**DEVELOPMENT OF CONTINUOUS SOLVENT EXTRACTION
PROCESSES FOR COAL DERIVED CARBON PRODUCTS
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Quarterly Report

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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. 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. The Hydrotreatment Facility is being prepared for trials with coal liquids. Raw coal tar distillate trials have been carried out by heating coal tar in the holding tank in the Hydrotreatment Facility. The liquids are centrifuged to warm the system up in preparation for the coal liquids. The coal tar distillate is then recycled to keep the centrifuge hot. In this way, the product has been distilled such that a softening point of approximately 110°C is reached. Then an ash test is conducted.

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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 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 continuous processes for hydrogenation as well as continuous production of carbon foam.

2.0 EXPERIMENTAL

2.1 Hydrotreatment of coal liquids

The Hydrotreatment Facility is being prepared for trials with coal liquids. Raw coal tar distillate trials have been carried out by heating coal tar in the holding tank in the Hydrotreatment Facility. The liquids are centrifuged to warm the system up in preparation for the coal liquids. The coal tar distillate is then recycled to keep the centrifuge hot. In this way, the product has been distilled such that a softening point of approximately 110°C is reached. Then an ash test is conducted.

Results to date show that the ash level is around 1% which is higher than our specification for binder pitch. Probably this was probably due to the coal liquids mass flow rate being too high in the centrifuge, since a flow controller was not used. Accordingly, future plans are for a pump to be able to meter coal liquids at a more precise rate, thus enabling lower ash content.

In addition, air blowing experiments are being trialed with coal liquids in a one-liter reactor to obtain a high softening pitch.

Flow curves have been established using 10 different pressures, different lengths of tubing, different diameters of tubing, and two types of liquids, water and oil. Using this data, the tubing size was estimated such that a flow rate of 3 gallons/hour can be obtained in the Hydrotreater. The tubing was then connected to the nominal 5 gallon reactor, charged with 4 gallons of coal tar distillate and pressurized.

Development of a continuous hydrotreatment capability means that 55-gallon drums of solvent must be handled in Engineering Research Building room 317. The electronic controllers had to be reconnected the controllers so that they would be outside of the reaction area for safety reasons. A ramp was built so that the drums can pass over the lip of the walk-in fume hood.

The catalyst basket has been re-charged with a fresh supply of catalyst for use in the 5 gallon reactor in preparation for the continuous hydrotreater. Because the catalyst is received in the oxide form it must be sulfided with Dimethyl Sulfoxide (DMSO). After sulfiding, the reactor was purged while hot to remove the DMSO vapor. The reactor was then filled with coal tar distillate to remove any residual DMSO from the catalyst basket and then drained.

The 5 gallon hydrotreater was loaded with coal tar distillate and operated under a continuous hydrogen pressure of 1000 psi. Some valves were found to be leaking and were replaced. Two runs were completed.

The 1 gallon reactors were cleaned. The products from the hydrotreater were combined with coal and hydrogenated using a standard protocol for one 1 hour. Along with this run another run was completed at a higher temperature and another run was done using tetralin as a control. Centrifugation is accomplished for 30 minutes at 4000 rpm.

The pilot plant has been retrofitted with a mini pilot system to separate solids from the heavy oil solutions. This involved installing three seven gallon pressure rated tanks and subsequent connective piping into and from the Sharples-Pennwalt centrifuge. One vessel is a stirred tank reactor with heater bands where the solvent and products are heated to 100 °C. The heated solution is then sent through a heated pipe to the centrifuge. The flowrate to the centrifuge is controlled with two valves. The underside of the centrifuge is fitted with two of the tanks. One is for the solvent which is used to preheat the system and the other is for the centrifuged product. All solids are caught in a 20 gallon catch can which can be removed and emptied. Handling of the materials is kept to a minimum by the ability to blow the material from the tanks back to the reactor or to a storage container. A small fume hood was constructed to put over the bowl area of the centrifuge to minimize escaping vapors to the surroundings.

The first test run with the solvent and product were run this week. The materials ran through the system well, however, there were some vapors leaking from the system and subsequently a very strong odor in the highbay area. For future runs, especially if more material is used, a better fume capturing unit will be necessary. We also will need to better control the flowrate with a pump to increase the residence time of the materials in the centrifuge. This should further remove enough solids to achieve the desired <.1 % ash level in the final product.

