DEVELOPMENT OF CONTINUOUS SOLVENT EXTRACTION PROCESSES FOR COAL DERIVED CARBON PRODUCTS
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ABSTRACT

The purpose of this DOE-funded effort is to develop continuous processes for solvent extraction of coal for the production of carbon products. The largest applications are those which support metals smelting, such as anodes for aluminum smelting and electrodes for arc furnaces. Other carbon products include materials used in creating fuels for the Direct Carbon Fuel Cell, 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, coking and composite fabrication continued using coal-derived samples. These samples were tested in direct carbon fuel cells.

Methodology was refined for determining the aromatic character of hydro treated liquid, based on Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared (FTIR).

Tests at GrafTech International showed that binder pitches produced using the WVU solvent extraction protocol can result in acceptable graphite electrodes for use in arc furnaces. These tests were made at the pilot scale.

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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 creating fuels for the Direct Carbon Fuel Cell, 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 development of carbon composites. Composite electrodes were fabricated for use as a carbon fuel cell electrode. Carbon foam samples were tested for armor applications.

2.0 Technical

2.1 Composite Electrode Rods

As a means to demonstrate low cost methods to produce coke and carbon composites (Task V in this effort), carbon composite rods suitable for use in direct carbon fuel cells (DCFCs) were fabricated. A schematic for a DCFC is shown below in Figure 1, with a photograph of an actual electrode assembly shown in Figure 2. The carbon composite fabrication processes have been described in reporting for fourth quarter 2005 under DE-FC26-03NT-41873. To recapitulate, the DCFS uses carbon rods which are oxidized in a molten hydroxide or molten carbonate bath. The result is a highly efficient means to convert carbon to carbon dioxide while extracting electrical energy. Because the specific Gibbs Free Energy is extremely high—in the range of 32 MJ/kg, it is thought that this can result in a high specific energy system, as well as a high efficiency system.
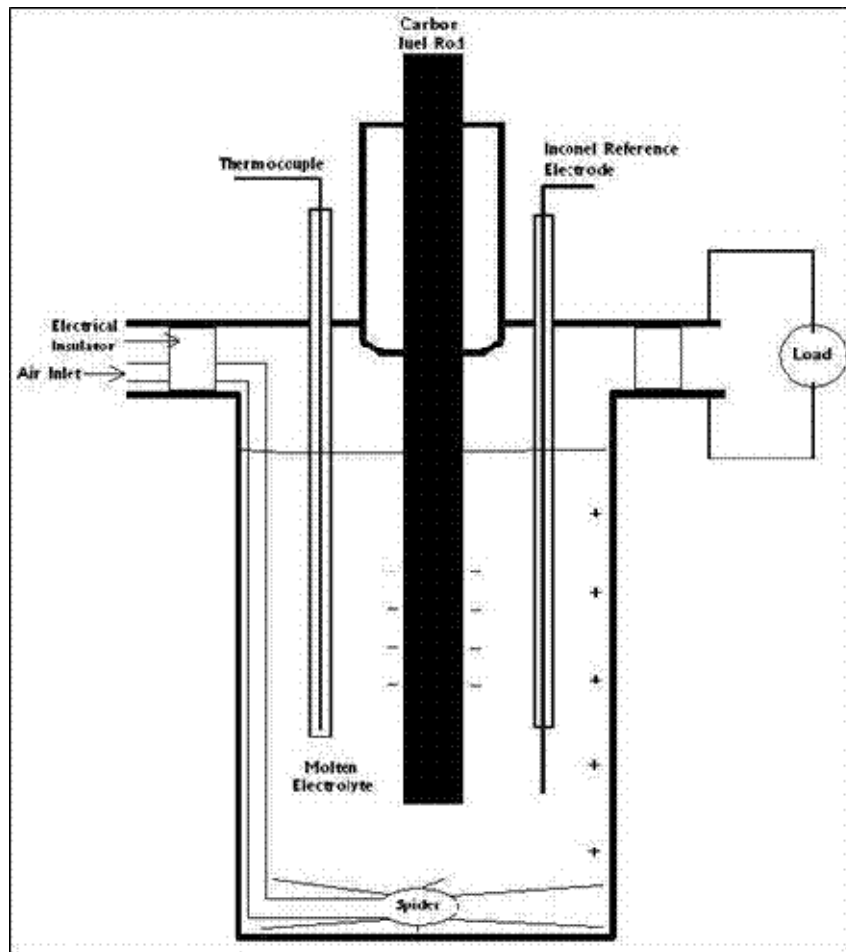
Figure 1. Schematic of Science Applications Research Associates (SARA) Direct Carbon Fuel Cell (DCFC).

Figure 2. Direct Carbon Fuel Cell (DCFC) Apparatus Tested at WVU.

2.1.1 Composite Performance in Electrical Systems

Several types of rods were tested. Rods were fabricated from petroleum coke supplied by SARA. Based on resistivity measurements, it is believed that the petcoke was higher resistivity than normal anode grade coke. Thus the petcoke was likely a fuel grade coke. The petcoke was blended with Solvent Extracted Carbon Ore (SECO) produced under this contract. SECO is produced by using n-methyl pyrollidone as a coal solvent.   Blends tested include 100/0, 75/25, 50/50, 25/75, 0/100

Two types of Graphite rods were tested. The first type was obtained from a previous experiment at West Virginia University. The second type of graphite rod was obtained from GrafTech.

Electrolytes trialed include NaOH, Li_2CO_3 + Na_2CO_3 eutectic, and NaOH + LiOH.

Rods were tested at temperatures of 600 °C, 625 °C, 650 °C, 675 °C, and 700°C and air flow rates of 0.25, 0.50, 0.75, 0.90 liters/minute (SLM).

Electrolytes trialed include NaOH, Li_2CO_3 + Na_2CO_3 eutectic, NaOH + LiOH.

Results of trials in the DCFC device are shown in Figures 3 through 11. General observations include the following:

a. Graphite rods exhibited lower current density than lower grade carbon rods. This is likely related to the lower activity of graphite compared to lower grade carbon.

b. Higher temperatures resulted in superior performance in all cases. This was expected due to the activity of carbon/graphite as well as the mobility of carbon in the electrolyte.

