenation reaction 5A with CBB, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 109.2 °C.

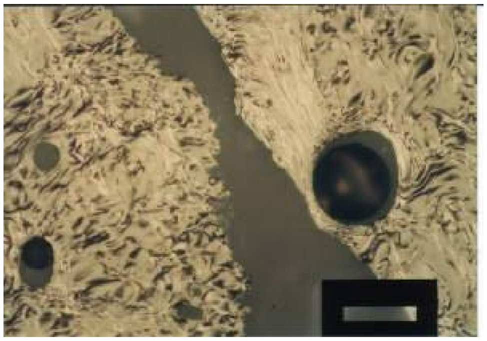

Figure B.15 Photograph of coke produced from hydrogenation reaction 5B with CBB, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 126.9 °C.

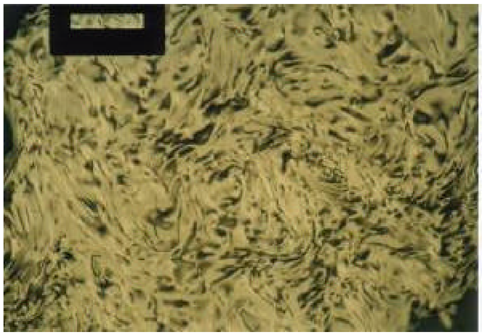

Figure B.16 Photograph of coke produced from hydrogenation reaction 5C with CBB, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 153.6 °C.

Figure B.17 Photograph of coke produced from hydrogenation reaction 5D with CBB, 400 °C, 1000 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 106.1 °C.

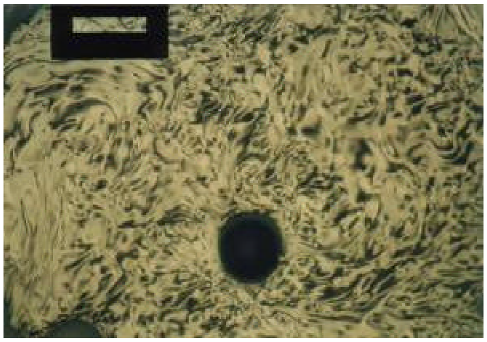

Figure B.18 Photograph of coke produced from hydrogenation reaction 6A with CBB, 400 °C, 1000 psig argon, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 105.2 °C.

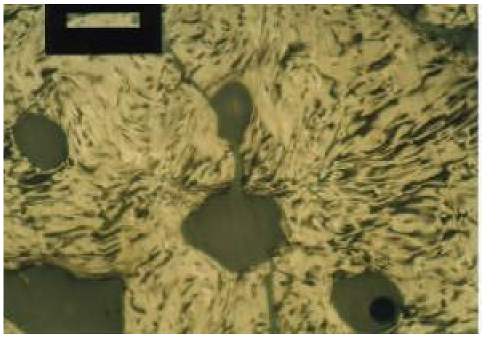

Figure B.19 Photograph of coke produced from hydrogenation reaction 6B with CBB, 400 °C, 1000 psig argon, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 146.8 °C.

Figure B.20 Photograph of coke produced from hydrogenation reaction 6D with CBB, 400 °C, 1000 psig argon, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 119.3 °C.

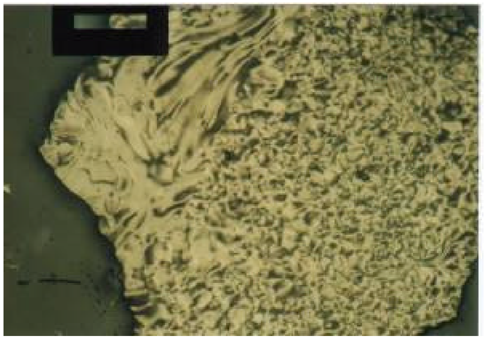

Figure B.21 Photograph of coke produced from hydrogenation reaction 7A with CBB, 400 °C, 500 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 113.2 °C.

