DEVELOPMENT OF CONTINUOUS SOLVENT EXTRACTION PROCESSES FOR COAL DERIVED CARBON PRODUCTS DE-FC26-03NT41873

Quarterly Report

PERIOD OF PERFORMANCE: April 1, 2005 – June 30, 2005

Submission date: August 11, 2005

Principal Investigator: Elliot B. Kennel

Co-Investigators: Stephen P. Carpenter, Dady Dadyburjor, Manoj Katakdaunde, Liviu Magean, Peter G. Stansberry, Alfred H. Stiller, John W. Zondlo

West Virginia University
Department of Chemical Engineering
College of Engineering and Mineral Resources
PO Box 6102
Morgantown WV 26506

Subcontractors: GrafTech International 12900 Snow Road Parma, OH 44130

Koppers Inc. 1005 William Pitt Way Pittsburgh, PA 15238

DISCLAIMER:

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

The purpose of this DOE-funded effort is to develop continuous processes for solvent extraction of coal for the production of carbon products. These carbon products include materials used in metals smelting, especially in the aluminum and steel industries, as well as porous carbon structural material referred to as "carbon foam" and carbon fibers.

During this reporting period, efforts have focused on the facility modifications for continuous hydrotreating, as well as developing improved protocols for producing synthetic pitches.

TABLE OF CONTENTS

1.0 EXECUTIVE SUMMARY	5
2.0 TECHNICAL	6
2.1 Pitches and Cokes from Coal Extraction	
2.2 Binder Pitch Requirements	
3.0 EXPERIMENTAL	8
3.1 Coal Selection	8
3.2 Solvent Selection	
3.3 Catalytic Solvent Hydrogenation	10
3.4 Coal Extraction	
3.4.1 Evaluation of Hydrogenated Solvent in 1-gallon Batch Trials	
3.4.2 Coal Refining Unit (CRU) Operation	
3.5 Solid Separations	
3.6 Solvent Recovery	
4.0 RESULTS	
4.1 Characterization of Catalytic Hydrogenation of Coal Tar Distillate	
4.2 Results of 1-Gallon Batch Reactions	
4.3 Production of Coal Extract in the CRU	27
LIST OF FIGURES	
LIST OF FIGURES	
Figure 1. Dried and crushed Kingwood coal ready for storage	
Figure 2. Completed and loaded catalyst basket	
Figure 3. Flow diagram of the continuous hydrogenator.	
Figure 4. Top view of catalyst containment system.	
Figure 5. Flow rate of corn oil through 1/8 inch tube 10 ft long as a function of pressure	
Figure 6. Flow rate of fluids through 5 ft section of 0.04 in ID stainless steel tubing	
Figure 7. Flow rate of coal tar distillate through 0.02 inch ID x 5 foot length capillary tube	
Figure 8. Flow rate of coal tar distillate through capillary tubing (0.02"ID X 10") at 350 °C	
Figure 9. Schematic of the Coal Refining Unit	
Figure 10. Typical 1H NMR spectrum of coal tar distillate, 60MHz.	
Figure 11. 1H NMR spectrum of coal tar distillate aliphatic region, 60MHz	21
Figure 12. FTIR spectra of feed and hydrogenated coal tar distillate	
Figure 13. Change in FTIR ratio as a function of hydrogenation conditions.	
Figure 14. Boiling point distribution of hydrogenated coal tar distillate.	
Figure 15. Changes in pressure versus time at reaction temperature	
Figure 17. Viscosity versus temperature of select coal solutions	25 26
Figure 18. Softening point of coal extracts versus amount distillate removed	
Figure 19. Reconfiguration of the CRU with installation of filtration system	
Figure 20. Current configuration of the CRU with the installation of the vacuum retort.	29
20) Current Company of the Cite with the institution of the working record	29
LIST OF TABLES	
Table 1. Binder pitch specifications	8
Table 2. Properties of Bituminous Coal Used for Extraction.	
Table 3. Catalyst properties.	
Table 4. NMR Spectrum Interpretation.	
Table 5. Conditions used to hydrogenate coal tar distillate.	
Table 6. Analyses of hydrogenated coal tar distillates.	
Table 7. Conversion of Kingwood coal summary.	26

1.0 EXECUTIVE SUMMARY

The purpose of this DOE-funded effort is to develop continuous processes for solvent extraction of coal for the production of carbon products. These carbon products include materials used in metals smelting, especially in the aluminum and steel industries, as well as porous carbon structural material referred to as "carbon foam" and other carbon composites.

Carbon products represent a multibillion dollar national industry, which is currently highly dependent upon imported feedstocks. The two primary feedstocks are petroleum distillation bottoms and coal tar. The latter is obtained as a byproduct from metallurgical coke ovens. Both are in short supply and must be imported to support North American industries such as metals smelting operations. Hence the development of environmentally sound methods to utilize coal-based feedstocks represents an opportunity to reduce imports of fossil fuel products, as well as to enhance the overall economics of production.

During this reporting period, highlights include the description of the continuous hydrogenation process, and optimization of the coal digestion process.

2.0 TECHNICAL

2.1 Pitches and Cokes from Coal Extraction

Solvent extraction of coal encompasses a wide range of processes or techniques all aimed toward bringing into solution a specific portion, or a majority, of the coal mass.^{1,2,3} The process most relevant in the current project is extractive chemical disintegration, known more commonly as direct coal liquefaction or, simply, coal extraction.^{5,6} Under these reaction conditions, coal can be converted into a pitch-like material suitable for binders and coke feedstock.^{7,8}

Invariably, direct liquefaction requires that the carbon-to-hydrogen atomic ratio of the coal decrease, which can be accomplished by a variety of means. The more extensively coal is hydrogenated, the more it appears pitch-like and the more anisotropic are the cokes derived there from. Large-scale plants constructed in Germany, before and during World War II, relied on high hydrogen pressure and temperature together in order to achieve high coal conversion to distillate products. Of equal significance was the development in catalysis for coal dissolution and hydrogenation. The effects of catalytic metal additives were an essential and critical part in these plant designs. 13

The United States government and private industry invested heavily in direct coal liquefaction technologies in the last quarter of the 20th century, in part, because of the embargo imposed by the Organization of Petroleum Exporting Countries (OPEC) in the 1970's. Similar to the earlier German work, the U.S. strategy employed severe temperatures and pressures. Successful demonstrations include the Exxon Donor Solvent (EDS), the Solvent Refined Coal (SRC) I and II, and the H-Coal processes. In all of these operations the criticalities of the solvent were paramount. One can easily make the argument that the solvent is more important than the coal in these circumstances. In order to convert coal into fuels boiling within the naphtha and gasoline range, up to 10wt% hydrogen weight percent hydrogen (based on dry, ash-free coal) could be added to the coal.