c.   Rods produced from Solvent Extracted Carbon Ore (SECO) exhibited very high open circuit voltage (over 1.0 volts compared to less than 0.8 volts for graphite rods under comparable conditions).   However, the current density and power density was significantly lower for the SECO case (less than .0250 W/cm^2 for SECO rods versus .085 W/cm^2 for graphite rods). The reason for this is not clear, although it is speculated that additional parametric studies might show that that the SECO rods can exhibit higher current density in different temperature regimes.
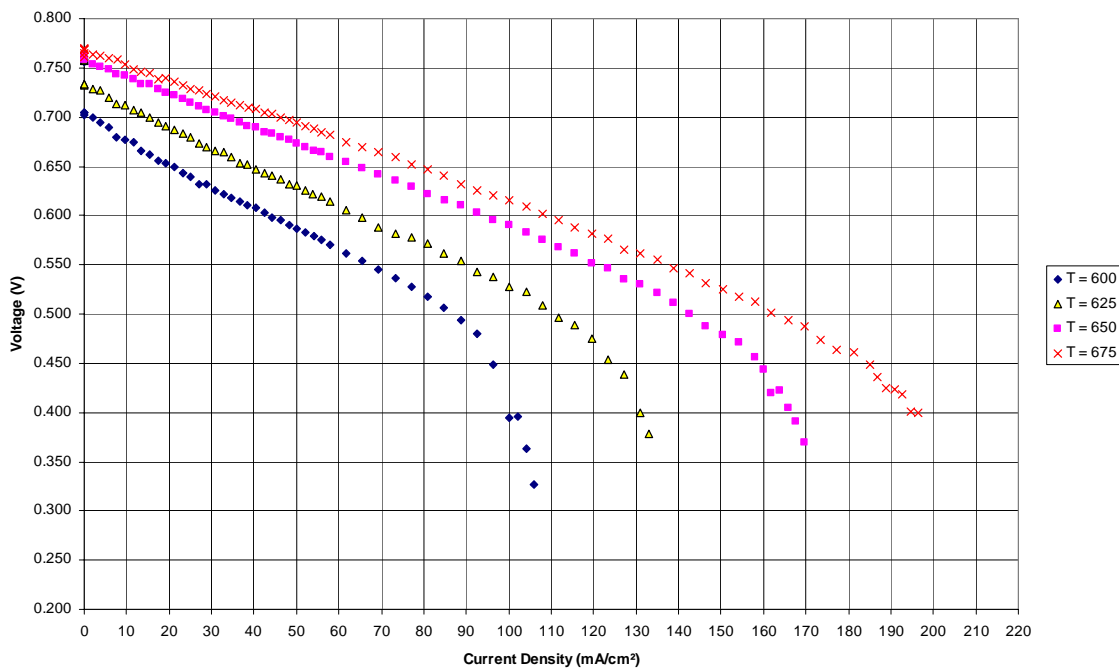
Figure 3. Cell Voltage versus Current Density for a Graphite Rod, Flow = 0.5 SLPM.
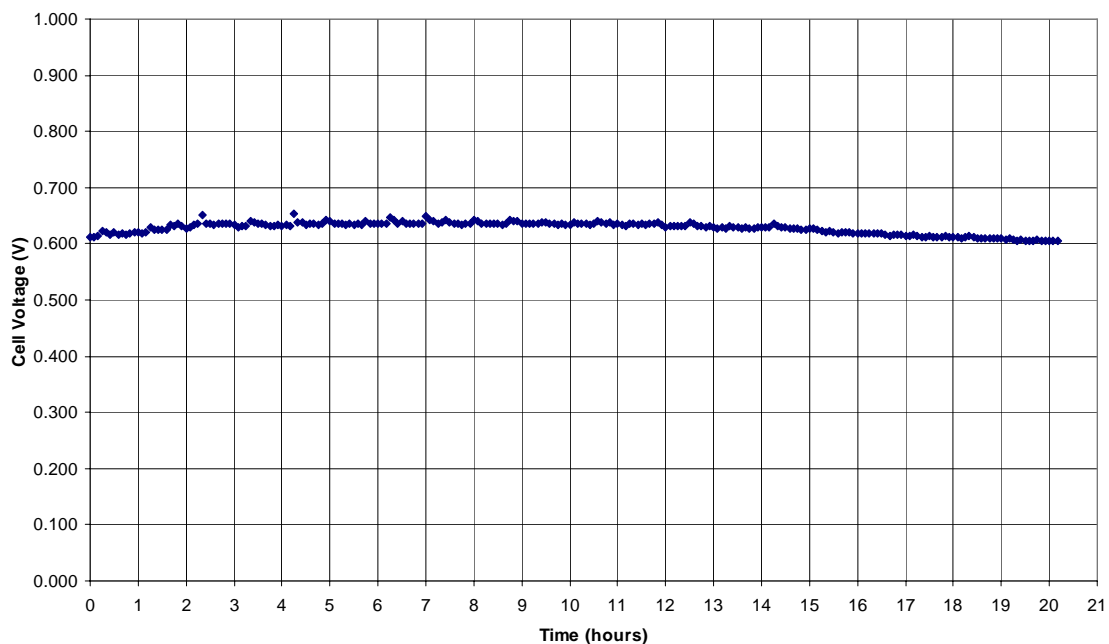
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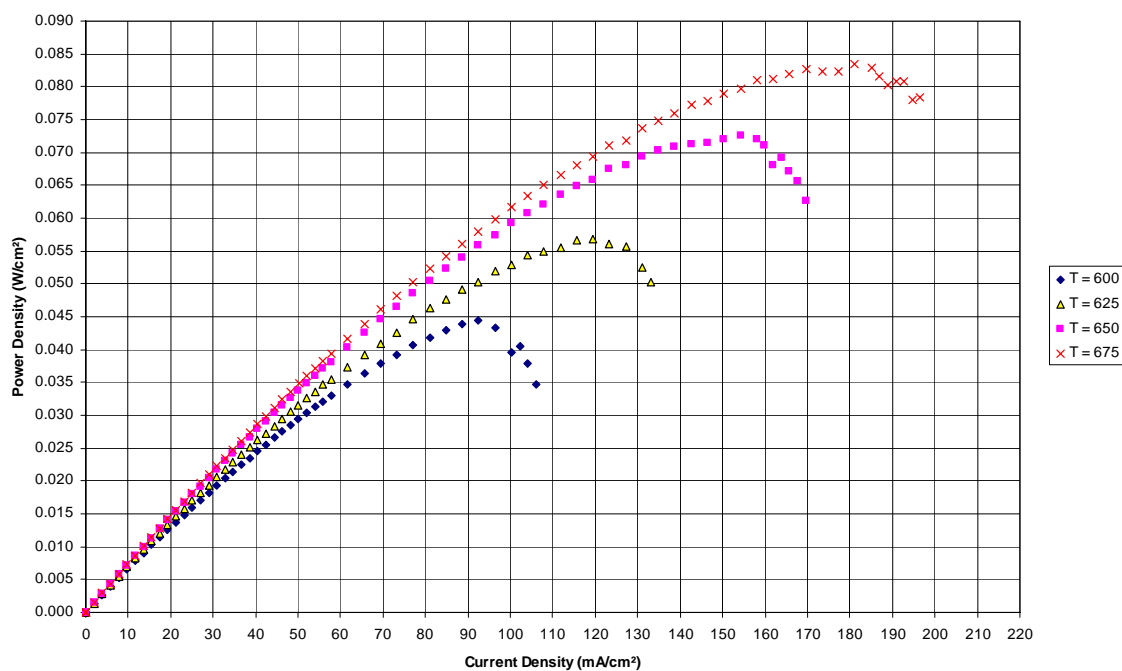
Figure 5. Power Density versus Current Density, Graphite Rod, Flow = 0.5 SLPM.
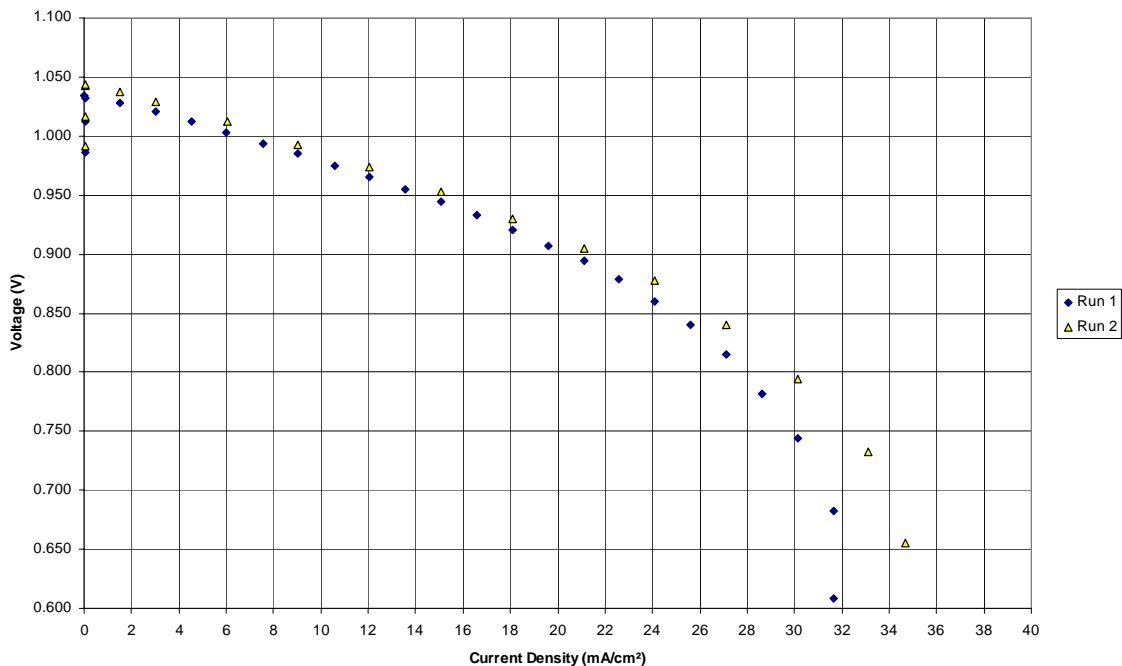
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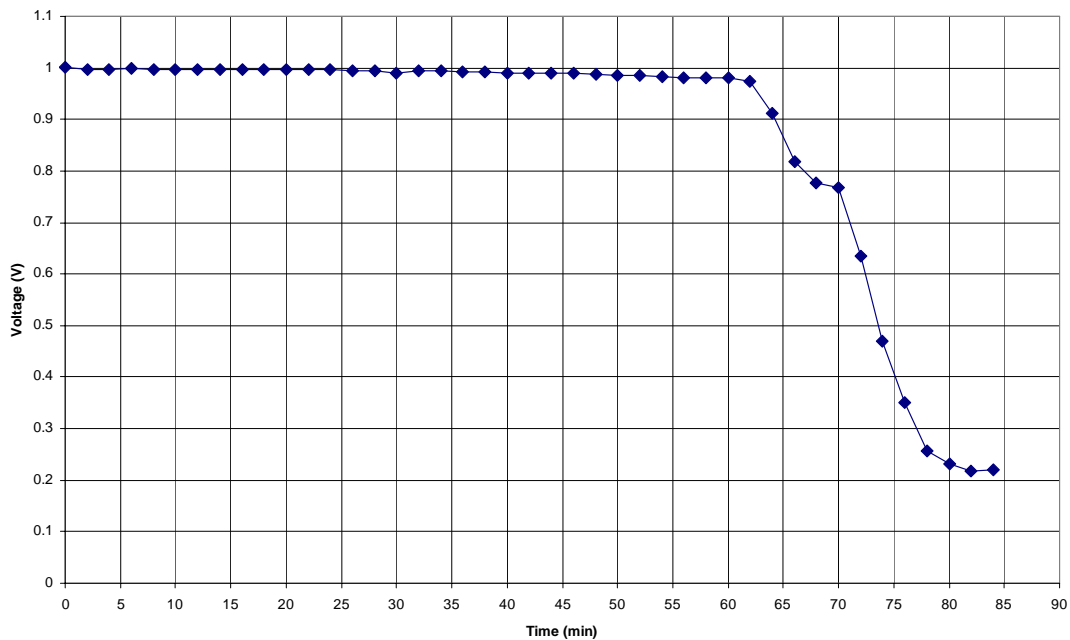
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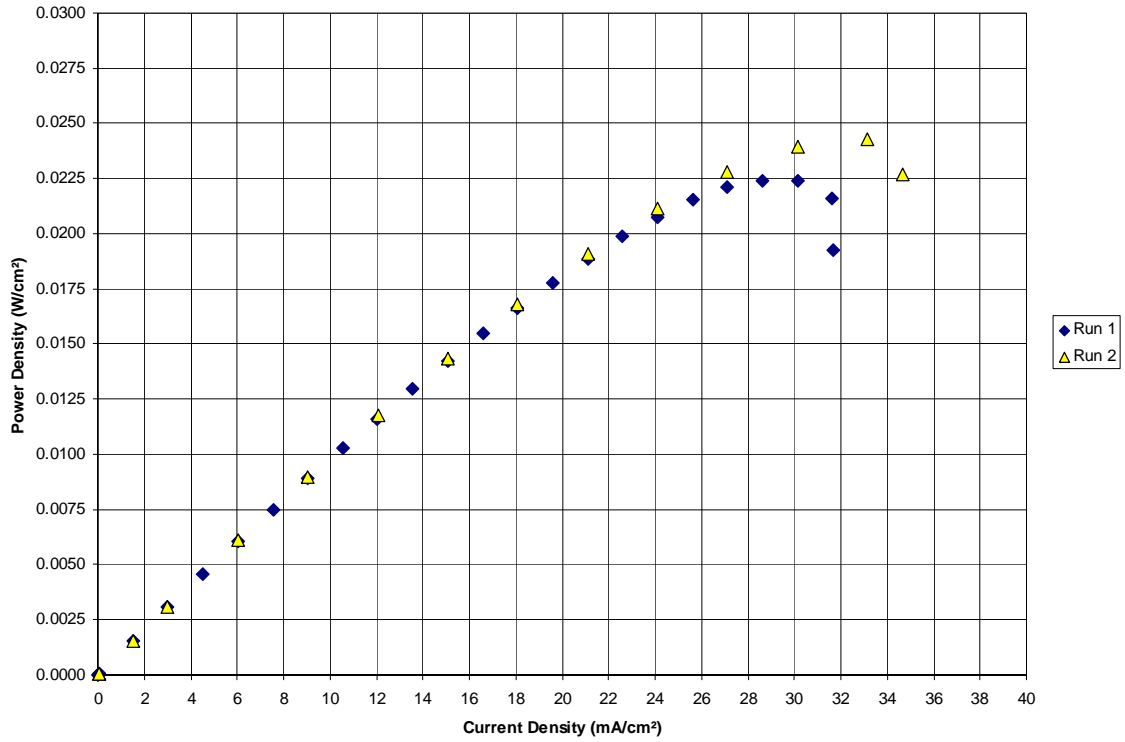
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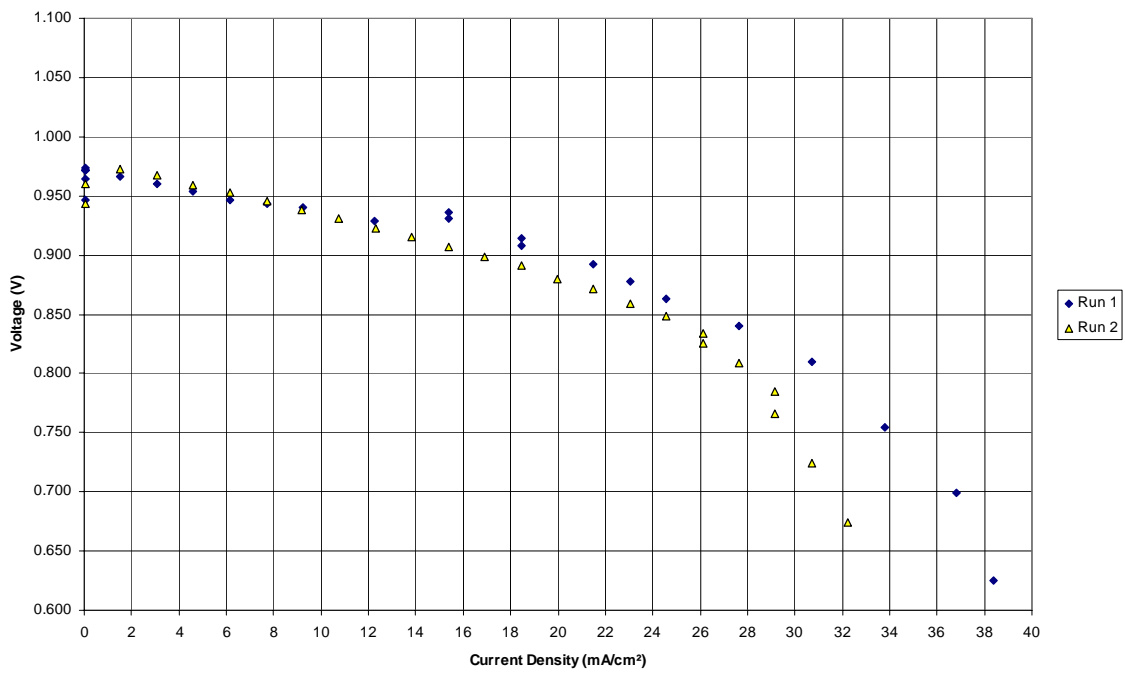
Figure 9. Cell Voltage versus Current Density, GrafTech Baked Rod, Air Flow = 0.50 SLPM, T = 600°C.
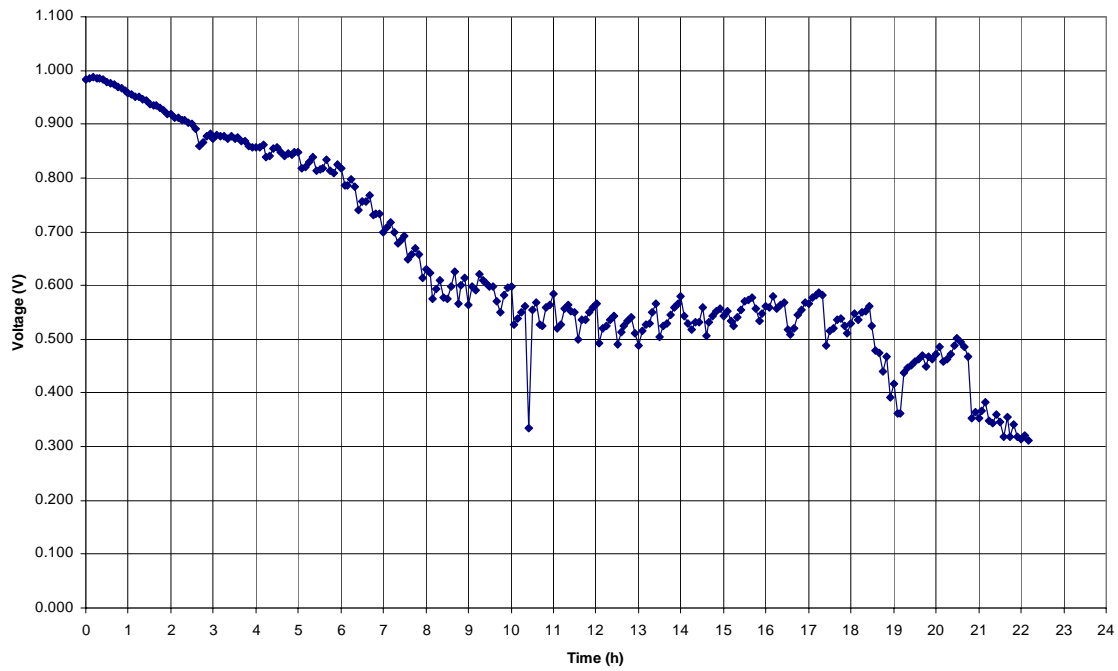
Figure 10. Voltage over Time, GrafTech Baked Rod, Air Flow = 0.50 SLPM, T = 600°C.
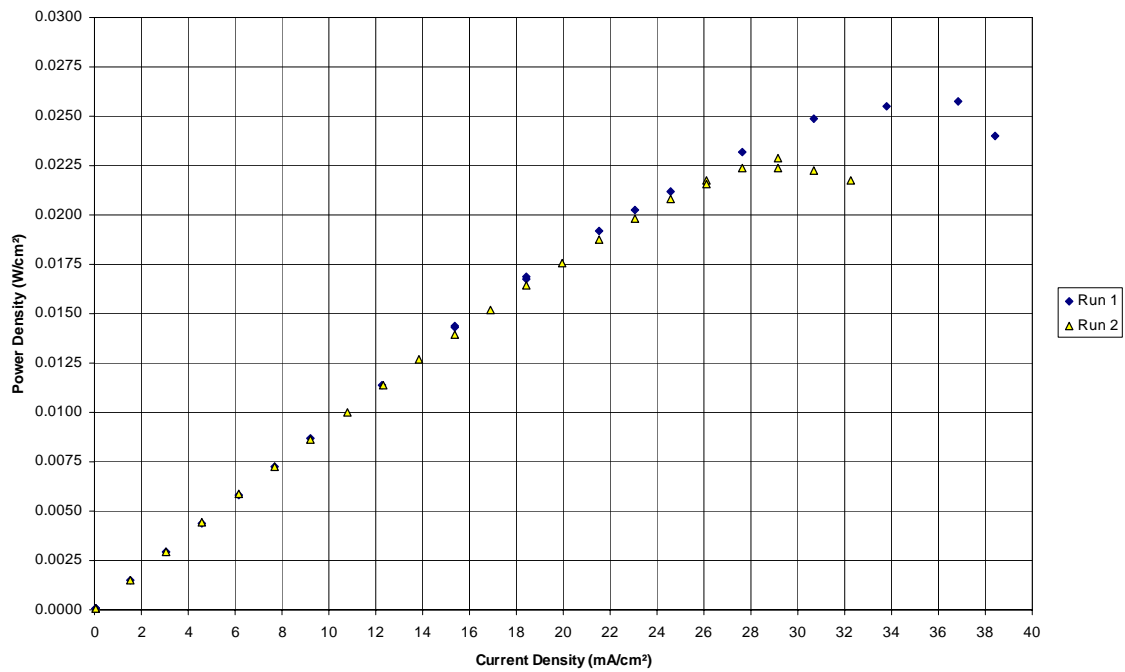
Figure 11. Power Density versus Current Density, GrafTech Baked Rod, Air Flow = 0.50 SLPM, T = 600°C.