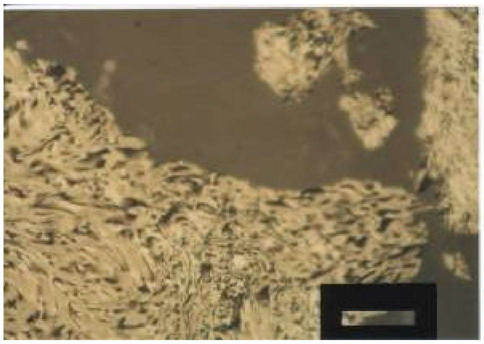

Figure B.22 Photograph of coke produced from hydrogenation reaction 7B with CBB, 400 °C, 500 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 158.4 °C.

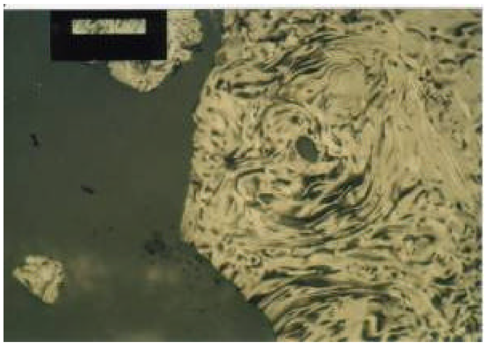

Figure B.23 Photograph of coke produced from hydrogenation reaction 7C with CBB, 400 °C, 500 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 142.4 °C.

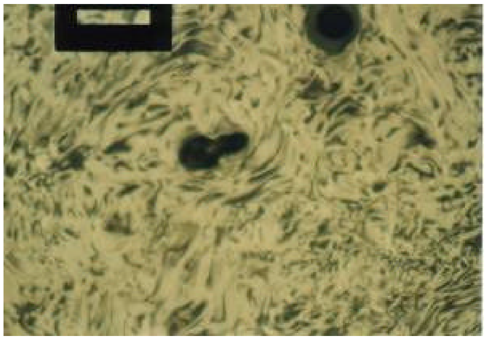

Figure B.24 Photograph of coke produced from hydrogenation reaction 7D with CBB, 400 °C, 500 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 97.5 °C.

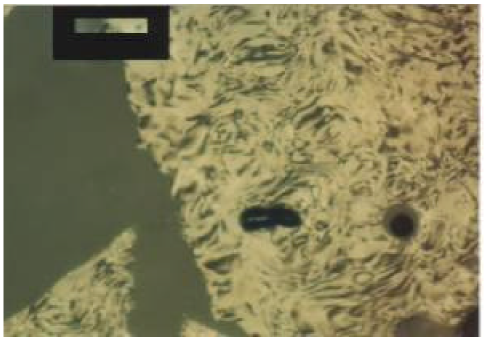

Figure B.25 Photograph of coke produced from hydrogenation reaction 8A with CBB, 400 °C, 500 psig argon, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 86.6 °C.

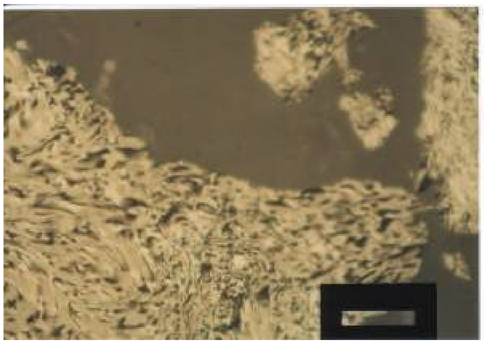

Figure B.26 Photograph of coke produced from hydrogenation reaction 8B with CBB, 400 °C, 500 psig argon, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 172.9 °C.

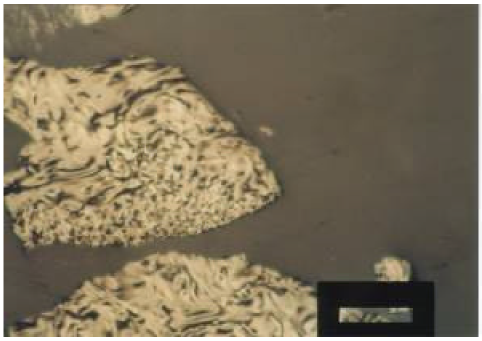

Figure B.27 Photograph of coke produced from hydrogenation reaction 8C with CBB, 400 °C, 500 psig argon, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 108.9 °C.