It has been known for a long time that cokes of high quality can be derived by the carbonization of coal extracts. In Germany, for example, around 1937, M. Pott and H. Broche developed a solvent extraction process with the goal to hydrogenate further the cleaned coal extract into fuel oil. In the Pott-Broche extraction, a bituminous coal was dried, ground, and slurried with a 4:1 mixture of tetralin and isomeric cresols. Typically, the slurry of coal and solvent was reacted between 425 °C to 430 °C and 1,400 psi to 2,200 psi for 60 to 90 min, which was adequate to dissolve approximately 75 percent of the coal mass. After solvent extraction, the slurry was hot filtered in batches through ceramic filters after which the filtrate was vacuum distilled to yield an extract with a melting point of about 200 °C, typically containing less than 0.05 weight percent ash.

The original intention was to produce an extract product suitable for further hydrogenation and upgrading into distillate fuels, but it was realized that the product was of such low ash that the coal extract was perfectly suitable as feeds for high quality cokes for use in carbon electrodes. Later it was discovered that the tetralin/cresols blends could be replaced with middle distillate cuts obtained from other hydrogenation processes, thus reducing the cost of the

coal extraction drastically. These middle oils contained partially hydrogenated aromatics (hydroaromatics) that facilely donate their hydrogen to the coal.

The National Coal Board (NCB) in England undertook a considerable program to convert coal by solvent extraction into fuels, binders, and coke feeds. ^{15,16,17} A process was developed to produce a needle coke substitute by dissolving one part bituminous coal in three parts anthracene oil (a coal tar distillate) at 410 °C for 1 hour. It is significant that no external hydrogen overpressure was applied yet high yields were attained. About 80wt% of the coal dissolved and the solution hot filtered to produce a filtrate containing 0.1wt% ash. The filtrate was fed to a delayed coking unit, the coking overheads recycled as solvent, and the coke processed into graphite electrodes. Industrial-scale tests conducted on the coal-based electrodes compared favorably to conventional cokes despite no attempts to optimize electrode formulations and processing. ¹⁸

The Center for Applied Energy Research (CAER) extracted coal with anthracene oil (perhaps comparable, the anthracene oil used in the CAER study probably was not the same as the NCB anthracene oil) between 200 °C and 450 °C for periods up to 3 hours. ¹⁹ Similar to the NCB process, no external hydrogen pressure was applied. Generally, within the range of process variables studied, extraction yields increased with temperature and reaction time. The extracts had softening point temperatures between 210 °C and 260 °C, too high for binder pitch, but suitable for melt spinning into carbon fibers. The important conclusion was that mild coal extraction can produce clean pitches of potential high value, the properties of which can be influenced by the selection of feed coals and process variables.

U. S. Steel had a process development unit for the production of pelletized formcoke. An integral component in the process was the catalytic hydrogenation of heavy coal oil to promote coal dissolution and product quality. The hydrogen content of a high-boiling coal tar was increased from 5.4 to about 7.0 percent over a fixed bed of supported Ni/W catalysts under 2,500pisg hydrogen and 400 °C. One pertinent aspect of the project showed that, after some adjustment of properties, a binder pitch made of coal extract (SRC-I material) can be successfully used to make formcoke of low volatile matter content and adequate strength and stability.

NETL-supported efforts at West Virginia University studied extractions of a range of bituminous coals between 350 °C and 450 °C. It was demonstrated that the coal extracts formed highly anisotropic cokes with low coefficient of thermal expansion in test graphite bars and that the extracts performed well as binder pitch and filler in laboratory carbon anodes. ^{21,22, 23,24} Control of the coal extract properties was affected by the extent or degree of hydrogen added to the original coal by using an active hydrogen transfer solvent tetralin and hydrogen pressure.

With the possible exception of the Pott-Broche process, the pitches made from coal using the NCB or CAER methods would not perform as well as conventional coal tar binders because the softening point temperature is too high. The high softening point is a result of the low level of hydrogenation during the extraction step; since no hydrogen pressure was used, no catalysis was involved, and the hydrogen donating ability of anthracene oil was limited. Softening points can be lowered by leaving more of the solvent components in the pitch, but this will decrease coke yield.

The procedure in the current project borrows key elements from established processes and what is known about the behavior of coal in solvent extraction. Since the production of fuels is not sought, only a low level of hydrogenation would be necessary to bring the coal into solution with the properties appropriate for blending with conventional coal-tar pitch. In our

approach, coal dissolution and hydrogenation are accomplished primarily by the ability of the solvent to transfer hydrogen to the coal, with no applied hydrogen pressure required in the extraction reactor. This effort uses hydrogenated coal tar distillate as a solvent, which is an improvement over the NCB and CAER processes for binder pitch development. It is anticipated that coal extract binders can be produced more economically by increasing the hydrogen content of the solvent in a separate hydrogenation step and then to use the hydrotreated solvent with coal in the extraction reactor.

2.2 Binder Pitch Requirements

Binder pitch must meet certain minimum specifications in order to perform satisfactorily. GrafTech has provided target values for binder pitch used in their applications, which are shown in Table 1. Additional requirements include storage stability, additive sensitivity, bake structure, in-stock coking value, polyaromatic hydrocarbon characterization, and, ultimately, final graphite properties.

Table 1. Binder pitch specifications

Viscosity @ 160 °C	20 Poise Maximum
Mettler Softening Point	110-115 °C
Ash Content	<0.5 wt%
Modified Conradson Carbon	55 wt% Minimum
Glass Transition Temperature, Tg	40 °C Minimum
Quinoline Insoluble, QI	4-16 wt%
Size of QI	25 µm Maximum
Mesophase Content	0 %
Sulfur Content	Low
Penetration Temperature	165 °C Maximum
Flash Temperature, Cleveland Open Cup	> 200 °C

3.0 EXPERIMENTAL

3.1 Coal Selection

The bituminous coal used for extraction was selected based on the findings of Stansberry et al.²⁵ The coal contains a large proportion of vitrinite with a reflectance of about 1.1, exhibits extensive thermoplastic behavior, and readily dissolves in specific solvents, such as N-methyl pyrrolidone (NMP). These coal characteristics are also conducive to direct liquefaction.^{16,26}

Table 2 lists some of the salient coal properties. The coal, located within 30 miles of the campus, was collected in coarse form at the mine site and transported to West Virginia University in ten 55-gallon steel drums.²⁷

Table 2. Properties of Bituminous Coal Used for Extraction.

Table 2. I Toperties of Ditummous Coal Oscu for Extraction.				
Kittanning				
Preston/WV				
1.08				
imate, %dry				
33.17				
57.91				
8.92				
nental, %dry				
77.44				
4.95				
1.18				
1.58				
14.85				
1.52				
Petrographic Composition, %vol				
67.5				
4.2				
13.9				
14.4				

The as-received coal contained about 25-35wt% water. The moisture content was lowered to 1-2wt% by spreading the coal 5-inches deep in three 26"x38" metal trays and inserting the trays into a drying oven set to 70-90 °C for about 8 hours. Initial screening of the material showed that about 5% of the coal was on the order to 3-4 inches in size. About 85% of the coal was between ¼" and +6 mesh. It took about four eight-hour drying cycles to process one 55-gallon drum.