2.2 Carbon Foam Composites

For a variety of reasons, increased national attention has been placed on miner safety, especially in West Virginia coal mines. Carbon foams have been suggested as possible material candidates for constructing a miner "safe house". Basically, the idea is to create small structures that would survive potential accident scenarios such as cave-ins, fires and explosions.   These structures could carry auxiliary supplies of air, water and other basic necessities, as well as backup communications capabilities.   Carbon foam is considered as a potential construction material because it is fire resistant, impact resistant, and explosion resistant.

Accordingly, WVU along with GrafTech International Ltd, a subcontractor on the present effort, have actively sought to develop safehouse designs incorporating carbon foam, usually as a trilayer with metal faceplates.

2.3 Solvent Hydrotreating

2.3.1. Hydrotreating Reactor Operating Procedure

Preparation

1. Coal Tar Distillate (CTD) should be sufficiently fluid to pump. If not, heat to about 70 C in 55 gallon drum overnight.

2.   Make sure reactor is depressurized.   Release pressure by opening Valve 1 and 2 to release gas to the vent tank. The vent tank valve should be open to allow gas to be bled in the fume hood at a slow rate. Valve 3 should be closed.

3.   Weigh the barrel of CTD and record in the lab book. Open valve 4 and turn on the air-actuated pump (prime if necessary). Transfer 27 Lbs max of CTD to the reactor.

4. Close Valves 1-4.

Hydrogen tank change out.

1. Valve off the hydrogen tank as well as the valve downstream from the regulator and the black valve downstream from the regulator valve.

2.   Remove the empty hydrogen tank. Note that hydrogen regulator threads are left-tighten, right-loosen.

3. Bring in the new hydrogen tank and strap. Attach the regulator.

4. Check for hydrogen leaks using the combustible gas detector and/or Snoop (soap bubbles).

Hydrotreater Protocol

1. Make sure valves 1, 2, 3 & 4 are off, and make sure that the fume hoods are on and functioning and that water coolant is flowing to the Magnadrive and water cooling heat exchanger.

2. Purge the reactor by pressurizing to ~100 psig and releasing the gas to the holding tank. Nitrogen is preferred since it is inert, but hydrogen can also be used.

3. If necessary, tighten bolts on reactor to 200 ft-lbs torque using a torque wrench. The sequence of bolt tightening is based on a "star pattern" posted above the reactor. The bolts should be tightened by increments using a torque wrench to 100, 150, 200, 200 and 200 psig, or until the torque wrench no longer rotates the bolts.

4. Turn on heat to the reactor.

5. Monitor the temperature and pressure every five minutes or as directed by the supervisor.

6. ***If the reactor has not been externally pressurized and the pressure goes above 200 psig at less than 400 ^{o}C, this means that the reactor may be overfilled, and a potential overpressure situation may be created. Immediately turn off the heater power, turn off the magnadrive, and then vent the product line, Valve 3. Release at least 3.0 liters should be released. If this is not effective, immediately initiate the emergency shutdown procedure.

7. The target reactor temperature can be determined by the supervisor, but should be less than 450 ^{o}C. If the reactor temperature exceeds 460 ^{o}C, immediately initiate the reactor shutdown procedure.

8. As the reactor approaches within 25 ^{o}C, of the target, adjust the temperature limit device to ensure temperature overshoot is minimized.

9. Pressurize the reactor by opening the valve at the hydrogen tank. The target pressure can be determined by the supervisor, but should never exceed 2200 psig. If the pressure reaches this level, vent the reactor gas from Valve 1. If this not effective, immediately initiate the emergency shutdown procedure.

10. Within 5 minutes of pressurizing the reactor, a flammable gas detector should be used to determine if any flammable gas is present near the system.

11. When hydrogenation is complete, record final time, temperature, and pressure.

12. Turn off valve to hydrogen source.

13. Turn off stirrer and heater switch.

14. Using insulated gloves, open the reactor outlet, Valve 3, to the product drum and slowly empty liquid contents of reactor. This process should take 15 minutes or longer. When the pressure drops to 1000 psig, valve off the flow and take a test tube sample for Fourier Transform Infrared (FTIR) or Nuclear Magnetic Resonance (NMR) testing. Then resume draining the reactor. When the reactor seems to be completely drained, turn off Valve 3, and open Valve 1 to refill the reactor.

16. At the end of the day turn off the following:

   a. Turn off the lever switches to the hydrotreater and Magnadrive, by pulling both levers down.

   b. Ensure that the hydrogen gas is valved off at the bottle, at the regulator and also with the black valve after the regulator.

2.3.2. Characterization of Hydrotreated Solvent

Fourier Transform InfraRed (FTIR) spectroscopy has been used to observe enhancements in the aliphatic content of treated solvents. This is based on the donor solvent model, in which naphthalene acquires four donatable hydrogen atoms via the hydrotreatment process, resulting in the formation of tetrahydronaphthalene (Tetralin®). Thus hydrogen is added to the system in an aliphatic state, as shown in the figures below.
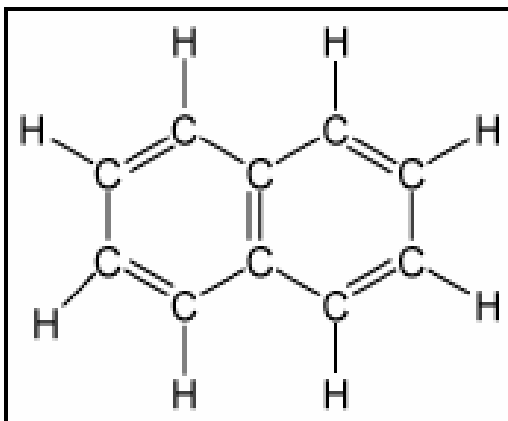
Figure 12. Naphthalene Structure.
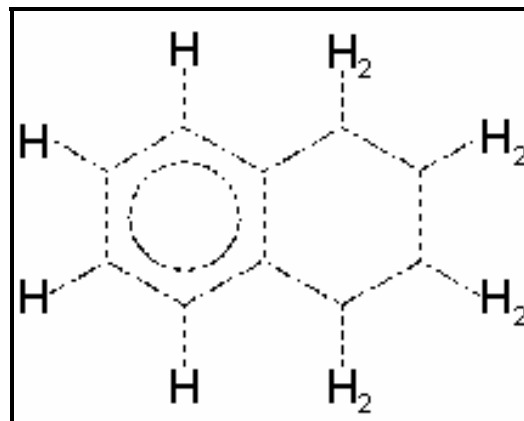
Figure 13. Tetrahydronaphthalene (Tetralin®) Structure.