Other projects that are ongoing are the construction and installation of the new condenser for the coking/foaming table and the construction of ballistic foam samples. The condenser needs to have the tubes welded in place and then the unit will be leak tested. A couple of the ballistic samples have been made and several others will be made in the near future.

2.2 Coal Dissolution and Swelling

The model describing coal dissolution concerns two distinct phenomena; the swelling of coal, and the extraction of coal. Historically, literature has incorrectly related swelling with extraction. While some high swelling coals may also have high solvent extraction ratios, poorly extracting coals (such as lignite) have the highest observed swelling ratios, as observed by Jose M. Rincon¹. Swelling provides a solvent with access to large soluble molecules, but a solvent capable of swelling the coal is not necessarily capable of dissolving it. It is desirable that swelling phenomena be modeled because pre-swelling of coals can increase the coal's susceptibility to H-donor solvents.

The swelling data is smooth and consistent. Increased extraction temperature and extraction time increased the swelling ratio. This is contrasted by the extraction yield, which is virtually zero until a temperature of 185°C is reached. After an extraction

temperature of 185°C and above is reached, the dissolution yield reached a maximum quickly, within a matter of minutes. The extraction can be roughly modeled by a step function, where nothing happened before 185°C and yield was increased drastically at and above 185°C. This is shown graphically in Figure 1.

Figure 1. Concentration of coal in NMP as a function of time at various temperatures.

3.0 RESULTS AND DISCUSSION

3.1 Alternate Coking Protocol

WVU has developed a patent-pending process to increase the level of anisotropy in samples of pitch. In other words an anisotropic (needle grade) coke can be produced from low quality isotropic pitch feedstock. Briefly, the concept involves the use of dynamic mechanical shear force to cause graphite domains to align.

Hot plate microscopy was performed on a hydrogenated coal extract, made in December 2002 using Marfolk Eagle Seam coal, extracted in Tetralin at 400 °C for 1 hour in a 5 gallon reactor, fairly mild hydrogenation condition, centrifuged, and evaporated in a rotary evaporator. This pitch is designated HO91. The coke produced by this method was observed using the Hitachi Scanning Electron Microscope. Anisotropic orientation of the crystalline structure was observed.

Figure 2. Needle Coke striations

Figure 3. Needle Coke (control).

Figure 4. Needle Coke (control).

Figure 5. Needle Coke (control).

Figure 6. Needle Coke (control).

Figure 7. Alternate process coke oriented platelets.

Figure 8. Alternate process coke platelet formations.

Figure 9. Alternate coke process platelets.

Figure 10. Alternate process coke with uncoked pitch and oriented coked plate formations

Figure 11. Alternate process coke highly oriented crystalline formation, similar to needle coke.

Figure 12. Shear Coke

Figure 13. Alternate process coke with nanoscale crystals, probably pyrite.

3.2 Laboratory Testing

Coal Tar Distillate CTDI062 and CTDI065 (liquids) samples were analyzed using an elemental analyzer. Simdis was used to determine the relative concentration of C_x compounds by comparing boiloff rates, as shown in the figures below.

Figure 14. Overlay of chromatograph results and rate diagram at which the sample is boiled off in a simulated distillation column, showing significant concentrations of C_7 , C_{13} , C_{16} compounds.

Figure 15. Time-Dependent boiloff rate using SIMDIST.

An NMR-Proton analysis of Coal Tar Distillate sample CTD L6 is shown below:

Figure 16. Proton analysis of CTD L6 full spectrum, showing aromatic content of nominally 77%, aliphatic content 23%.

Figure 17. Detail of aliphatic portion of CTD L6.

Figure 18. Additional detail of aliphatic area of the spectrum.

Figure 19. C-13 NMR Analysis on CTD Feed, full spectrum. The aromatic to aliphatic ratio is 84/16.

Figure 20. NMR Analysis shows an aromatic to aliphatic ratio, of 86/14, for CTD Feed using proton NMR analysis.

Figure 21. NMR Analysis on CTD feed, aliphatic area, using proton NMR.

Figure 22. Full-Spectrum proton NMR analysis on CTD (Level 2 hydrogenation). Aromatic to aliphatic ratio = 83/17.

Figure 23. C-13 full-spectrum NMR analysis on CTD Level 2 hydrogenation. The aromatic/aliphatic ratio is 93/4.

Figure 24. Proton NMR analysis of aliphatic area for CTD Level 2 hydrogenation.

Figure 25. Proton NMR analysis on CTD Level 3 hydrogenation, showing aromatic to aliphatic ratio of 82/18.