The 3-4 inch coal was ground in a jaw crusher to 8 mesh top size and combined with the remaining fractions. Screening removed any +1/4 inch material for particle size reduction in a jaw crusher to within 8 mesh. This material was then sized to 8 mesh, 20 mesh, 65 mesh, 150 mesh, and pan. All coal between 8-20 mesh was passed through a roll mill. The roll mill is carefully adjusted to crush coal to just below 20 mesh. The materials were screened again to collect any material above 20 mesh for further processing. All coal crushed below 20 mesh was sealed in 55 gallon drums and stored until ready for use, as seen in Figure 1.



Figure 1. Dried and crushed Kingwood coal ready for storage.

3.2 Solvent Selection

Clendenin examined both petroleum and coal derived liquids for coal extraction.²⁸ Although some of the petroleum derivatives showed promise in extraction efficiency, the most effective and processable solvents were coal tar distillates that were hydrogenated prior to contacting with coal, in accordance with the findings of other researchers.¹⁰ Therefore, coal tar distillates were chosen as the solvent of choice. Although the liquids are dependent upon the recovery coke oven, whose long-term existence in the U.S. is uncertain, the liquids would more than likely succeed in the West Virginia University method. Thus, based on these considerations, Koppers Industries was requested to supply six 55-gallon drums of coal tar distillate from their Stickney plant, which were delivered to the laboratories at West Virginia University.

3.3 Catalytic Solvent Hydrogenation

A Ni/Mo on alumina catalyst was supplied by Criterion. Properties of the catalyst are shown in Table 3. A basket was constructed from 316 stainless steel materials in order to suspend about 2.39 lbs of catalyst within the solvent medium of the 5-gallon stirred reactor. The basket was constructed in such a way to allow for solvent to flow through the screen, which held the catalyst particles securely. The solvent flowed from inside to outside of the basket, with the reactor stirrer set in the middle of the basket. The basket was propped up on legs to allow the solvent to flow under the basket, and the basket was short enough to allow for solvent to flow over the top of the basket when the agitator was activated, see **Figure 2**. The finished basket fit into the reactor snuggly, and allowed for the reactor thermowell to lower into the reactor properly.

Table 3. Catalyst properties.

Particle shape	Trilobe
Nominal pellet size (mm)	1.3
Ni, %dry	3.0
Mo, %dry	13.0
Surface area, m ² /g	155
Pore volume, cm ³ /g	0.45

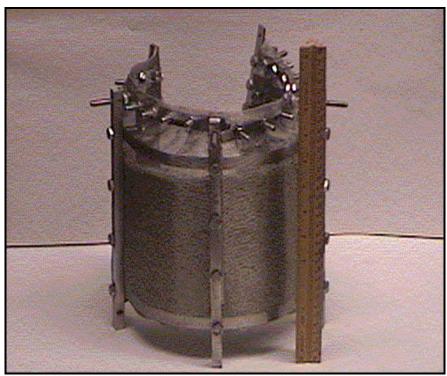


Figure 2. Completed and loaded catalyst basket

The catalyst is delivered in the form of metal oxides. The most active state of these metals for hydrogenation is the sulfide. Therefore, a sulfiding step was necessary before any solvent treatment can begin. The sulfiding step was done according to the guidelines provided by Criterion using dimethyl sulfoxide at a temperature around 210 °C. After sulfiding, the reactor was vented and purged with nitrogen, and kept sealed and unexposed to the atmosphere until needed.

Several batches of hydrogenated coal tar were prepared at different levels of hydrogen addition. Hydrogenation was accomplished by transferring 1.3kg of the coal tar distillate through an opening in the top of the reactor lid. The reactor was plugged, mixing commenced, and reactor furnace activated. Various temperatures, residence times, and hydrogen pressures were explored. In all cases, the reactor would not be pressurized with hydrogen gas until the reactor had first reached operating temperature. Following hydrogenation, the solvents were thoroughly characterized and correlations established. Each hydrogenated solvent was tested for extraction efficiency with coal and the extract solutions characterized. The results of the batch coal extractions were used to establish operating conditions for the Coal Refining Unit in scale-up operations.

The 5-gallon batch hydrogenation reactor was converted into a semi-continuous system by the installation of a high-pressure diaphragm pump to convey feed coal tar distillate at a controlled rate and an air-driven booster pump to deliver hydrogen gas at constant pressure. Figure 3 is a schematic diagram of the unit.

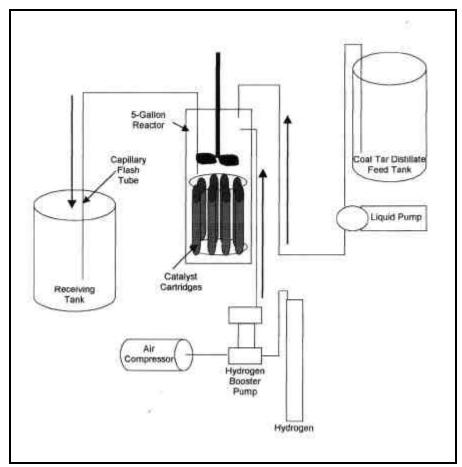


Figure 3. Flow diagram of the continuous hydrogenator.

During the course of batch solvent hydrogenation a rapid change in the solvent's FTIR aromaticity ratio was detected. The detection led to opening of the reactor for inspection where it was observed that the screen of the basket had sagged and had then been torn by the impeller. Despite the fact that the catalyst pellets had fallen to the bottom of the reactor and were, therefore, not availed to full mixing phenomena, catalytic hydrogenation was still evident, albeit at a lower level.

The design of the catalyst support structure was changed to a modular, tubular catalyst containment system. Stainless steel screen was cut and rolled into tubes 8 inches long and 1.5 inches in diameter. One end of the tube was folded over and held together by stitching with stainless steel wire. The Ni/Mo catalyst was poured into the tube and the end sealed as described. Eight tubes were assembled and placed inside the body of the reactor. Two metal coils acted as springs to hold the tubes against the wall and stainless steel rings secured the tubes from tipping. Figure 4 shows the configuration of the catalyst system. About 4 lbs of catalyst were used.



Figure 4. Top view of catalyst containment system inside of the 5-gallon semi-continuous hydrogenator

Rather than dimethyl sulfoxide, carbon disulfide was chosen as the material to convert the metal oxide to its sulfide form because this sulfiding agent is more volatile and the reactor could be purged more readily. Two hundred mL (173 mL required for stoichiometric conversion to the sulfides) of carbon disulfide were added to the reactor and heated to 220 °C for one hour. The reactor was cooled to about 150 °C, vented and purged with nitrogen gas.

Several batches of coal tar distillate hydrogenations confirmed the reliability of the new design. Spectroscopic analysis (FTIR) affirmed that the solvent was hydrogenated at the desired level.