The ratio of aromatic peak area to aliphatic peak area in the FTIR spectrum is used as an indicator of the effectiveness of the process. However, the modifications introduced in the current research effort have complicated the situation. Because coal tar distillation cuts have been substituted for pure Tetralin®, the donor solvent reaction may take place in several aliphatic compounds and not just in Tetralin®. Conversely, other aromatic-to-aliphatic conversions may occur without resulting in donatable hydrogen.

For this reason, Nuclear Magnetic Resonance (NMR) is the preferred technique to distinguish between donatable and non-donatable hydrogen. In other words, separate measurements identify hydrogen as aromatic hydrogen, aliphatic donatable hydrogen and aliphatic non-donatable hydrogen.

Although FTIR is not definitive in this respect, it is very fast and suitable for making measurements in a matter of a few minutes. Hence an algorithm was developed for determining the success of hydrotreatment based on the ratio of peak areas corresponding to aromatic hydrogen and to aliphatic hydrogen. As described in last quarter's report, a Nicolet FTIR spectrometer, built circa 1990, had been used to make this measurement in the past. However, due to the lack of repair parts, it became necessary to replace the Nicolet FTIR spectrometer with a more recent model manufactured by Perkin-Elmer.   The basic technique is to define a peak area by "chopping" the peak linearly, as illustrated by the calculations below.

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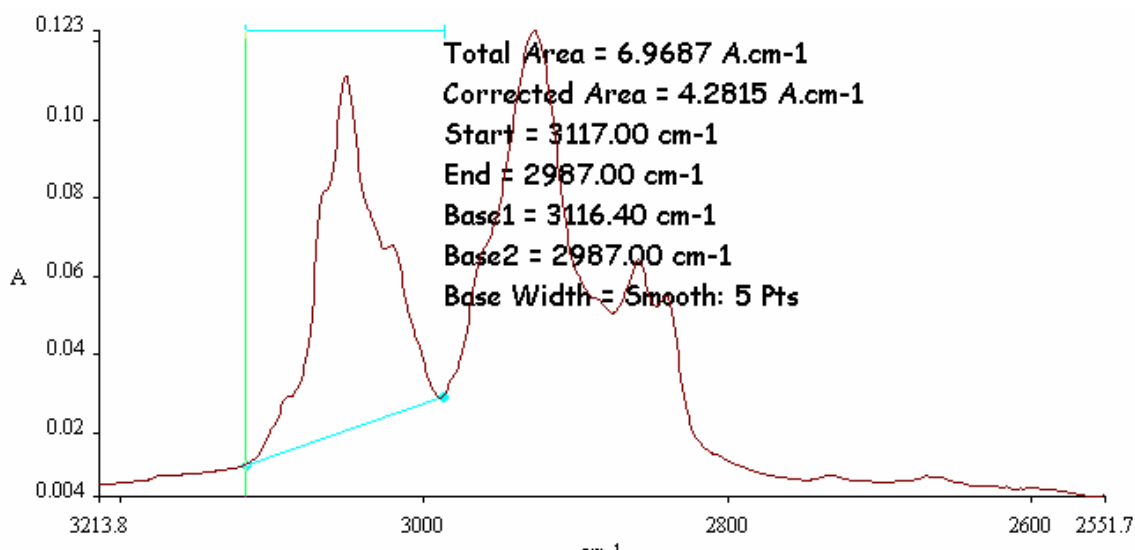
Figure 14. FTIR Aromatic Peak Measurement Algorithm.
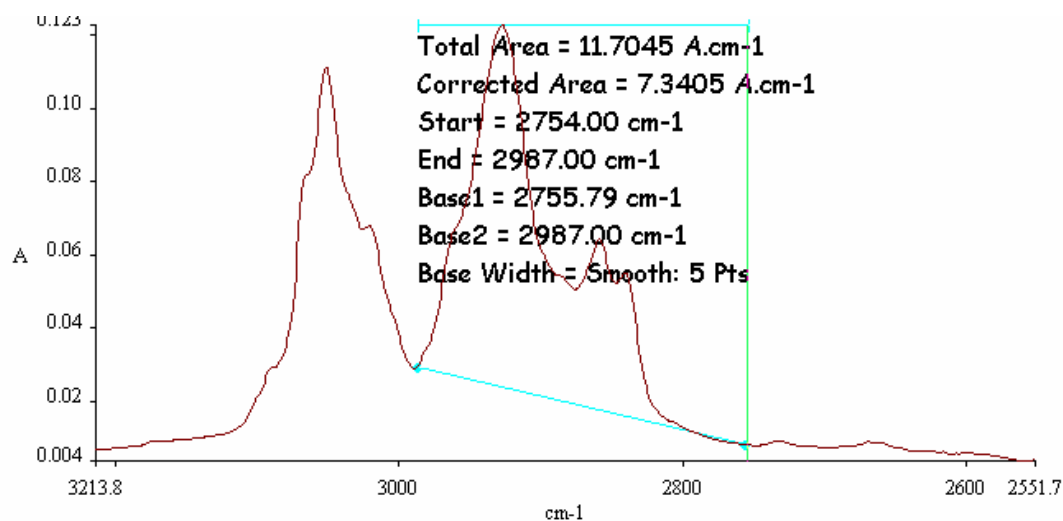
Figure 15.   Sample FTIR Aliphatic Peak Measurement Calculation.

To correlate FTIR measurements with the actual amount of donatable hydrogen absorbed, and to verify that results obtained using the Perkin-Elmer FTIR can be duplicated on other machines, different calibration standards were examined using both instruments and compared.

NMR spectra were obtained for pure naphthalene (100% aromatic), as well as Tetralin® (eight aliphatic hydrogens of which four can be donated; as well as four aromatic hydrogens).   Hence the spectrum of naphthalene is expected to show only aromatic hydrogens. The spectrum of Tetralin® is expected to show 1/3 of the hydrogen peak area corresponding to aromatic hydrogens, with a doublet peak corresponding to the paired hydrogen atoms in an aliphatic state.   These features are indeed observed in Figures 16 and 17 respectively.

Xylene is used as another control, due to its unique structure which shows peaks due to different states present in ortho, meta and para xylene. This is shown in Figure 18. The results of Xylene blends with Tetralin are shown in Figure 19.
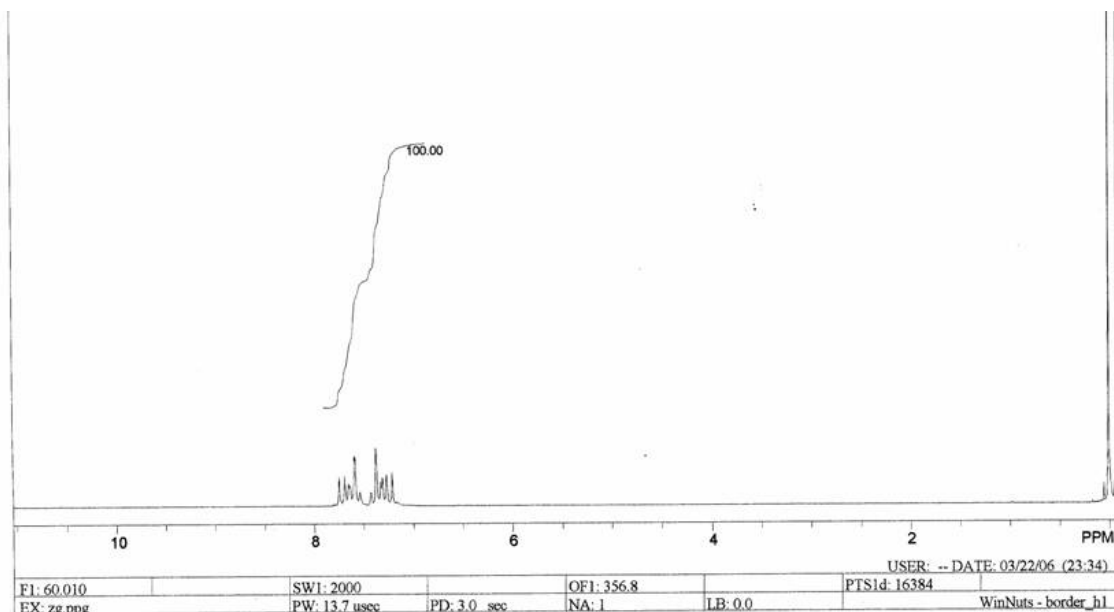
Figure 16. NMR Spectrum of Pure Naphthalene, Showing 100% Aromatic Composition.
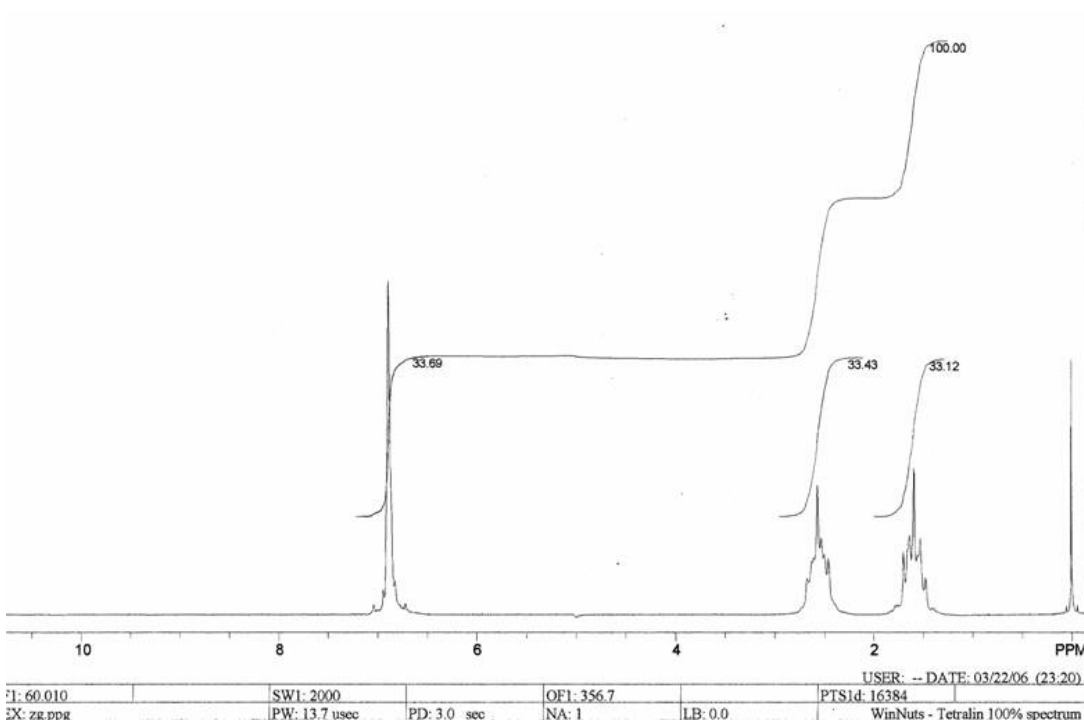
Figure 17. NMR Spectrum of Pure Tetralin®, Clearly Showing Peak Splitting from Donatable Hydrogen.
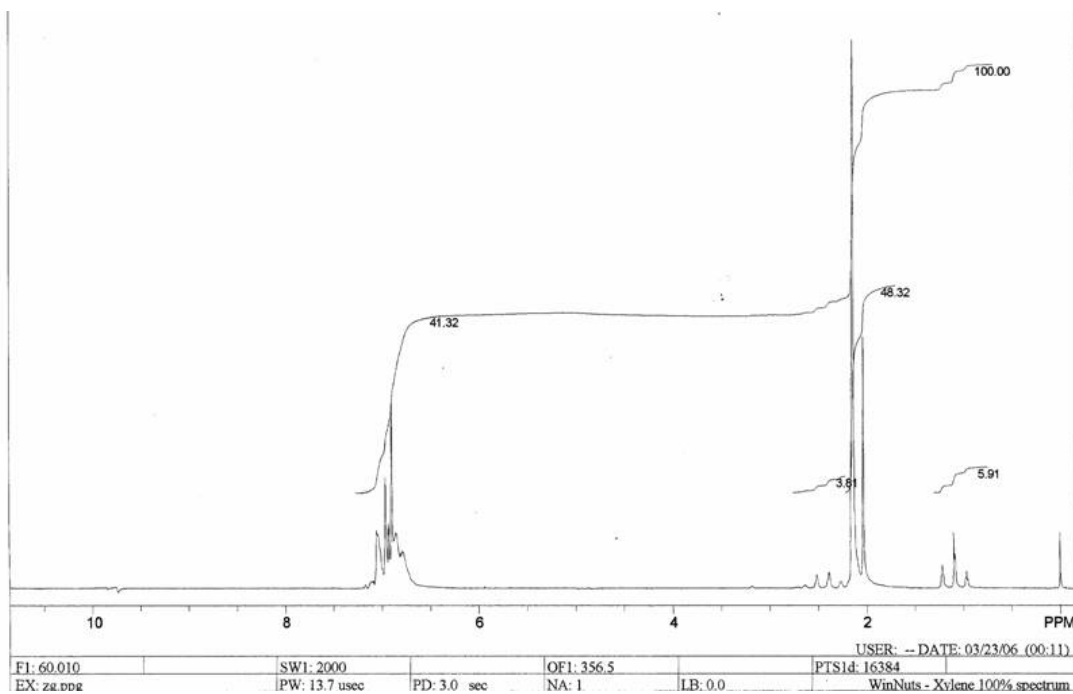
Figure 18. NMR Spectrum of 100% Xylene.
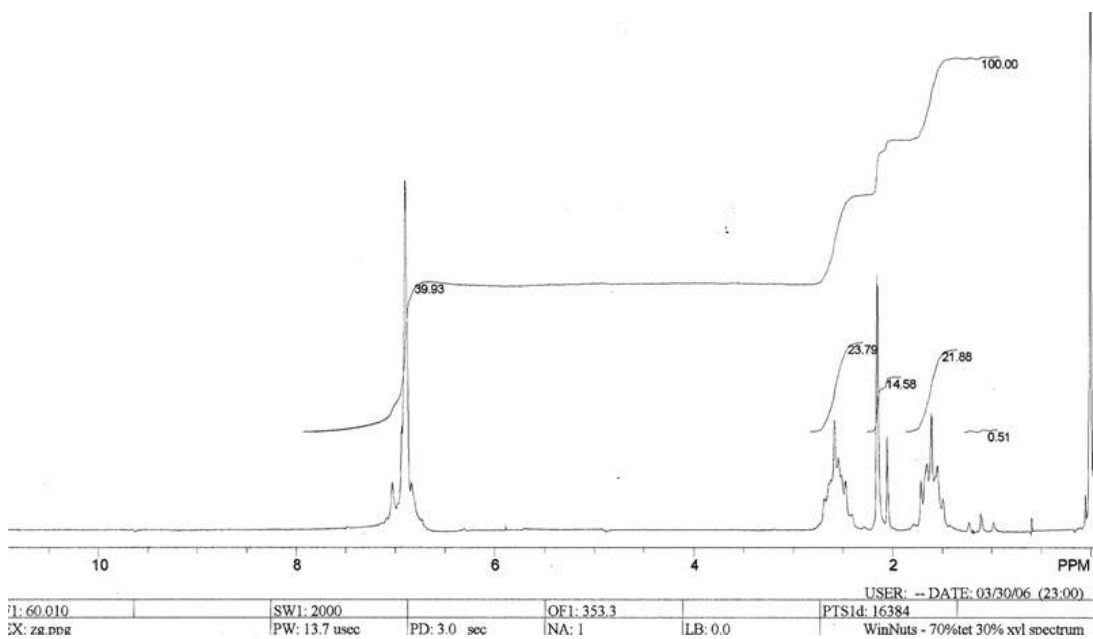
Figure 19. NMR Spectrum of 70% Tetralin® and 30% Xylene.
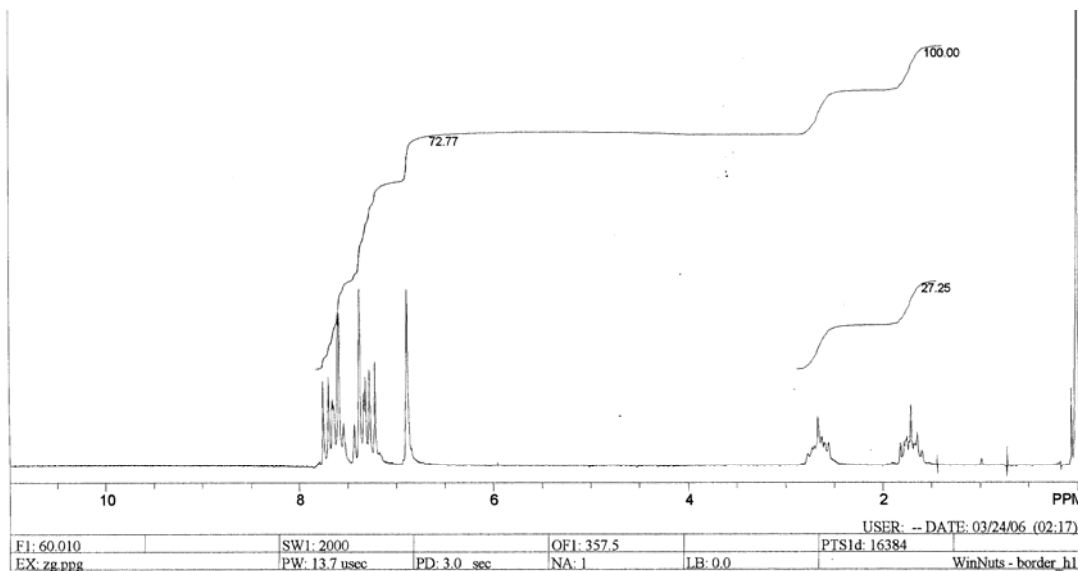
Figure 20. NMR Spectrum of 70% Tetralin® and 30% Naphthalene.