Figure B.28 Photograph of coke produced from hydrogenation reaction 8D with CBB, 400 °C, 500 psig argon, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 132.5 °C.

Figure B.29 Photograph of coke produced from hydrogenation reaction 9A with CBB, 400 °C, 100 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 73.9 °C.

Figure B.30 Photograph of coke produced from hydrogenation reaction 9B with CBB, 400 °C, 100 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 123.6 °C.

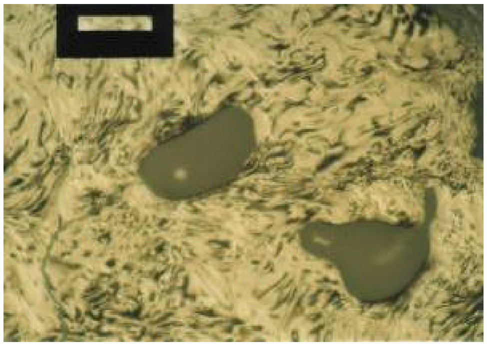

Figure B.31 Photograph of coke produced from hydrogenation reaction 9C with CBB, 400 °C, 100 psig hydrogen, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 132.0 °C.

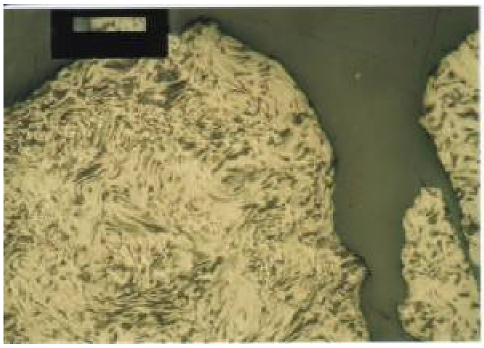

Figure B.32 Photograph of coke produced from hydrogenation reaction 10A with CBB, 400 °C, 100 psig argon, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 81.1 °C.

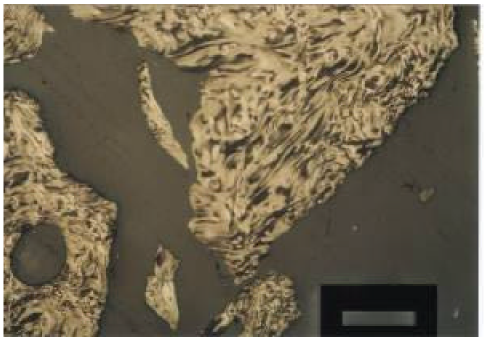

Figure B.33 Photograph of coke produced from hydrogenation reaction 10B with CBB, 400 °C, 100 psig argon, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 159.1 °C.

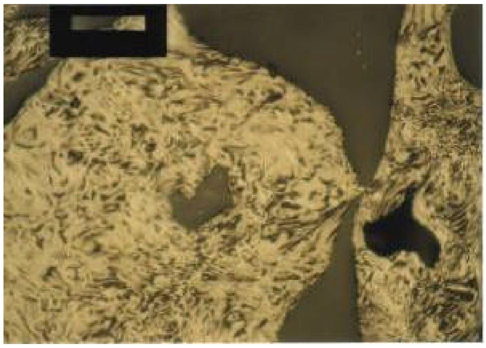

Figure B.34 Photograph of coke produced from hydrogenation reaction 10C with CBB, 400 °C, 100 psig argon, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 103.9 °C.

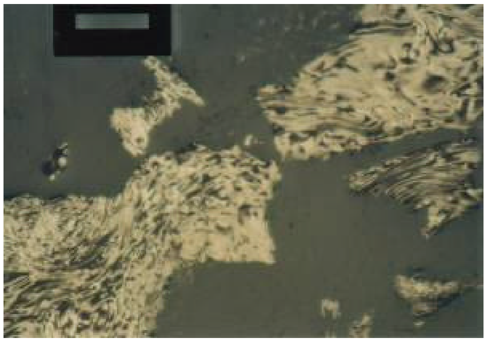

Figure B.35 Photograph of coke produced from hydrogenation reaction 10D with CBB, 400 °C, 100 psig argon, 3/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 120.3 °C.