Considerable thought was given to the means by which the hydrogenated products can be removed continuously from the reactor at a controlled rate while under high pressure and temperature. The system must be reliable, robust, and very simple, yet be able to maintain the solvent inside the reactor for the proper residence time. To meet all of these requirements, stainless steel capillary tubes of specific diameter were examined.

A few simple experiments were undertaken to determine flow rates over a range of pressures. Common grocery-store corn oil was chosen to simulate the feed coal tar distillate. A 1L stainless steel cylinder with valves on either end was tare weighed and filled with a known amount of corn oil. The vessel was pressurized with nitrogen and the other end opened rapidly to allow the corn oil to escape. A stop watch was used to record the time period between valve opening and when the vessel became emptied. All experiments were performed at room temperature with the tube uncoiled and straight. Figure 5 shows the measured flow rates through 1/8 inch OD tubing. In this particular instance the inside diameter was not determined. Obviously the flow rate was much too high, as anticipated, since the residence time of the fluid in the reactor should be on the order of 1 to 2 hours, yet the results demonstrated that the principle was sound.

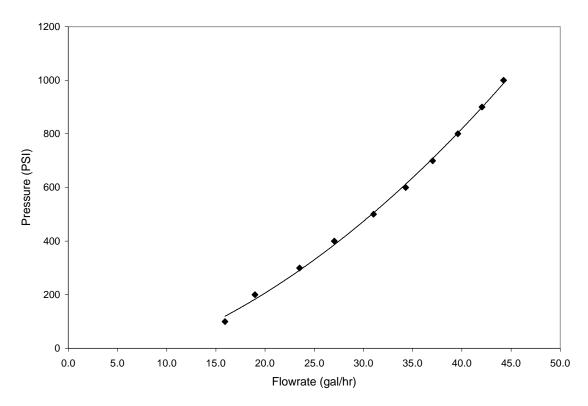


Figure 5. Flow rate of corn oil through 1/8 inch tube 10 ft long as a function of pressure.

Flow was also studied in a five foot section of tubing with 0.04 in ID. The flow rate of the oil through the 0.04 in ID capillary is shown in Figure 6. Flow rate with water was also determined for comparison with the oil.

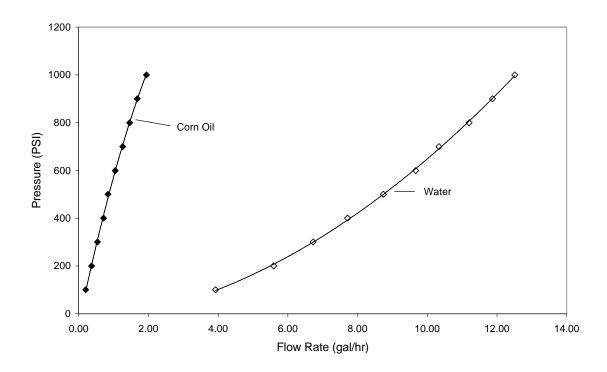


Figure 6. Flow rate of fluids through 5 ft section of 0.04 in ID stainless steel tubing.

Thus, the flow through the 0.04 in ID tube suggested that the flow rate would still be too great. Thus, the flow through the 0.02 in ID tube was determined by attaching the capillary to the 5-gal reactor and bringing the coal tar distillate temperature up to $275\,^{\circ}\text{C}$. The reactor was pressurized with nitrogen gas between 500 and 1000 psi and flow rates determined by measuring the mass of coal tar distillate escaping as a function of time. Figure 7 compares these results with other conditions.

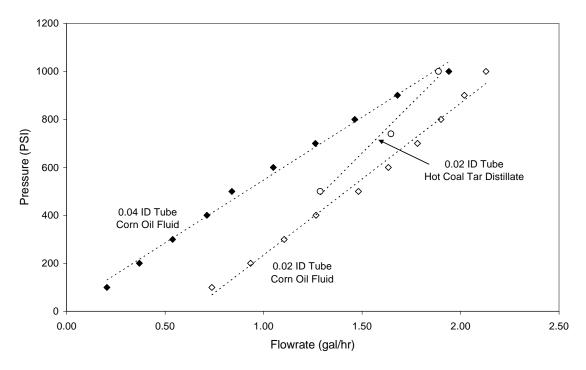


Figure 7. Flow rate of coal tar distillate through 0.02 in ID x 5 foot length capillary tube.

At 1000 psi the flow rate of the coal tar distillate is about 2 gal/hr. At the operating pressure of the hydrotreater (1500-1800 psi) the flow rate would still be excessive with this setup. Two of the 5 ft sections of the 0.02 ID capillaries were connected to make a 10 ft tube. Flow rates were determined using the coal tar distillate between 1500-1800 psig nitrogen and 350 °C to simulate more closely actual hydrogenation conditions. Figure 8 shows the results, where it can be seen that the desired flow rate is within the operating pressure to be used.

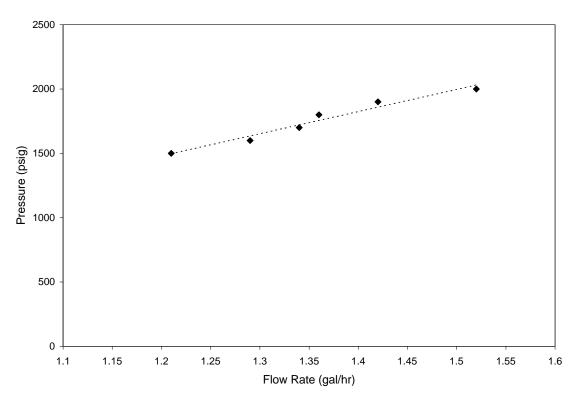


Figure 8. Flow rate of coal tar distillate through capillary tubing (0.02"ID X 10') at 350 °C.

3.4 Coal Extraction

3.4.1 Evaluation of Hydrogenated Solvent in 1-gallon Batch Trials

Solvent extraction efficiency was determined in batch 1-gallon bolted-closure autoclaves. The coal tar distillate was hydrogenated to different levels. In all coal extraction reactions 1,900g of solvent were placed along with 730g of dried coal (2.6:1 solvent-to-coal ratio). The reactors were purged of air by nitrogen. Any pressure developed during extraction was because of solvent vapor and reaction products. Different temperatures and reaction periods were examined. After extraction, the reactor was cooled to approximately 50 °C to 70 °C, vented of gases, and carefully opened. The products from these reactions were recovered using a vacuum line and an Erlenmeyer flask with a sidearm. Once the reactor had been emptied into the flask, the contents of the flask were reheated in an oven set to ~100 °C, and then the product was transferred to plastic, pre-weighed centrifuge bottles. The bottles were weighed on the Mettler scale and then placed into the Thermo Electron Corporation PR700M Centrifuge and spun for 30 minutes at 4000 rpm and 39 °C, which was the maximum temperature allowable for operation of the centrifuge. After centrifugation, the liquid product was decanted out of the centrifuge bottles into a glass, pre-weighed bottle and then the product mass was determined. This was the effective converted portion of the coal. The residue from the centrifugation was washed with warm tetrahydrofuran (THF) and filtered to remove any entrained solvent and product still left in This was done in an effort to close the mass balance and to determine coal conversion. The THF-insoluble portion left after filtration was dried in a vacuum oven and then weighed to determine unconverted coal. The THF was stripped from the soluble portion using a

rotary evaporator and the extract was also vacuum dried overnight. The conversion was calculated according to Equation 1.

