QUARTERLY TECHNICAL PROGRESS REPORT

AND KEY PERSONNEL STAFFING REPORT

NUMBER 10

**PRODUCTION AND SCREENING OF CARBON PRODUCTS
PRECURSORS FROM COAL**

CARBON PRODUCTS CONSORTIUM

CONTRACT NO. DE-AC22-95PC94063--12

REPORTING PERIOD:

April 1, 1997 to June 30, 1997

Submitted to:

**AAD Document Control Center
U.S. Department of Energy
Pittsburgh Energy Technology Center
PO Box 10940, MS 921-143
Pittsburgh, PA 15236-0940**

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**July, 1997
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1. Executive Summary

The U.S. DOE Office of Fossil Energy is interested in the coproduction of coal liquids and carbon precursors. The DOE project manager has arranged for Hydrocarbon Technologies, Inc. (HTI) to provide the WVU researcher team with samples of stage-one, mildly hydrogenated coal liquids. Distillation and extraction process are being developed which produce a potential carbon anode precursor from the HTI material. The results obtained thus far seem to indicate that a coal-derived, pitch-like material can be developed from the HTI liquefaction product after distillation to remove liquefaction solvent and NMP extraction to eliminate mineral matter. The physical properties of the liquid are not unreasonable when compared to other types of available pitches. The molecular arrangement and the optical structures present in the green coke of the de-ashed coal liquid may be suitable for the production of anodes for aluminum manufacture, but more testing needs to be conducted to confirm this.

2. Processing of HTI Samples

Vivek Pradhan of Hydrocarbon Technologies, Inc. (HTI) has prepared a quantity of mildly hydrogenated coal liquid (>100 pounds). No processing conditions, coal and catalyst type, or any other information are available at this time. However, the material is identified as *0-6 bottoms material collected during run 227-102 Periods 17, 18, 19, and 20* (sic).

The coal-derived material is a thick viscous liquid at room temperature. West Virginia University (WVU) conducted preliminary characterization of the product. The results are presented in the Table 1 below.

Table 1. . . . Characteristics of as-received HTI coal liquid.

Softening Point, °C	Room Temperature
Density, g/cm ³	ND
Coke Yield, wt%	38.8
THF Insolubles, wt%	13.7
Toluene Insolubles, wt%	16.4
Ash Content, wt%	10.7

The data indicate that the material is unsuitable for binder pitch or anode coke primarily because of the low coke yield, low softening point, and unacceptably high ash content.

The as-received HTI coal liquid was converted into green coke by heating at 5°C/min to 600°C and holding at this temperature for two hours. After cooling, a sample of the green coke was mounted in epoxy resin and polished for examination by polarized-light microscopy. Figure 1 is a photomicrograph displaying the type of optical texture developed. The optical units are of a coarse-grained-mosaic type indicating an inhibition in the growth and ordering of mesophase during carbonization, probably caused by the high content of inorganic matter. These optical structures are undesirable in anode fabrication.

Figure 1. Photomicrograph of green coke from as-received HTI coal liquid.

2.1 Distillation

The low softening point of the as-received material is most likely because of the presence of low molecular weight species present in significant quantity, probably from the liquefaction solvent. This solvent must be removed prior to coking. In order to increase the softening point temperature, the coal liquid was vacuum distilled using a conventional laboratory vacuum distillation apparatus. This unit consisted of a 500-mL round bottom flask to which was attached a condenser, a receptacle vessel, and a vacuum pump. An insulated heating mantle was used as a heat source.

Heat was applied to the coal liquid while the system was under vacuum. The molten coal liquid initially foamed a great deal, but subsided after a few moments. The temperature

was increased until about 20 wt% of clear, amber-colored liquid was removed from the original amount of coal liquid. The remaining coal liquid was cooled to room temperature while still under vacuum and then removed from the distillation flask. Characterization of this material was performed and the results presented in Table 2. A sample was also converted into green coke and a polished specimen prepared for optical microscopy, Figure 2.

Table 2. Characteristics of lightly distilled HTI coal liquid.

Softening Point, °C	95.0
Density, g/cm ³	1.270
Coke Yield, wt%	47.0
THF Insolubles, wt%	17.2
Toluene Insolubles, wt%	20.5
Ash Content, wt%	12.9

Figure 2. Photomicrograph of green coke from lightly distilled HTI coal liquid.

As expected, distillation raised the softening point from room temperature to about 95°C and produced a proportionate increase in coke yield, ash, and insolubility in tetrahydrofuran and toluene. There were no obvious changes in coke structure, as is evident in the photomicrograph.