Figure 26. Full-spectrum C-13 NMR analysis on CTD Level 3 hydrogenation.

Figure 27. Close-up of aliphatic region for proton NMR Analysis on CTD Level 3 hydrogenation.

Figure 28. Full-spectrum proton NMR Analysis on CTD Level 4 hydrogenation. (Aromatic/aliphatic ratio = 83/18).

Figure 29. Full-Spectrum C-13 NMR analysis on CTD Level 4 Hydrogenation (aliphatic/aromatic ratio 91/5).

Figure 30. Close-up of aliphatic region, using proton NMR Analysis on CTD Level 4 hydrogenation.

Figure 31. Full-spectrum Proton NMR analysis on CTD Level 5 Hydrogenation (80/20 aromatic/aliphatic ratio).

Figure 32. Full-spectrum C-13 NMR analysis on CTD Level 5 Hydrogenation (aliphatic/aromatic ratio = 85/15).

Figure 33. Close up of aliphatic region of CTD Level 5 hydrogenation using proton NMR.

3.3 Ultrasonic Dissolution

Information concerning modeling of the extraction and swelling of coals was gathered and parsed. This information will serve as the basis for and justification of a new model describing the swelling and extraction of coals. Specific information of interest involved coal dissolution by ultrasonic agitation is found in Liu et al (reference: Hong-Tao Liu, Tatsushi Ishizuka, Toshimasa Takanohasi, Masashi Iino; “Effect of TCNE Addition on the Extraction of Coals and Solubility of Coal Extracts”; Energy & Fuels, 7, 1108-1111).

“TCNE was added to a slurry of a coal in the CS₂-NMP mixed solvent just before the extraction was carried out under ultrasonic irradiation (38 kHz)...the extraction yield enhancement by TCNE described above may be attributed to the suppression of association between coal molecules.”

That extraction could be carried out under ultrasonic radiation provides a clue as to the mechanism of dissolution. Molecular motion is confined to translational, rotational, and vibrational; and certain frequencies affect certain molecular motions.

3.4 Carbon Fuel Cell Applications for Anode Coke Materials

We continue to consider means by which carbon composites based on anode-grade materials may be applicable to carbon fuel cells. As mentioned in previous reporting, the carbon fuel cell produces power by converting carbon to carbon dioxide through an intermediate carbonate state.

Carbon samples were ground mechanically and then ball milled to achieve micron-sized particles or as small as possible. Samples trialed include petroleum coke, binder pitch, and Cenfuel (an acid extracted coal fuel produced by Carbonxt, Inc) to make mixtures for the carbon fuel cell rods.

An inverted hydraulic press was modified to press the carbon rods for Dr. Zondlo in collaboration with SARA. The design worked in that it compressed the rod quite well; however the samples were usually cracked during extraction. GrafTech experience indicates that extrusion has been used at temperatures slightly below the softening point. This is done so that the rod will hold shape. The new die has been designed and machined by Bergen. It requires alignment pins which should arrive on Friday. Also, machined threads on the die are needed so that it can easily be attached to the hydraulic press.

A shell and tube heat exchanger to be used as a condenser for coking and foaming volatiles will be completed soon. The tank has been fitted with a series of one inch tubes which will flow water in an effort to cool the hot gases to a point of condensing within the container. The tubes are in the shell and welded. It needs to be leak tested and then have the end caps welded. This will complete the additional condenser.

There has been discussion regarding the appropriate course of action with respect to the current volatile condensing unit. It may be easier and perhaps beneficial to use it in series with the new condenser. This would add another zone through which the gases may be cooled and volatiles removed from the air.

4.0 CONCLUSION

More experimental work has been carried out on synthetic coal tar enamel coatings. Several commercial organizations have recently asked us whether a durable coating can be created with enhanced electrical conductivity. Accordingly, we have considered combinations of coal tar enamel with graphite powder additives. Coal tar enamel is similar to coal tar pitch, although additives are used to make a more plastic material. It was estimated that a concentration of 30% graphite may be enough in order to achieve adequate electrical conductivity. Accordingly, one hundred grams of coal tar enamel and 100 ml of NMP were combined in a metal 400 ml beaker with 30 grams of graphite and heated with a hot plate and stirred occasionally for approximately 20 minutes, or until the enamel was completely dissolved in the NMP. A sprayable consistency was obtained.

Samples were prepared and sent to Firefly Energy Inc for evaluation for use in a commercial application that they have that requires conductive coatings.

5.0 REFERENCES

None.