% Coal Conversion =
$$\underline{[(Mass Dry Coal) - (Mass THF Insolubles)]} X100$$
 (1)
(Mass Dry Coal)

3.4.2 Coal Refining Unit (CRU) Operation

The Coal Refining Unit is capable of processing 40 lbs/d of coal resulting in about 35 lbs/d of extract. Sixty pounds of hydrotreated coal tar distillate would be mixed with 20 pounds of coal (3:1 solvent:coal ratio) in a slurry tank that is warmed to about 60 °C. The ratio of solvent to coal is slightly higher in the CRU unit than the 1-gal batch reactors to make the solutions more fluid and processable. The slurry tank was lifted by a winch and cable and the mixture fed into the 10-gallon feed vessel by gravity.

Figure 9 is a schematic representation of the system. The stirred 10-gal feed tank was heated to 350 °C to digest the coal partially to lessen the likelihood of blockage. Nitrogen pressure was applied to the 10-gal feed tank to maintain a pressure differential between it and the 1-gal extraction reactor of around 100 psig. The stirred 1-gal extractor reactor was preheated to 425 °C before both the high pressure feed and let down pumps were activated. The pumps were programmed to deliver a flow rate of 1gal/hr of solution. Immediately after the pumps were activated the valve below the feed tank was opened to initiate the extraction process. The products of extraction flowed into a holding tank. The coal extract solution was cooled while in the holding tank and transported to the Sharples centrifuge for solids removal.

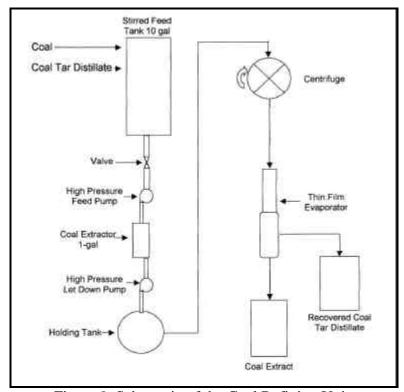


Figure 9. Schematic of the Coal Refining Unit.

3.5 Solid Separations

The coal solution from the Coal Refining Unit was cleaned of solids in a Sharples continuous decanter-type centrifuge. The holding tank can readily be removed from the CRU and attached to the centrifuge system to serve as a feed tank. Heater bands kept the temperature of the coal solution at about 100 °C in order to reduce viscosity. A separate tank was filled with about 5 gallons of coal tar distillate and heated to approximately 120 °C. The hot solvent was fed to the centrifuge through a metering pump and served to preheat the centrifuge and associated plumbing. A valve was switched from the hot solvent tank to the coal solution tank to begin centrifugation. Several flow rates of coal solution through the centrifuge were examined to determine the effects of residence time on ash content. Samples of centrate (over flow portion) were collected, vacuum distilled to remove solvent, and ash content determined. In all cases the centrifuge generated 3000 G of force.

Filtration of the coal solutions was also investigated. Three filtration devices with capacities of several gallons of solution per hour were tested for separation efficiency. The first unit was designed and assembled in house. It consisted of an outer steel cylinder about 22" ID x 24" L into which a perforated basket was inserted. Two-micron particle retaining filter paper, held in place by a compression ring, lined the perforation. A lid was bolted to the top of unit. Provisions to pour the coal solution, pressurize the system with nitrogen, and collect the filtrate in a tank were made.

The second filtration system was purchased from a commercial vendor. The unit is a vertical steel canister with an internal screen. A filter bag with a 1 μ m particle retention rating was fitted around the screen and attached with a metal band. The third filtration unit is similar to the second except the screen and filter bags were replaced with four 2"OD x 24"L 1 μ m glass fiber or 0.2 μ m sintered-metal cartridges. This device is commercially available and became the preferred system for coal solution purification.

3.6 Solvent Recovery

After solids removal, evaporation of the solvent from the coal solution was accomplished using a Pfaudler wiped-film evaporator with a surface area of 1.4 ft². The unit is heated with hot circulating oil maintained at about 290 °C under a vacuum of 29 in Hg. The coal solution was contained in a stirred heated vessel and metered into the evaporator by a Zenith gear pump. Flow rates of coal solution from several liters per hour to less than one liter per hour were examined to determine the effects of evaporation conditions on the softening point of the extract.

4.0 RESULTS

4.1 Characterization of Catalytic Hydrogenation of Coal Tar Distillate

The feed coal tar distillate and its hydrogenated derivatives were characterized by simulated boiling point distribution, elemental analysis, proton nuclear magnetic resonance, and Fourier-transform infrared spectroscopy. For NMR, samples of coal tar distillate were dissolved in carbon disulfide with tetramethylsilane as the reference compound. Neat samples of solvent

for infrared spectra were recorded using an attenuated total reflectance cell. **Figure 10** is a typical ¹H NMR spectrum for one of the hydrogenated coal tar distillates and **Figure 11** is an expansion of the aliphatic signals. ²⁹ **Figure 12** shows the infrared spectral region associated with carbon-to-hydrogen aliphatic and aromatic stretching modes for the coal tar distillate. ³⁰ Note that it is apparent that hydrogenation increases the relative area of the aliphatic region in the infrared.

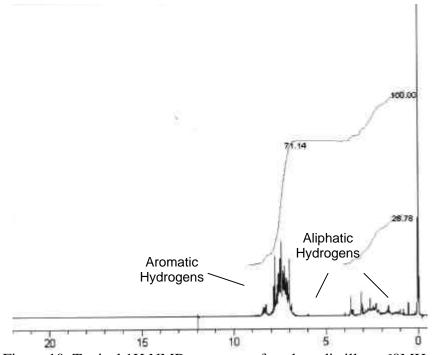


Figure 10. Typical 1H NMR spectrum of coal tar distillate, 60MHz.

Table 4. NMR Spectrum Interpretation.

ppm	Structure	Symbol		
5.5-9.0	Aromatic & Phenolic	H_{A}		
4.7-5.5	Olefinic	H_{O}		
3.3-4.5	Fluorene-type Hydrogen	H_{F}		
2.0-3.3	Hydrogen alpha to Ring	H_a		
1.0-1.6	Methylene & Methyl beta to Ring	$H_{\mathcal{B}}$		
0.5-1.0	Methyl gamma & Further to Rng	$\mathrm{H}_{?}$		

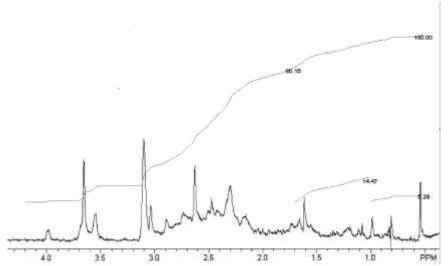


Figure 11. 1H NMR spectrum of coal tar distillate aliphatic region, 60MHz.