A comparison of theory, NMR results and FTIR results is shown in Figures 21 and 22. FTIR appears to underestimate the amount of aromatic hydrogens present in the sample.
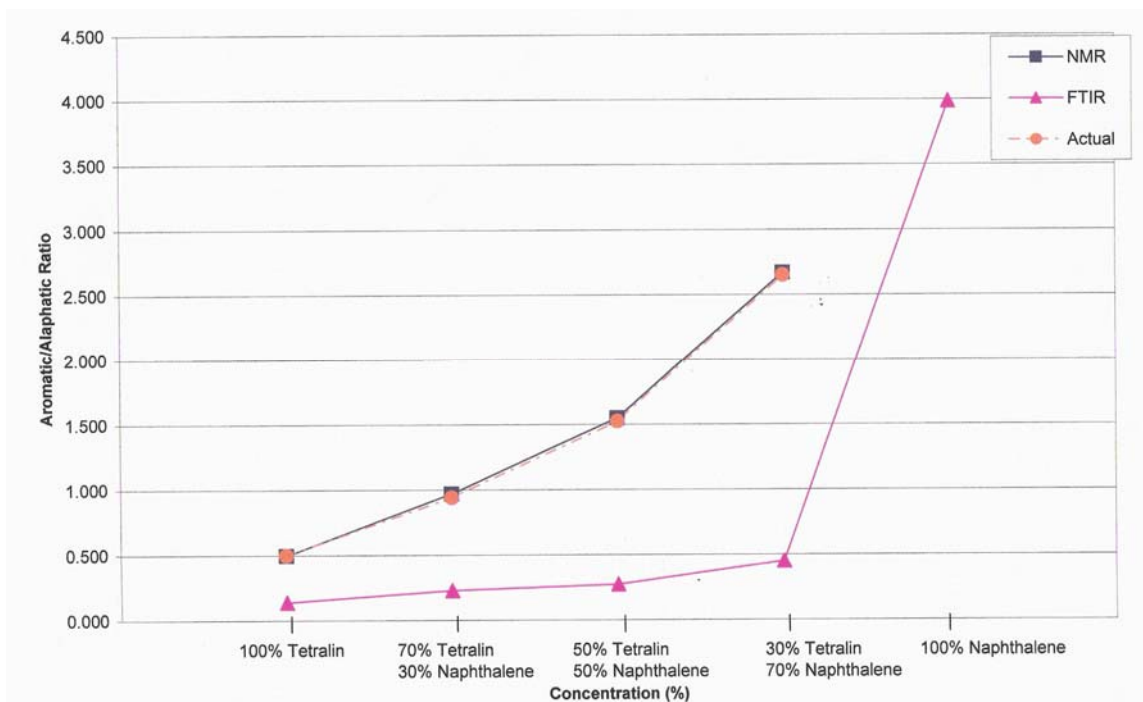
Figure 21.   Correlation of NMR and FTIR derived ratios of aromatic to aliphatic hydrogen for Naphthalene/Tetralin® blends.
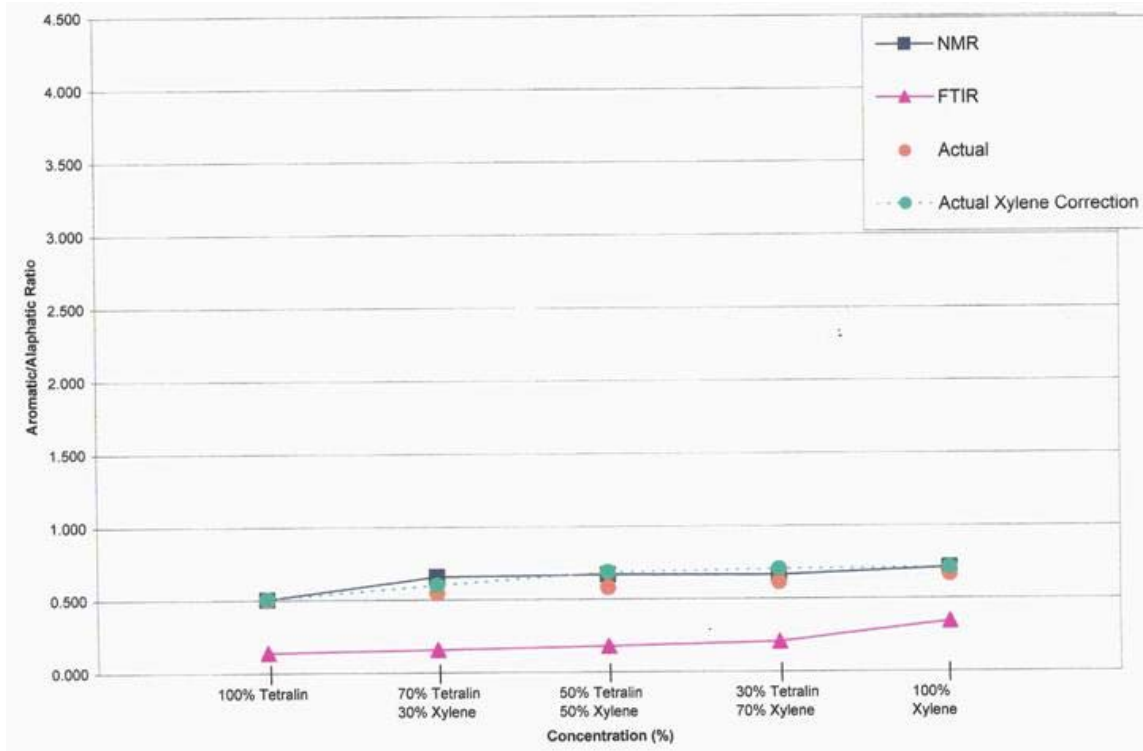
Figure 22. Correlation of NMR and FTIR derived ratios of aromatic to aliphatic hydrogen for xylene/Tetralin® blends.

2.4 Digestion

During this reporting period, an attempt was made to systematize the procedures for digesting coal. Additional consideration is given to the solids separation step used to prepare the coal extract.