2.2 Solvent Extraction

To determine if the properties of the coal liquid could be improved by removal of the ash forming constituents, the distilled material was dissolved in N-methyl pyrrolidone (NMP) in an approximately 1:10 wt ratio at the normal boiling point of NMP (202°C). The insolubles were separated from the dissolved coal by centrifugation, the NMP stripped by rotary evaporation, and the de-ashed product finally dried overnight in a vacuum oven at about 170 °C. Analyses of the distilled and NMP-extracted coal liquid and its resultant green coke structure are presented in Table 3 and Figure 3, respectively.

**Table 3. . . . Characterization of lightly distilled and NMP-extracted HTI coal
. . . . liquid.**

NMP Solubles, wt% (based on weight of distilled liquid)	80
Softening Point, °C	93.6
Density, g/cm ³	1.172
Coke Yield, wt%	35.6
THF Insolubles, wt%	ND
Toluene Insolubles, wt%	ND
Ash Content, wt%	0.5

Figure 3. Photomicrograph of green coke from lightly distilled and NMP-extracted HTI coal liquid.

As is evident in Figure 3, removal of the ash forming material leads to a coke structure that is more amenable for the production of anode-type coke. Mesophase coalescence is much more pronounced but, nevertheless, coke yield and softening point temperature are still considered too low. Since it is believed that HTI produced the coal liquid without any additional processing or treatment, the as-received product presumably still contains a significant amount of liquefaction solvent. The presence of the solvent would doubtlessly lead to the low softening point temperature as well as contribute to low coke yield.

2.3 Vacuum Distillation with Solvent Extraction

To remove liquefaction solvent to a greater extent, a 1-L autoclave was arranged to function as a vacuum distillation unit. Essentially this entailed closing all the service ports on the autoclave except for one, which was connected to a heated transfer line. The transfer line was attached to a receiving container to collect distillate material. Finally, the receiving container was connected to a cold trap and vacuum pump.

About 600-mL of as-received coal liquid were sealed in the autoclave and a stirrer mechanism activated while the system was under vacuum. The reactor contents were brought to a temperature of 350°C and distillation continued until about 250 mL (42 vol%) of a dark liquid were collected. The reactor furnace was then removed and an external water quench initiated to bring the temperature of the system down rapidly to about 150°C. The reactor was opened and the deeply distilled contents allowed to solidify before removal and weighing. The deeply distilled product was characterized with the results presented in Table 4 and Figure 4.

Table 4. Characterization of deeply distilled HTI coal liquid.

Softening Point, °C	144.7
Density, g/cm ³	1.374
Coke Yield, wt%	67.0
THF Insolubles, wt%	23.3
Toluene Insolubles, wt%	31.1
Ash Content, wt%	18.7

Figure 4. Photomicrograph of green coke from deeply distilled HTI coal liquid.

Vacuum distillation in this instance produced an ash-laden coal liquid with a softening point temperature of about 145 °C and an ash content near 19 wt%. The high ash content

also prevented the development of anisotropy as is evident in the photomicrograph, Figure 4.

A sample of the deeply distilled coal liquid was mixed with boiling NMP in a 1:10 wt ratio. The solution was filtered hot through medium-porosity filter paper and a Buchner funnel. NMP was removed from the filtrate by rotary evaporation and the NMP-soluble material and insoluble residue dried overnight in a vacuum oven at about 170 °C.

The properties of the deeply distilled and NMP-extracted coal liquid are listed in Table 5. Mass balance consideration indicates that nearly 100 percent of the organic matter was brought into solution by NMP. Furthermore, the softening point temperature of 124.0 °C and density of 1.205 g/cm³, as well as solubility in tetrahydrofuran and toluene, are more in line with values for commercially available solids-free pitches. However the coke yield is somewhat low, perhaps because of residual liquefaction solvent.

Table 5. . . . Characteristics of deeply distilled and NMP-extracted HTI coal . . . . liquid.

Yield of NMP-Solubles (based on distilled coal liquid)	80.1
Softening Point, °C	124.0
Density, g/cm ³	1.205
Coke Yield, wt%	48.3
THF-Insolubles, wt%	1.63
Toluene Insolubles, wt%	12.7
Ash Content, wt%	0.7

Figure 5 is a photomicrograph of the green coke obtained from the deeply distilled coal liquid. Similar to the optical structures depicted in Figure 3, mesophase development is significantly enhanced after the removal of inorganic matter by NMP extraction.

Figure 5. Photomicrograph of green coke from deeply distilled HTI coal liquid.

3. Summary

The results obtained thus far seem to indicate that a coal-derived, pitch-like material can be developed from the HTI liquefaction product after distillation to remove liquefaction solvent and NMP extraction to eliminate mineral matter. The physical properties of the liquid are not unreasonable when compared to other types of available pitches. The molecular arrangement and the optical structures present in the green coke of the de-ashed coal liquid may be suitable for the production of anodes for aluminum manufacture, but more testing needs to be conducted to confirm this.