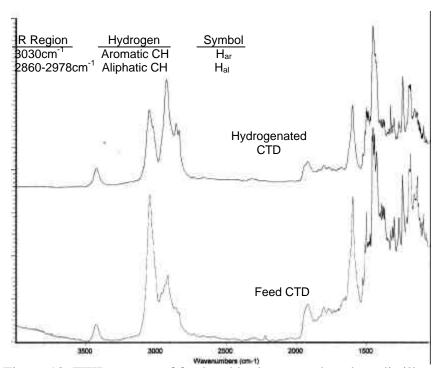


Figure 12. FTIR spectra of feed and hydrogenated coal tar distillate.

Several reaction conditions were examined to determine the effects of hydrogenation. Table 4 identifies the conditions.

Table 5. Conditions used to hydrogenate coal tar distillate.

Hydrogenation Level	Run ID	Conditions	
Level 2	Run I032	350 °C, 500 psig Hydrogen, 1 Hour	
Level 3	Run I034	375 °C, 750 psig Hydrogen, 1 Hour	
Level 4	Run I035	275 °C, 1320 psig Hydrogen, 1 Hour	
Level 5	Run I049	275 °C, Repressurized Hydrogen, 1 Hour	
Level 6	Run I062	275 °C, Repressurized Hydrogen	
Level 7	Run I065	300 °C, Constant H 1000 psig, 1 Hour	
Level 8	Run I069	325 °C, Constant H 1800 psig, 3 Hour	
Level 9	Run I071	350 °C, Constant H 1800 psig, 2 Hour	

Table 6 lists the elemental composition and the ratio of the integrated areas of $H_A/(H_{a} + H_{\beta} + H_{?})$ and H_{ar}/H_{al} by ^{1}H NMR and FTIR, respectively. The more either ratio decreases the more aliphatic the coal tar distillate becomes. The symbols used to define the hydrogen types were shown in **Figure 10** and **Figure 11**.

Table 6. Analyses of hydrogenated coal tar distillates.

Tuble of finally sets of hy all offended court and distinutes.							
					C/H		FTIR
Material	C	Н	N	S	Atomic	¹ H Ratio	Ratio
Feed CTD	93.05	6.27	1.04	0.59	1.236	5.93	1.395
Level 2	93.11	6.35	1.16	0.36	1.222	4.99	1.154
Level 3	92.68	6.39	0.84	0.24	1.209	4.56	1.140
Level 4	92.37	6.40	0.82	0.22	1.202	4.46	1.136
Level 5	92.30	6.47	0.77	0.15	1.189	3.90	1.000
Level 6	92.53	6.25	1.45	0.78	1.234	3.38	1.100
Level 7	93.31	6.39	1.73	0.78	1.217	2.30	0.973
Level 8							0.773
Level 9							0.551

Correlations among the hydrogenation conditions, C/H atomic ratio, proton NMR, and FTIR data are reasonably good. For example, **Figure 13** shows how the FTIR ratio changes for the level 8 and 9 hydrogenations as a function of time. Also included are the results for levels 2 through 7, the conditions of which are listed in Table 5. Figure 14 shows that the boiling point distribution does not change dramatically with hydrogenation.

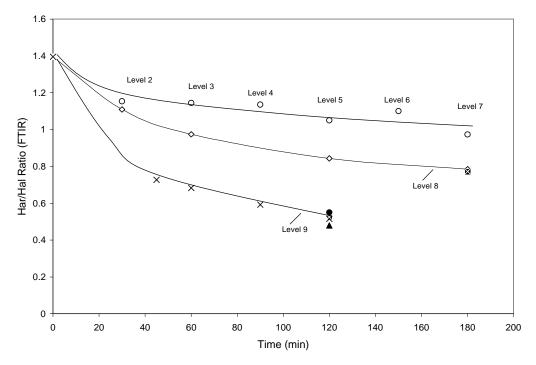


Figure 13. Change in FTIR ratio as a function of hydrogenation conditions.

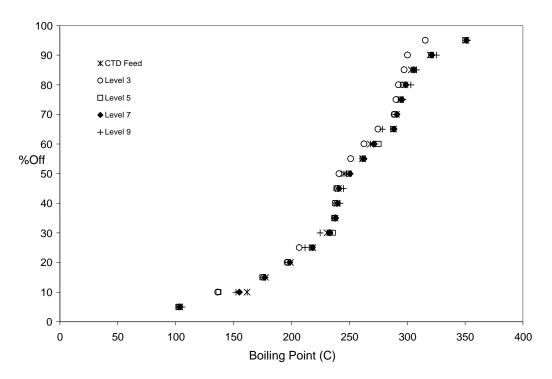


Figure 14. Boiling point distribution of hydrogenated coal tar distillate.

4.2 Results of 1-Gallon Batch Reactions

The effectiveness of the coal tar distillates for coal extraction was determined in batch 1-gal reactors, as described in section 5.3.1. The solvent tetralin was used as a control. The effects of extraction temperature, time, and solvent composition on processing performance were observed in order to establish conditions to be used in the Coal Refining Unit. Although hydrogenation did not appear to alter boiling point distribution profiles, there were noticeable differences in pressure during the extraction period. For example, Figure 15 shows that process pressure increases with the level of solvent hydrogenation as well as with time. Tetralin has a normal boiling point of about 210 °C, thus its vapor pressure is high compared to the coal tar distillates. It is possible that the higher pressure generated during extraction with the hydrogenated solvent could reflect its greater activity during upgrading of the coal molecules. Figure 16 shows the effects of solvent composition and extraction temperature on process pressure. It is important to the economics of the process that pressures are kept as low as practicable.

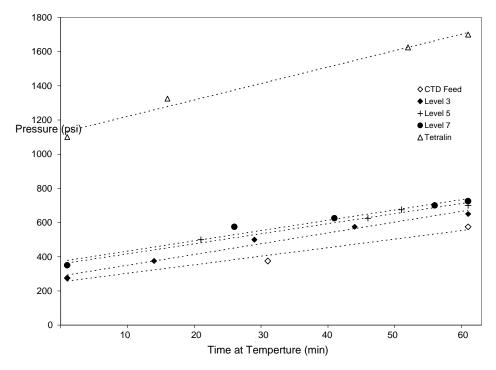


Figure 15. Changes in pressure versus time at reaction temperature for hydrogenated coal tar distillates in the extraction of Kingwood coal. Conditions: 425 °C, autogenous pressure.