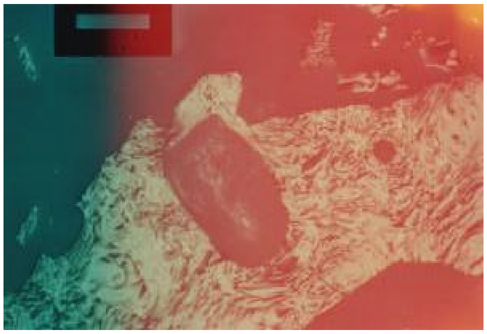

Figure B.36 Photograph of coke produced from hydrogenation reaction 11A with HCO, 400 °C, 1000 psig hydrogen, 2/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 140.6 °C.

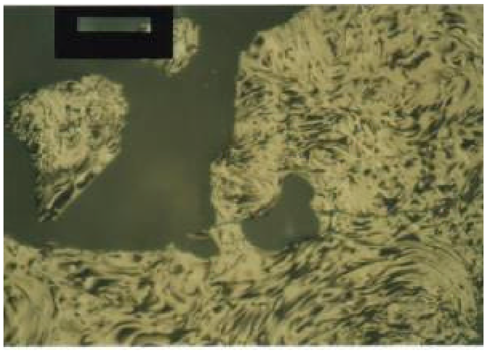

Figure B.37 Photograph of coke produced from hydrogenation reaction 11B with HCO, 400 °C, 1000 psig hydrogen, 2/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 127.5 °C.

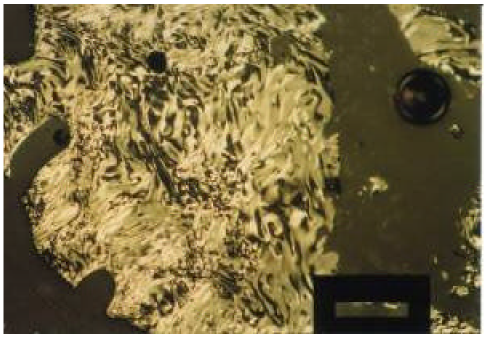

Figure B.38 Photograph of coke produced from hydrogenation reaction 11C with HCO, 400 °C, 1000 psig hydrogen, 2/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 167.5 °C.

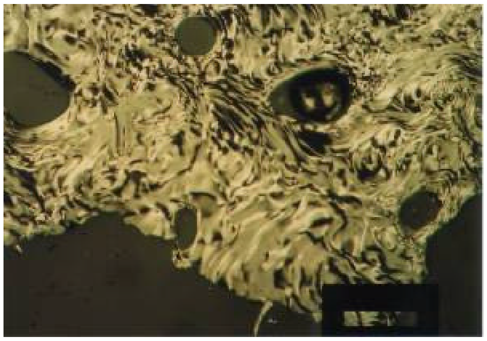

Figure B.39 Photograph of coke produced from hydrogenation reaction 11D with HCO, 400 °C, 1000 psig hydrogen, 2/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 154.2 °C.

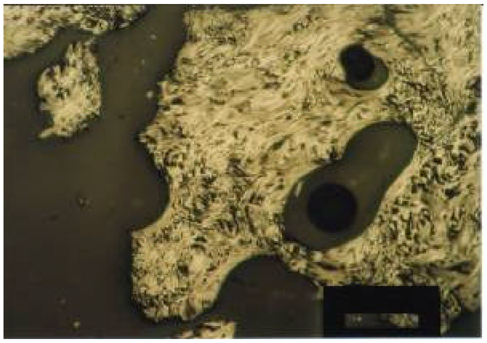

Figure B.40 Photograph of coke produced from hydrogenation reaction 12A with HCO, 400 °C, 1000 psig hydrogen, 1/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 162.1 °C.