In 2005, data showed that a single pass through a Sharples Pennwalt decanter-type centrifuge was marginal for the achievement of the ash content of the Synpitch. The requirement for acceptable binder pitch is that the ash content following proximate analysis should be 0.5% or less. Trials with the Sharples Pennwalt typically resulted in ash content between 0.5% and 1.0%. Thus a decision was made to use nitrogen pressure filtration instead. The pressure filtration method resulted in ash content of about 0.2 % ash or below, well below the target.

However, pressure filtration results in the need to filter only a few gallons of extract at a time. The desire to avoid a second pass in the reactor necessitates frequent ash testing and frequent changing of the filters. These steps would be cumbersome for an industrial scale process.

Pennwalt India recommends using two centrifuges in series in order to reduce the ash content by more than a decade. This possibility should be investigated further before a protocol is nominated for industrial production.

A second issue is the need to open the reactor to air during the filling procedure. In order to avoid the formation of vapors, the reactor must be cooled down before opening the unit. This results in a down period of at least an hour. This lag time could be eliminated by forming a slurry of crushed coal that can be pumped at low pressure (but at near-operating temperature), in semi-batch mode. This possible change will be considered in the context of Task VI, which researches alternate feedstocks.

The digestion reactor is only partially operational at the present time, due to failure of one of the heaters used on the digester reactor. This results in a very long heat-up time. As a consequence, only a single batch of 17 pounds of coal can be accommodated in an operating shift.

By repairing the heater, the capability of the facility can be upgraded to three runs per shift, resulting in 51 pounds per day. By installing a closed loop system to avoid the need for breaking the reactor seal to load material, then cooldown time can be eliminated and at least eight batches or 136 pounds can be produced per shift.

2.4.1 Reactor Operating Procedure

The procedure for filling the digestion reactor is summarized below.

1. A slurry is created by combining the Hydrogenated Coal Tars, from the Hydrotreater in the ERB, with the crushed coal in a small feed vessel. The coal is crushed to a particle size of approximately -50 mesh and dried to eliminate any free moisture. The normal ratio is 2:1.

2. Verify that the reactor vents are all open.

3. Turn on the heat to the feed vessel.

4. Stir the feed vessel at 450 rpm for about 30 minutes or until the mixture is fluid enough to be easily transferred into the 10 gallon reaction vessel. The temperature set point is 90 $^{\circ}$C.

5. After ensuring that the reactor vents are open, the feed vessel is then hoisted above the reaction vessel and the slurry is drained into the reactor.

6. Once all of the contents of the feed vessel are in the reaction vessel, the reactor is then sealed and the feed port plug is torqued to 150 ft-pounds to ensure that a good seal is made.

7. Close all vents on the reaction vessel. The reactor is now prepped for the reaction.

8.   After the reactor is completely sealed, the stirrer rotational speed is increased to 750 rpm and the reaction heater is turned on and set at 420 °C.

9.   The process temperature, reactor pressure, and the hour and minute of the day, is recorded every 15 min. to insure that successive runs are consistent with each other as well as giving early warning signs that could indicate a problem with the reactor at reaction temperatures.

10.   Once the process temperature reaches the reaction temperature of 420 °C, a data point is then taken every 5 min. for one hour to record the relationship between the reaction and the process pressure in the reactor.

11.   Once the process temperature has remained at 420 °C for one hour, the reaction is assumed to be over, the process heater is turned off and the reactor is ready to be cooled. The reaction vessel is equipped with cooling coils inside of the vessel through which an aerosol is fed to accelerate the cooling process.

13.   To begin cooling, the air compressor must first be turned on and allowed to pressurize before water should be added to the system to prevent the water from filling up the coils and flashing violently.

14.   Once the compressor is pressurized and a steady flow of air is flowing through the coil, the aerosol is added.

15.   Verify that the valve on the aerosol nozzle is completely closed.

16.   Completely open the water valve against the wall that feeds the aerosol nozzle.

17.   Slowly open the aerosol nozzle injecting water into the air stream flowing through the cooling coils inside the reaction vessel. After the valve is opened slightly, the flow of steam should be monitored coming out of the reactor.

18.   The exit stream vents the steam directly outside so to monitor the flow the stream outside must be monitored. Once a steady flow of steam is flowing from the reactor, the process temperature and pressure should again be monitored and recorded.

19.   After the process has been cooled to a filtration temperature of 150°C, the water should be shut off to the aerosol nozzle, followed by closing the valve on the nozzle.

20. The air compressor should be turned off and allowed to decompress on its own through the cooling coils.

21. Upon cooling to 150°C the reactor is still under pressure. The stirrer should be slowed back to 450 rpm before the reactor can be vented.

22. Open reactor the vent slightly to allow the pressure to vent slowly. Releasing the pressure too quickly will cause the contents in the reactor to be pushed out of the reactor through the vent line. Once the pressure in the reaction vessel reaches zero psi, close the vents on the reactor to prepare to use the air ram.

Air Ram

1. During the heating and reaction process some of the un-dissolved coal settles in the section of pipe between the valve and the vessel and forms a plug that becomes compacted by the high pressures during the reaction process. This plug is broken free by forcing nitrogen at high pressures through the bottom of the reactor. When the vents are closed and the pressure is at zero in the reaction vessel, the tank that supplies nitrogen to the air ram should be turned on. The regulator should be set between 200 and 400 psi.

2. After pressurizing the air ram, open the valve to the reactor before opening the valve to the air ram, then close the valve to the air ram before closing the valve to the reactor.

3. Repeat Step 2 repeatedly, stepping up the pressure as needed, until the plug breaks loose.

4. After the plug is broken free check the pressure in the reaction vessel. If the pressure is over 70 psi, slowly vent the pressure for the reactor. If not, check to make sure the vent valve is closed and then open the valve to the nitrogen line to prepare for filtration.

5. When pressurizing the reaction vessel, that the pressure in the reaction vessel must remain below 70 psi. Once the reaction vessel is under pressure, the receiving vessel is checked to ensure it is empty. If not drain the contents into buckets while taking a sample (to determine ash content) from each bucket.

6. When the receiving vessel is empty, check to make sure the drain valve is closed. Next, make sure that new filters are in the filter.

7. If more than three passes have already been run though this set of filters, changes filters. If not, open the valve at the bottom of the reactor and then open the valve leading into the filter.

8. Check flow into the receiving vessel to make sure that it is flowing. Once the filtration is done the pressure in the reactor will drop below 30 psi.

9. The nitrogen feed should be turned off and the valves under the reactor should be closed.

10. Open the vent valve to relieve any leftover pressure and begin the process again.

11. The process described above requires making several samples of ~5 gallon batches of tar. These batches are kept for a few days until confirmation is received that they are of acceptable quality. Then they are transferred to a 55 gallon drum. Such drums are also used such to contain the raw materials (hydro-treated coal tar and raw coal). Tar and the raw products are considered Class IIIB liquids (combustible but not flammable). Therefore, it is not permitted to store this material in plastic, but metal cans are allowed up to 5 gallons, and 55 gallon DOT-compliant drums are also permitted.

2.5 Composite Fabrication and Characterization

GrafTech artificial graphite electrodes have been selected as a test case for the industrial practicality of the synthetic pitch (Synpitch) fabrication process. GrafTech carried out pilot scale testing of graphite electrodes fabricated using a blend of Synpitch with a Koppers control pitch.

These tests were carried out using 500 pounds of material processed by Koppers Inc. Unfortunately, during the distillation process, the pitch was somewhat over-distilled. As a consequence, the softening temperature of the Synpitch was measured at about 120 ^{o}C versus the target of 110 ^{o}C. This discrepancy made it difficult to analyze the other properties of the pitch.

GrafTech has suggested that the discrepancy in softening temperature may make it advisable to re-accomplish the pilot scale tests near the composition intended for commercial electrodes. Nevertheless, the results suggest that blends of 10% to 25% Synpitch are likely to be commercially viable.
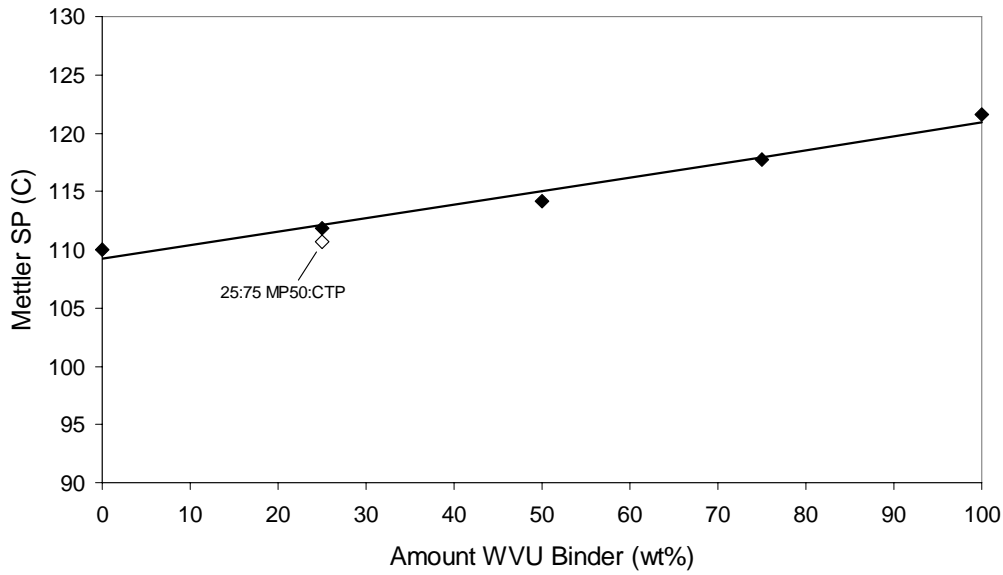
Figure 23. Mettler softening point for blends of Synpitch and Koppers control binder pitch. The results are approximately linear. Had the Synpitch softening point been 110 ^{o}C as planned, then a flat curve would have been expected.

Another characteristic of solvent-extracted Synpitch is that the pitch has zero quinoline insolubles (QIs). QIs are microscopic carbon rich particles created in the partially pyrolyzing conditions of metallurgical coke ovens. The QI content of coal tar pitches varies somewhat according to the conditions of metallurgical coke (metcoke) production. Higher QIs are associated with high temperature operations, such as which may occur during periods of peak production. The nominal operating temperature of metallurgical coke ovens are around 1100 ^{o}C, and might be raised by a few tens of degrees in such cases. Conversely, lower QIs may result from somewhat lower material throughput and operating temperatures.

QI content has an effect on the coke yield of the pitch. Low QIs are associated with low coke yield. On the other hand, if the QI content is too high, it may be difficult to achieve adequate wettability and overall quality. Thus, one of the attractive features of Synpitch is that it might be blended with coal tar pitches that are too high in QI content.