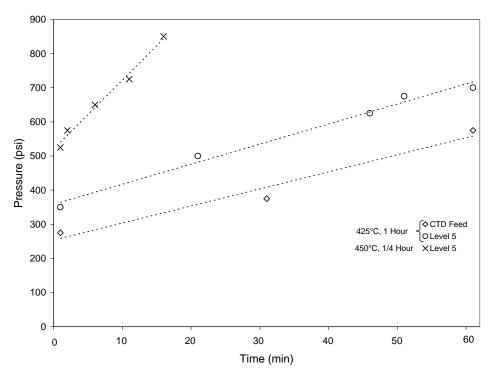


Figure 16. Changes in pressure versus time and temperature for hydrogenated coal tar distillates in the extraction of Kingwood coal, autogenous pressure.

Table 7 summarizes the conversion of coal for a range of conditions and solvents. All conversions were over 80% except for the two runs at 450 °C and 15 minutes. The lower extraction might because of the shorter residence time, but it is probable that the hydrogen donating capability of the solvent is expended rapidly under these conditions, leading to retrogressive reactions.

Viscosity of the coal solutions following centrifugation (centrate) was determined. Low viscosity simplifies pumping and solids-removal operations. The results in Figure 17 indicate at above 60 °C all solutions exhibited similar viscosity, with the more highly hydrogenated solvents being less viscous at the lower temperatures.

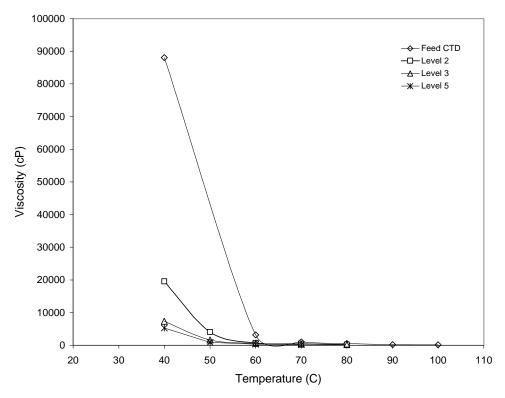


Figure 17. Viscosity versus temperature of select coal solutions.

Table 7. Conversion of Kingwood coal summary.

Solvent	Conditions	Conversion, wt%
Feed CTD	425 °C, 1 Hour	82.5
Level 2	425 °C, 1 Hour	84.7
Level 3	425 °C, 1 Hour	82.4
Level 4	425 °C, 1 Hour	82.5
Level 4	450 °C, ¼ Hour	75.7
Level 5	425 °C, 1 Hour	80.5
Level 5	450 °C, ¼ Hour	74.5
Level 6	425 °C, 1 Hour	87.9
Level 7	425 °C, 1 Hour	86.3
*Level 8	425 °C, 1 Hour	83.5
*Level 9	425 °C, 1 Hour	86.6
Tetralin	425 °C, 1 Hour	91.9

^{*} Conversion determined using tubing mini reactor.

The coal solutions were vacuum distilled using common laboratory glassware and a vacuum pump. Softening point temperatures were measured as a function of distillate material removed, as shown in Figure 18. Note more of distillate is recovered as the degree of hydrogenation increased to achieve an equivalent softening point. For example, about 43% of

the distillate using the unhydrogenated coal tar would have to be removed to produce a pitch with a 100 °C softening point while about 53% would have to be distilled using the level 5 solvent. This implies that more solvent could be recovered for recycle using highly hydrogenated solvents.

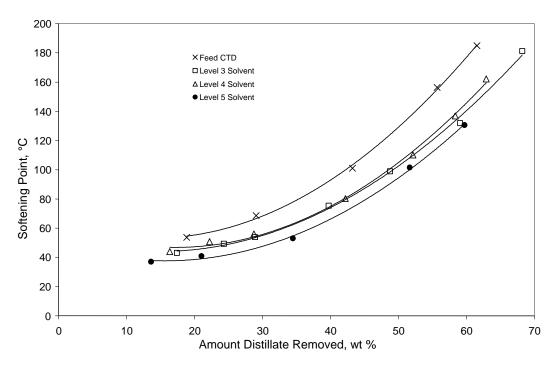


Figure 18. Softening point of coal extracts versus amount distillate removed. Extraction conditions: 425 °C, 1 hour.

4.3 Production of Coal Extract in the CRU

Difficulty was encountered with blockage at the opening to the entrance of the highpressure feed pump. Several attempts were made to unblock the feed pump before one successful CRU extraction was completed. This product was processed by centrifugation.

The centrifuge is manufactured by Sharples and is a decanter type. In all trials, the unit generated 3000 times the force of gravity (3000G). The centrifuge was pre-heated by passing about 5 gallons of 100 °C coal tar distillate to prevent the precipitation of the coal solution and to maintain low viscosity. Considerable odors and vapors emanated during this process and the centrifuge had to be shut down until an enclosure was fitted around the unit and an exhaust system installed. The exhaust fumes first past through a canister of activated carbon to ensure complete removal of organic vapors.

After pre-heating, the 100 °C coal solution was fed to the centrifuge by a metering pump. Various flow rates from about 18gal/hr to less than 1gal/hr were investigated and the centrates analyzed for ash content. Ash contents were high (above 3wt%) at the higher flow rates but only moderately low (about 1wt%) at very low flow rates.

It became apparent that the centrifugation unit was not going to produce coal extracts with ash contents 0.5wt% or less. The centrifugation step was replaced with a filtration unit, Figure 19. Filtration of the coal solutions directly from the 10-gallon reactor through 1-2µm

glass fiber cartridges or sintered metal tubes became the preferred method of solids removal. Ash contents below 0.4wt% in the coal extract pitch can routinely be obtained.

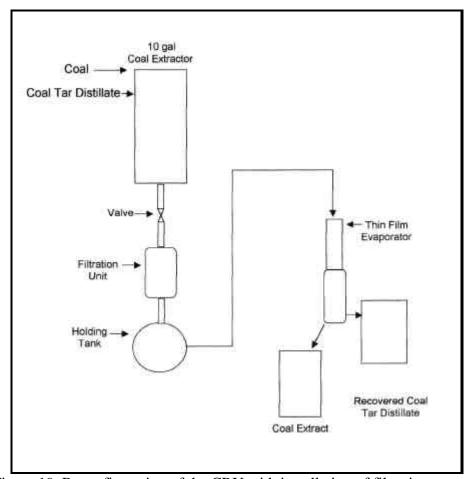


Figure 19. Reconfiguration of the CRU with installation of filtration system.

The cleaned coal solutions were metered from a heated tank to the Pfaudler thin film evaporator. The unit was heated by circulating hot oil at 290 °C at a vacuum of 29 in Hg, which were the maximum process variables achievable. Feed rates between 4gal/hr to a few tenths gal/hr were tried and softening point temperature of the concentrate (coal extract) measured. Acceptable softening points can only be attained at very low through puts.