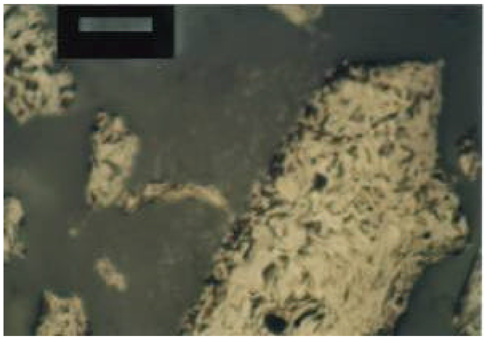

Figure B.41 Photograph of coke produced from hydrogenation reaction 12B with HCO, 400 °C, 1000 psig hydrogen, 1/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 127.3 °C.

Figure B.42 Photograph of coke produced from hydrogenation reaction 12C with HCO, 400 °C, 1000 psig hydrogen, 1/1 solvent-to-coal ratio, 1 hour. Pitch has softening point of 124.6 °C.

APPENDIX C

Elemental Analysis Data

Table C.1 Elemental Analysis Results from Select Hydrogenation Reactions

Sample Name	Nitrogen %	Carbon %	Hydrogen %	Sulfur %
COAL	0.800726593	82.03022003	4.413304329	0.735073268
COAL	1.393814802	81.14820099	4.715521336	0.717331052
DACL-L	1.032134652	80.14930725	7.481013775	0.579850316
DACL-L	0.862452507	80.86106873	7.994864464	0.644888937
1A Pitch	1.289442658	86.89827728	6.020725727	0.555523694
1A Pitch	1.146941423	86.70263672	6.294783115	0.777996659
1A THF Insoluble	0.973333001	83.5721817	4.165088654	0.930670857
1A THF Insoluble	2.090841293	81.47145081	4.185832977	0.884985149
1A Recycle Solvent	0.725984573	81.89357758	8.269141197	-0.187794656
1A Recycle Solvent	1.008112788	83.33693695	8.15523243	0.559279799
DACL-H	0.906315863	88.18888092	5.546836376	0.797720015
DACL-H	1.585921168	88.83122253	5.896028996	0.731309056
2C Pitch	1.652619839	89.20326233	5.505034924	0.599318624
2C Pitch	1.708004594	90.18683624	5.730174065	0.712649286
2C THF Insoluble	2.166527987	83.86855316	4.133490562	0.742859304
2C THF Insoluble	1.865050554	82.3000412	4.167425632	0.956396997
2C Recylce Solvent	1.917423368	85.35504913	7.15696907	0.555400014
2C Recylce Solvent	1.046489358	85.84366608	7.338793755	0.587919772
3B Pitch	1.497819662	90.98829651	5.667295933	0.824364841
3B Pitch	1.079764724	90.07225037	6.002172947	0.6290766
3B THF Insoluble	2.174021721	79.99674225	4.448624134	0.908544421
3B THF Insoluble	2.215703249	81.45055389	4.648269653	0.934747279
3B Recycle Solvent	1.771402955	82.48386383	8.351308823	0.737286687
3B Recycle Solvent	1.974727035	81.22819519	8.534269333	0.609703422
RACL	0.874046028	86.2507019	6.809337139	0.668987215
RACL	1.559338689	87.0880661	6.714583397	0.777099848
4C Pitch	1.617382884	91.69573212	5.396313667	0.761683703
4C Pitch	1.28988862	90.63007355	5.214667797	0.660184264
4C THF Insoluble	1.346327186	79.64372253	4.090205193	0.956537008

Table C.1 (Continued) Elemental Analysis Results from Select Hydrogenation Reactions