The QI content of blends of Synpitch and Koppers pitch are shown in Figure 24 below. The results show that a blend of 25% Synpitch results in a very close match to the target value. The effect of QI upon Modified Conradson Coke Yield is shown in Figure 25. The Modified Conradson Coke Yield is also very nearly the target value at 25% Synpitch content.
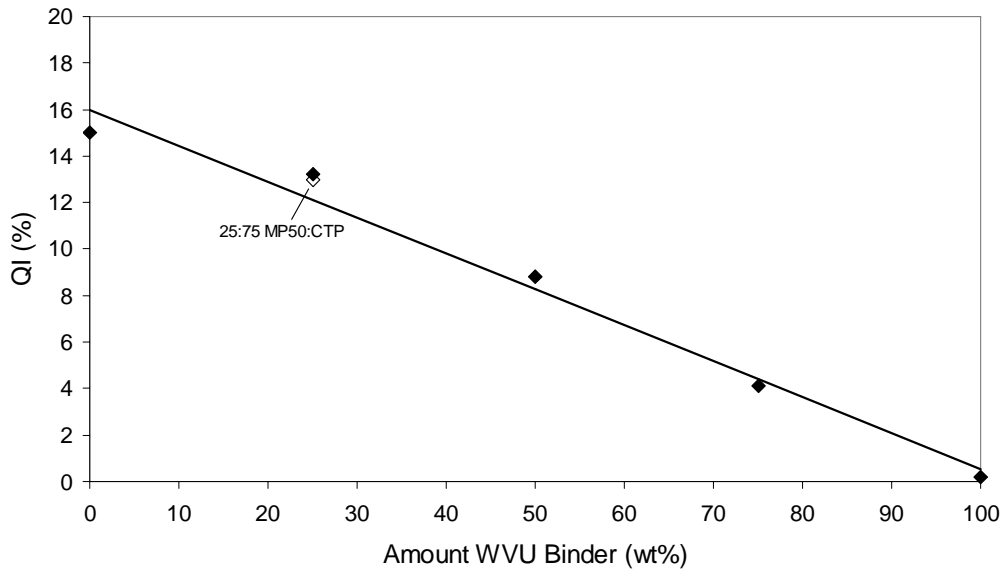
Figure 24. QI Content of Blends of Synpitch and Koppers Control.
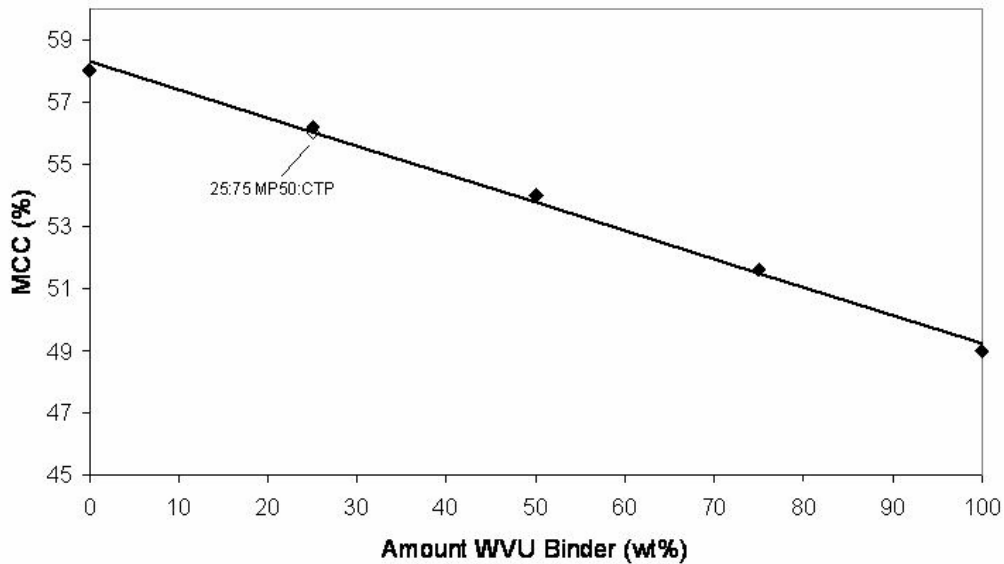
Figure 25. Modified Conradson Coke yield for blends of Synpitch and Koppers control pitch.

The density of electrode grade artificial graphite is measured at three different points. First, the density is measured in the "Green" or non-heat-treated state. After impregnation pitches are used, the density is measured again at the "Baked" stage. This step typically adds mass to the sample. Finally, the entire sample is "Graphitized" at a temperature of about 3000 $^{\circ}$C.

The results show that initially there was a deficit in density for the Green samples containing 25% Synpitch. However, after the baking process, the samples gained enough weight to make up for the discrepancy. After graphitization, the measured density was slightly lower than the target value, but well within limits of acceptability, as shown in Figure 26 below.
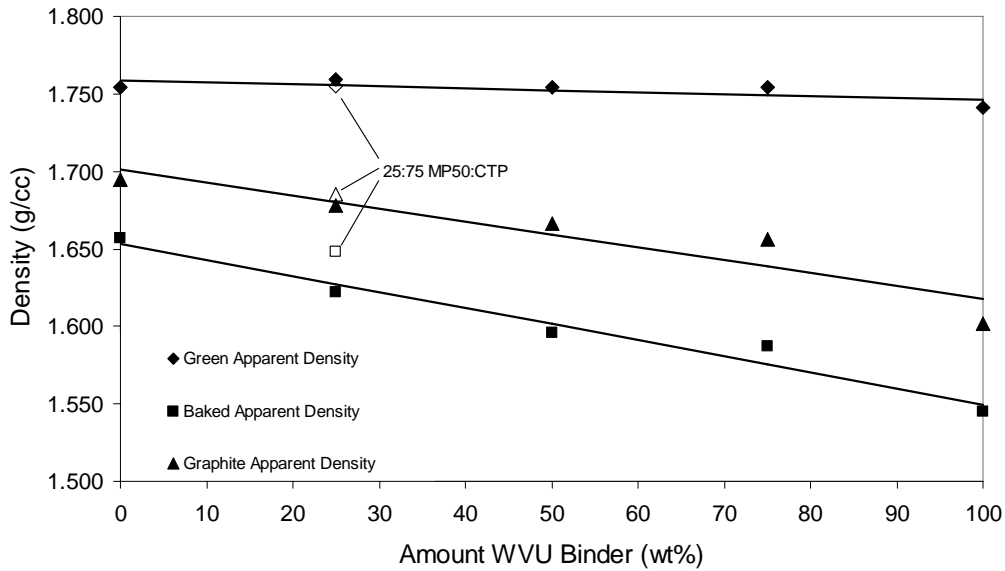
Figure 26. Density measurements for blends of Synpitch and Koppers control pitches.

Artificial graphite containing Synpitch exhibited significantly lower strength than samples made using Koppers control material, as shown in Figure 27. The discrepancy at 25% Synpitch content is considered significant, but within acceptable limits.
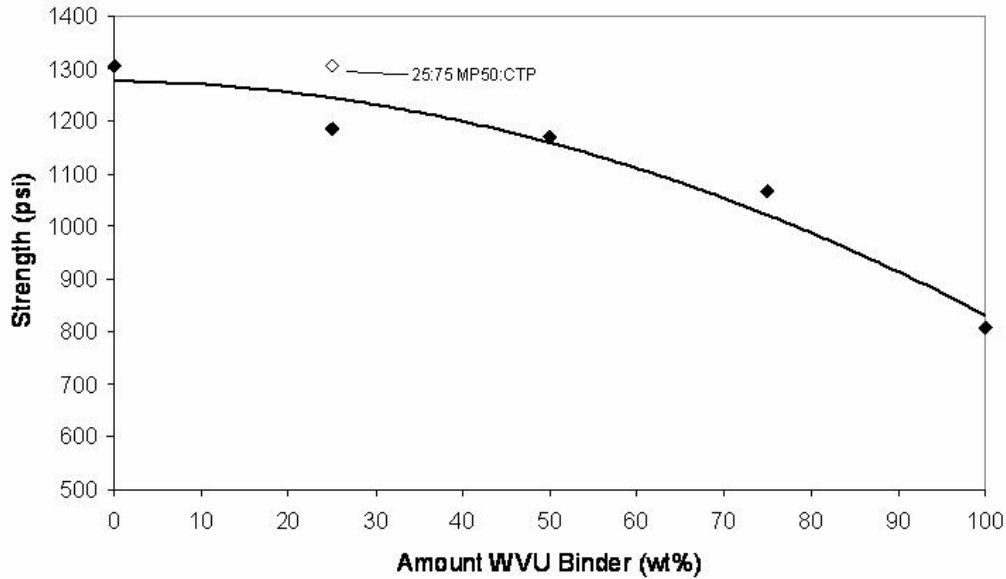
Figure 27. Strength versus Synpitch Content.

Electrical resistivity is a key property for arc furnace electrodes. Obviously, electrical losses in the electrode itself result in wasted electricity as well as unnecessary heating of the electrode.

Synpitch exhibit a significantly poorer resistivity than the control sample from Koppers, as shown in Figure 28 below. The addition of 25% Synpitch resulted in an increase in electrical resistivity of about 20%. The reason for this increase in resistivity is not clear. It may be that the higher reactivity of Synpitch may interfere with the formation and growth of anisotropic domains.

Another interesting feature of the resistivity measurements is the apparent nonlinearity of the curve, and in particular, the presence of local minima in resistivity for a composition of 75% Synpitch. It had been expected that resistivity might more closely follow a rule-of-mixture relationship. Thus, determination of the cause(s) of increased resistivity of composites containing Synpitch and potential remedies may be worthy of additional future research.
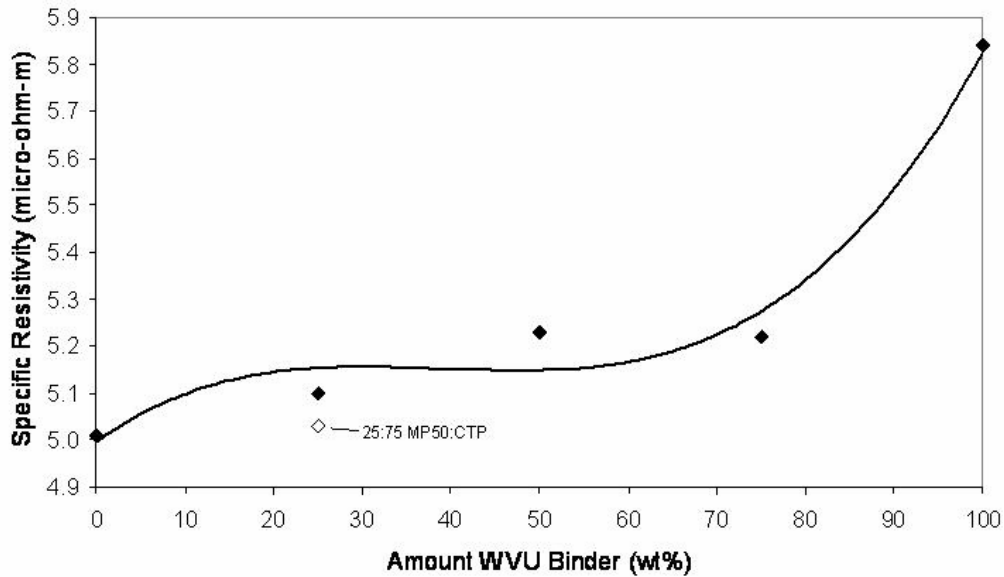
Figure 28.   Electrical Resistivity versus Synpitch Content.

The coefficient of thermal expansion is important in order to match existing equipment and standards. Although in principle zero-CTE materials would be attractive for high temperature systems such as arc furnaces, in actual practice such systems are designed to accommodate a certain amount of thermal expansion. Accordingly it is desirable to either meet the specification, or else achieve a somewhat lower CTE value. As shown in Figure 29 below, a blend of 25% Synpitch appears to be approximately optimal from this standpoint.
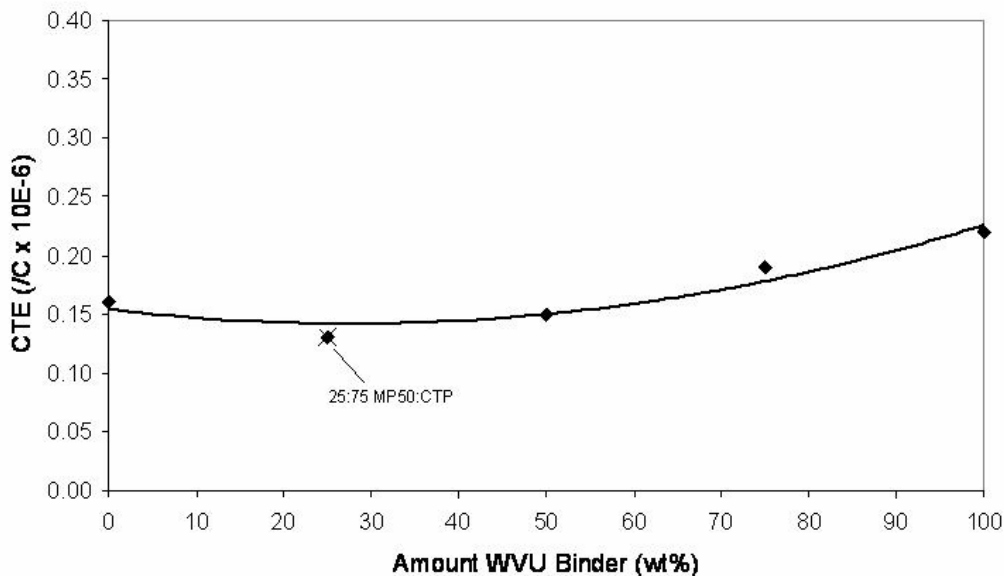
Figure 29. Coefficient of Thermal Expansion (CTE) versus Synpitch Content.