Because the production of evaporated coal solution was unacceptably slow, the CRU was reconfigured again. To test whether vacuum distillation would provide the necessary through put, the thin film evaporator was replaced with a 20gal vacuum retort, as shown schematically in Figure 20.

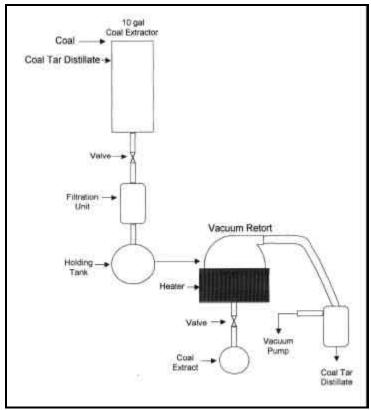


Figure 20. Current configuration of the CRU with the installation of the vacuum retort.

A trial run (CRU #031805) with this configuration, from coal dissolution to distillation, was successfully completed without any difficulty. Samples of coal extract could be withdrawn from the vacuum still through a sealed port to monitor softening point temperature as distillation progressed. The heat to the still was removed once a softening point temperature of $110\ ^{\circ}\text{C}$ was measured and the system allowed cooling to ambient conditions while still under vacuum.

About 10 lbs of the product was sent to GrafTech for characterization. WVU determined the ash content of the coal extract to be 0.57 wt%, slightly above specifications. Also, the Mettler softening point temperature is 124.1 °C, nearly 10 °C higher than specified. The softening point temperature was higher than expected because the vacuum still continued to function after the heat was removed.

References.

_

¹ Lowry, H. H. *Chemistry of Coal Utilization*; John Wiley & Sons; New York, 1945; Volumes I & II.

² Van Krevelen, D. W. Coal: Typology, Physics, Chemistry, Constitution; Elsevier, New York, 1993.

³ Dilo Paul, A. *The Solvent Extraction of Coal*; DOE; September 30, 2002.

- ¹¹ Wu, W. R. K. and Storch, H. H. *Hydrogenation of Coal and Tar*, U.S. Bureau of Mines, Bulletin No. 633, 1968.
- ¹² Gordon, M. K. Report on the Petroleum and Synthetic Oil Industry of Germany, published for the Ministry of Fuel and Power, London, His Majesty's Stationary Office, B10S Overall Report No. 1, 1947.
- ¹³ Donath, E. E. and Hoering, M. Fuel Processing Technology, 1, 3-20, 1977.
- Lowry, H. H. and Rose, H. J. Pott-Broche Coal-Extraction Process and Plant of Ruhrol G.M.B.H., Bottrop-Welheim, Germany, U. S Bureau of Mines, Information Circular I.C. 7420, 1947.
- ¹⁵ Kimber, G. M. Graphitising Carbons from Coal Via Solvent Extraction: Effects of Processing Conditions on Product Quality, 13th Biennial Conference on Carbon, pg. 316-371, Irvine, CA, 1977.
- ¹⁶ Clarke, J. W., Kimber, G. M., Rantell, T. D., and Shipley, D. E. Reactivity of British Coals in Solvent Extraction, Coal Liquefaction Fundamentals, ACS Symposium Series 139, 1980.

⁴ Oele, A.P., Waterman, H.I., Goedkoop, M.L., and Van Krevelen, D.W., Fuel, 30, 169, 1951.

⁵ Schindler, H. D. *Coal Liquefaction a Research Needs Assessment*. DOE Coal Liquefaction Research Needs Panel Assessment. Final Report, Vol. II., under contract DE-AC01-87ER30110, 1989.

⁶ Probstein, R. F. and Hicks, R. E. *Synthetic Fuels*; McGraw-Hill Book Company, New York, 1982.

⁷ Stansberry, P. G., Zondlo, J. W., and Stiller, A. H., Chapter 7, *Coal-Derived Carbons*, in Carbon Materials for Advanced Technologies, T. D. Burchell, ed., Pergamon Press, New York, NY, 1999.

⁸ Donath, E. E. *Hydrogenation of Coal and Tar* in Chemistry of Coal Utilization, Supplementary Volume, Chapter 22, John Wiley & Sons, Inc., New York, 1963.

⁹ Merrick, D. Coal Combustion and Conversion Technology; Elsevier, New York, 1984.

¹⁰Bockrath, B. C. Chemistry of Hydrogen Donor Solvents, Coal Science, Vol. 2, Academic Press, New York, 1983.

¹⁷ Kimber, G. M. A History of Coal Liquefaction in United Kingdom, 1967-1992, ACS Div. Fuel Chem., Vol. 42, No. 1, pg. 308-312, 1997.

¹⁸ Kimber, G. M., Brown, A., and Kirk, J. N. High Temperatures-High Pressures, <u>13</u>, pg. 133-137, 1981.

- ²² Stansberry, P. G., Zondlo, J. W., Andrews, R. J., and Withers, J. C., *Development of Carbon Fiber Precursors from Coal Extracts*, American Chemical Society, Fuel Chemistry Division Preprints, 2001.
- ²³ Seehra, M. S., Pavlovic, A. S., Babu, V. S., Zondlo, J. W., Stansberry, P. G., and Stiller, A. H., Carbon, 32, 431-435, 1995
- ²⁴ See, for example, the series *Chemistry of Coal Utilization*, Vol. I and II, Supplementary Volume, and Second Supplementary Volume.
- Stansberry, P. G., DeVanney, K, and Gray, R. J., Characterization of Coal Solvent Extraction Processes Using Petrographic, Chemical, and Physical Methods, Final Report to DOE under contract DE-FC26-98FT40350, 2004.
- ²⁶ Given, P. H., Spackman, W., Davis, A., and Jenkins, R. G. Some Proved and Unproved Effects of Coal Geochemistry on Liquefaction Behavior with Emphasis on U. S. Coals, Coal Liquefaction Fundamentals, ACS Symposium Series 139, 1980.
- ²⁷ Rick Craig, President, Kingwood Mining Company, LLC, RR 1 Box 294C, Newburg, WV 26410, June 23, 2004.
- ²⁸ Clendinen, L. M. *Development of Coker Feeds from Aromatic Oil and Bituminous Coal Digests*, M.S. thesis, Department of Chemical Engineering, West Virginia University, 2004.
- ²⁹ Bartle, K. D. and Jones, D. W. *Nuclear Magnetic Resonance Spectroscopy*, Chapter 23 in Analytical methods for Coal and Coal Products, Vol. II, Academic Press, New York, 1978.
- ³⁰ Speight, J. G. *Assessment of Structures in Coal by Spectroscopic Techniques*, Chapter 22 in Analytical methods for Coal and Coal Products, Vol. II, Academic Press, New York, 1978.

¹⁹ Berk.

²⁰ Miller, C. T. Clean Coke Process: Process Development Studies, Final Report Vol. II, DOE under contract No. EX-76-C-01-1220, 1978.

²¹ Stansberry, P. G., Zondlo, J. W., and Wombles, R. H., Light Metals, 581-585, 2001.