Sample Name	Nitrogen %	Carbon %	Hydrogen %	Sulfur %
4C THF Insoluble	1.498970151	78.39524078	3.837160587	0.960397959
4C Recycle Solvent	0.724746406	93.58480835	5.362288475	0.444027484
4C Recyce Solvent	1.129940271	94.20589447	5.697498322	0.512170851
HCO	0.968861938	93.08518219	4.987132549	0.557442606
HCO	1.007636428	93.94626617	5.31794548	0.542826772
5B Pitch	0.756639302	89.6841507	4.952497482	0.683298409
5B Pitch	1.546139002	89.81164551	5.324268341	0.584444702
5B THF Insoluble	0.853470564	79.47361755	3.838719606	0.943519771
5B THF Insoluble	0.859390855	78.86706543	4.102155685	0.943781793
5B Recycle Solvent	0.891899347	91.45198059	5.842988014	0.729324162
5B Recycle Solvent	0.886314631	90.00209045	5.740687847	0.644795418
CBB	0.982173145	91.86216736	5.572559834	0.718307495
CBB	0.635398149	91.83862305	5.446722507	0.62724328
6D Pitch	1.281929374	91.20168304	5.251701832	0.885590434
6D Pitch	1.303733945	91.64124298	5.369911671	0.792035282
6D THF Insoluble	0.854979277	81.79877472	3.842562437	0.653879762
6D THF Insoluble	1.296254277	83.40203094	3.986491203	0.911690235
7A Pitch	1.9395684	92.09086609	5.295227051	0.808043718
7A Pitch	1.426768184	90.92002106	5.252641201	0.735275447
7A THF Insoluble	0.660272121	81.20497894	4.100767612	0.900794447
7A THF Insoluble	1.825739503	83.76688385	4.077264786	0.85759294
6D Recycle Solvent	-0.204879567	94.5942688	5.649143219	0.910861075
6D Recycle Solvent	-0.698981762	91.18883514	5.370734215	0.652718902
7A Recycle Solvent	0.877761841	90.97460175	5.855251789	0.598276138
7A Recycle Solvent	0.586638629	91.55131531	5.651697636	0.659404576
8D Pitch	1.751173615	92.32575226	5.134294987	0.675103962
8D Pitch	1.724418998	92.68335724	4.955196381	0.907358825
8D THF Insoluble	1.571769238	81.08649445	4.167609692	0.838398814

Table C.1 (Continued) Elemental Analysis Results from Select Hydrogenation Reactions

Sample Name	Nitrogen %	Carbon %	Hydrogen %	Sulfur %
8D THF Insoluble	2.260994196	81.7248764	4.246864319	0.782370448
9B Pitch	1.078383446	91.92891693	5.153922081	0.698048353
9B Pitch	1.15290308	91.17565918	5.233355045	0.687234581
9B THF Insoluble	1.202765226	82.38817596	4.087132454	0.809182346
9B THF Insoluble	1.401732683	82.05186462	4.069063663	0.865704477
8D Recycle Solvent	0.624038637	88.60739899	4.976284981	0.860951901
8D Recycle Solvent	0.561470747	90.58050537	5.55779314	0.662091851
9B Recycle Solvent	0.940030575	90.99137115	5.815058708	0.613212407
9B Recycle Solvent	0.798502684	93.19036865	5.780529976	0.598441362
10D Pitch	1.523295164	88.74085236	4.861751556	0.863550842
10D Pitch	1.500685215	89.34506226	5.272848129	0.739778459
10D THF Insoluble	1.478106976	80.26706696	4.123864174	0.583087683
10D THF Insoluble	0.924294233	83.76509857	4.256327152	0.700130343
11B Pitch	1.298616171	89.80078888	5.242455482	0.65870893
11B Pitch	1.633161306	89.37313843	5.110965252	0.628293216
11B THF Insoluble	1.480561495	77.2186203	3.998501539	0.664203823
11B THF Insoluble	1.919276714	77.84881592	3.898455858	0.759484112
10D Recycle Solvent	0.883579671	89.75298309	5.607596397	0.552561283
10D Recycle Solvent	0.660242021	89.41329193	5.333270073	0.372020066
11B Recycle Solvent	0.891836584	90.4691391	5.688763142	0.401919603
11B Recycle Solvent	0.804223597	90.17233276	5.189516068	0.368410617
12C Pitch	1.577460408	87.77875519	5.434559822	0.665524304
12C Pitch	0.612488925	86.80805206	5.248411655	0.616027951
12C THF Insoluble	1.572936773	76.87220764	4.223587513	0.716712952
12C THF Insoluble	1.151239634	76.7490387	3.991147995	0.719765246
12C Recycle Solvent	0.672605038	90.575737	5.792259693	0.439225942
12C Recycle Solvent	0.652494192	90.34770203	5.68773365	0.400908679