The results of tests on the pitch blends and composite artifact are summarized in Tables 1 and 2 below.

Table 1. Blended Pitch Properties.

Measurement	25:75 Syn:CTP	25:75 MP50:CTP
Mettler SP, °C	111.8	110.7
MCC, %	56.2	56.0
TGA (500 °C), %	59.4	61.0
QI, %	13.2	13.0
TI, %	32.7	28.6
Ash, %	0.23	0.19

Table 2. Artifact Properties.

Measurement	25:75 Syn:CTP	25:75 MP50:CTP
Green Apparent Density, g/cm^3	1.759	1.755
Baked Apparent Density, g/cm^3	1.622	1.648
Graphite Apparent Density, g/cm^3	1.678	1.685
Specific Resistivity, $\mu\Omega$m	5.10	5.03
Flexural Strength, psi	1186	1247
CTE, /C10E-6	0.13	0.13

2.6 Studies with Luscar Material for Anodes

A small amount of binder pitch was produced using Luscar Ltd Sub-Bituminous Coal Valley coal as part of Task VI. Some important differences were noted with this material. First, the mineral matter is generally in the form of a clay rather than a rocky state as is the case with West Virginia bituminous coals. Second, the liquefied coal results in a lower pitch yield than bituminous coal, suggesting that the liquefied coal contains more light molecules than conventional pitch.

The purpose of this study was to produce a set of pilot anodes made with a blended pitch consisting of 80% standard coal tar pitch and 20% synthetic pitch. The synthetic pitch was produced using the WVU coal extraction process. The pilot anodes were produced using the blended pitch and a standard coke formulation (including butts) at one pitching level (16.0 %).

Table 1 describes the basic pitch properties, Table 2 the dry mix formula for the laboratory pilot anodes, and Table 3 the baking profile. The processing conditions are listed in tables 4-9 for the blended pitch and comparison standard pilot anode series. Six pilot anodes (4 inch diameter x 6-7 inch height) were fabricated from each mix for the given pitching level of 16%.

Generally, the results indicate that the pitch containing the synthetic material produced laboratory pilot anodes of acceptable quality. Additional work would be required to determine optimum pitching level to maximize anode quality.

Table 3.   Analysis Report from Koppers Analytical Services Group.

Analytical Services Group			
Analysis Report			
Received From:	Harmarville	Follansbee	WVU
Description:	20% Luscar Pitch	Standard Pitch	Luscar Pitch
	80% Standard Pitch	C97-1019	2005-1368
	2005-1383		
Softening Point, °C:	112	109.4	112.3
Toluene Insolubles, %:	24.8	27.5	18.3
Quinoline Insolubles, %:	10.4	13.1	0.1
Beta Resins, %:	14.4	14.4	18.2
CVC, %:	54.5	57.8	42.3
Ash, %:	0.14	0.07	0
Specific Gravity:	1.31	1.34	1.574
Sulfur, %:	0.58	0.68	0.17
Metals, ppm:			
calcium Ca:	26	25	16
iron Fe:	124	147	51
lead Pb:	9	9	ND
nickel Ni:	2	1	1
phosphorous P:	N.D.	1	ND
potassium K:	25	31	4
silicon Si:	251	271	182
sodium Na:	14	ND	34
vanadium V:	2	3	2
zinc Zn:	44	57	4

Table 4. Standard Domestic Dry Mix Formula

Coarse Coke	31.5%	4725 g
Intermediate Coke	14.6%	2190 g
Fine Coke	37.0%	5550 g
Butts	16.9%	2535 g
Total		15000 g

The petroleum coke material was supplied by a US smelter and contained butt material.

Table 5. Baking Protocol

Baking: Anodes were baked to ~1100°C under N_2 purge.

0-600°C	10°C/hr.
600-1170°C	25°C/hr.
1170°C	14 hrs. Hold

Actual temperature center retort ~1100-1120°C.

Table 6. Laboratory Anode Forming Information—Luscar Blended Pitch.

FORMING DATA

4" Dia. Anode Cylinders - Atm.Vibrating Press

Date: 10/17/2005   Customer: **WVU-DOE**

Type of Pitch: **20/80 Blend**

Pitch #	2005-1383	Vibrator Run #'S	W-1	W-2	W-3	W-4	W-5	W-6
Analysis		Sample log #'S						
Softening Point, °C:	112	Pitch %	16					
Toluene Insolubles, %:	24.8							
Quinoline Insolubles, %:	10.4	Vacuum	No					
CVC, %:	54.5							
Ash, %:	0.14	Motor Wt. %	90					
Viscosity		Probe, PSIG	83					
150°C:								
160°C:		Probe, PSI						
180°C:								
		Frequency HZ	51					
C/H , Pitch:								
		Amptitude, Inches	227	231	231	238	222	235
Metals,PPM:								
		Mixer Temp. °C	194					
calcium Ca:	26							
iron Fe:	124	Mix Temp. °C	150					
lead Pb:	9							
nickel Ni:	2	Mold Temp. °C	150					
phosphorous P:	N.D.							
potassium K:	25	G-Force	7.5	7.5	7.51	7.57	7.43	7.62
silicon Si:	241							
sodium Na:	14							
sulfur %:	0.58							
vanadium V:	2							
zinc Zn:	44							

Table 7. Luscar Blended Pitch Anode Data 16% Pitching Level

Anode No,	Koppers Sample No.	Pitch Wt. %	Block GAD (g/cc)	Block BAD (g/cc)	InSitu C-V (wt.%k	% Shrinkage
W-1	2005- 1390	16	1.608	1.544	67.20	1.35
W-2	2005- 1391	16	1.600	1.536	67.11	1.36
W-3	2005- 1392	16	1.594	1.534	67.23	1.49
W-4	2005- 1393	16	1.604	1.565	76.51	1.35
W-5	2005- 1394	16	1.601	1.536	67.01	1.30
W-6	2005- 1395	16	1.590	1.529	67.18	1.48

Table 8. Luscar Blended Pitch Anode Core Data

Production Data	Core Baked Apparent Density (g/cc)	E.R. (μ Ohms-m)	Air Perm. (nPm)	CO_2 Reactivity % Wt. Loss	% Dust	% Attr.	% Residue	Air Reactivity % Wt. Loss	% Dust	% Attr.	% Residue	Crush Strength (Mpa)	Flexural Strength Stress (Mpa)	CTE Avg. Alpha (E^{-6}/°C @300°C)	Thermal Conductivity (W/m-K)
W-1	1.542	59.2		3.72	0.18	0.25	95.82					45.36	7.98	4.293	
W-2	1.538	62.0						27.57	6.28	1.91	64.22	44.52	6.66	4.410	
W-3	1.540	61.4	0.50	3.55	0.11	0.22	96.11						5.61	4.471	2.66
W-4	1.546	59.0	0.60					26.63	5.16	1.33	66.87		6.37	4.400	2.66
W-5	1.543	58.5	0.70	4.32	0.41	0.57	94.69						7.46	4.162	2.57
W-6	1.544	59.3						25.88	5.47	2.98	65.65	48.83	3.96	4.407	
Count	6	6	3	3	3	3	3	3	3	3	3	3	6	6	3
Avg.	1.542	59.9	0.60	3.86	0.23	0.35	95.54	26.70	5.64	2.07	65.58	46.23	6.339	4.357	2.628
Std. Dev.	0.003	1.4	0.10	0.40	0.15	0.19	0.75	0.84	0.58	0.83	1.32	2.29	1.432	0.112	0.055

Table 9. Standard Pitch Laboratory Anode Forming Information

- FORMING DATA			
4" Dia. Anode Cylinders - Vac./Atm.Vibrating Press			
Date: 7/22-8/3/99		**Customer:** Koppers	
		Type of Pitch: Standard	
Pitch #	C97-1019	Vibrator Run #'S	S13-19
Analysis		Sample log #'S	99-2563/2568
Softening Point, °C:	109.4	Pitch %	16
Toluene Insolubles, %:	27.5		
Quinoline Insolubles, %:	13.1	Vacuum	no
CVC, %:	57.8		
Ash, %:	0.07	Motor Wt. %	90
Viscosity		Probe, PSIG	83
160°C:	1280		
180°C:	378	Probe, PSI	13.68
Metals,PPM:		Frequency HZ	50
calcium Ca:	25	Amptitude, Inches	0.243
iron Fe:	147		
lead Pb:	9	Mixer Temp. °C	191
nickel Ni:	1		
phosphorous P:	1	Mix Temp. °C	160
potassium K:	31		
silicon Si:	271	Mold Temp. °C	150
sodium Na:	ND		
vanadium V:	3	G-Force	7.4/11.0
zinc Zn:	57		

Table 10. Standard Pitch Anode Data 16% Pitching Level

Sample No.	Koppers Sample No.		Pitch Wt. %	Block GAD (g/cc)	Block BAD (g/cc)	InSitu C-V wt. %	% Shrinkage
S13	C99-	2563	16	1.632	1.556	68.0	0.479
S14	C99-	2564	16	1.640	1.556	67.6	0.051
S16	C99-	2565	16	1.632	1.551	67.7	0.196
S17	C99-	2566	16	1.633	1.552	67.4	0.267
S18	C99-	2567	16	1.643	1.552	67.5	-0.385
S19	C99-	2568	16	1.637	1.547	67.9	-0.347
Avg.				1.636	1.552	67.6	0.12

Table 11. Standard Pitch Anode Core Data

Sample No.	Core Baked Apparent Density (g/cc)	E.R. (µ Ohms m)	Air Perm. (nPm)	ISO CO2 Reactivity				ISO Air Reactivity				Crush Strength (MPa)	Flexural Strength Stress (MPa)	CTE Avg. Alpha (E-6/°C @300°C)	Thermal Conduct. (W/mK)
				% Wt. Loss	% Dust	% Attr.	% Residue	% Wt. Loss	% Dust	% Attr.	% Residue				
S13	1.555	60.1	0.38					20.55	4.45	1.88	73.11		7.10	3.846	2.74
S14	1.562	60.4		10.33	2.69	1.36	85.61					45.62			
S16	1.553	60.1	0.41					20.52	4.41	1.82	73.23		5.71	3.817	2.54
S17	1.560	59.7		11.22	2.46	1.55	84.76					45.20			
S18	1.553	59.4	0.32					25.41	4.55	1.30	68.73		5.63	3.890	2.76
S19	1.554	59.9		10.45	2.04	1.18	86.31					39.11			
Count	6	6	3	3	3	3	3	3	3	3	3	3	3	3	3
Avg.	1.556	59.9	0.37	10.67	2.40	1.36	85.56	22.16	4.47	1.67	71.69	43.31	6.15	3.851	2.68
Std. Dev.	0.004	0.4	0.05	0.48	0.33	0.19	0.78	2.81	0.07	0.32	2.56	3.6	0.83	0.037	0.12

3.0 References

None.