

PRODUCTION OF CARBON PRODUCTS USING A COAL EXTRACTION PROCESS

DE-FC26-02NT41596

Semiannual Report

For the period: September 11, 2003--March 10, 2004

Resubmitted: February 23, 2006

Principal Investigator:
Dady Dadyburjor, PhD

Co-Investigators:
Chong Chen, PhD
Elliot B. Kennel
Liviu Magean
Peter G. Stansberry, PhD
Alfred H. Stiller, PhD
John W. Zondlo, PhD

West Virginia University
Department of Chemical Engineering
College of Engineering and Mineral Resources
PO Box 6102
Morgantown WV 26505

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 technologies for carbon products from coal-derived feedstocks. Carbon products can include precursor materials such as solvent extracted carbon ore (SECO and synthetic pitch (Synpitch)). In addition, derived products include carbon composites, fibers, foams and others.

Key milestones included producing hydrogenated coal in the Hydrotreating Facility for the first time. The facility is now operational, although digital controls have not yet been completely wired.

In addition, ultrasound is being used to investigate enhanced dissolution of coal. Experiments have been carried out.

Table of Contents

Disclaimer.....	2
Abstract.....	3
List of Tables.....	5
List of Figures.....	6
1.0 Executive Summary	7
2.0 Technical.....	7
2.1 Isotropic and Mesophase-Based Fibers and Composites	7
2.1.1 Production of Fibers.....	7
2.1.2 Production of Composites	7
2.1.3 Processing Optimization.....	8
2.2 Coal Derived Carbon Foam	8
2.2.1 Pretreatment on Manufacture of Carbon Foams at Low Pressures.....	8
2.2.2 Evaluation of Properties of Foams.....	8
2.3 Production of Coal-Derived Pitches and Cokes.....	9
2.3.1 Construction of a Continuous Green Coker	15
2.3.2 Effects of Green Coking and Calcining Conditions	17
2.3.3 Development of Matrix and Mesophase Pitches	17
2.4. Technology Transfer.....	20
3.0 References.....	25

List of Tables

Table 1. Coal Conversion Results using Solvent Blends.....	10
Table 2. Overall Mass Balances of	11
Table 3. Softening point for products obtained via progressive hydrogenation.	12
Table 4. Solvent Protocols.	15

List of Figures

Figure 1. Stress vs. Strain for an uncalcined pitch composite using ceramic.	8
Figure 2. Stress-strain curve for a carbon foam sample fabricated in 30 minutes.	9
Figure 3. Coal Conversion Results.	10
Figure 4. Chromatography Column(s).....	13
Figure 5. Concentration of Small Coal (less than 106 microns) in solution as a.....	14
Figure 6. The initial design failed because the temperature was allowed to rise.....	16
Figure 7. A clamshell heater is used to heat a steel tube through which a coke.	16
Figure 8. Bench scale coking experiment.	17
Figure 9: Coal conversion efficiency for various solvents at	18
Figure 10. Coal conversion efficiency for various solvents at.....	19

1.0 Executive Summary

The purpose of this DOE-funded effort is to develop technologies for carbon products from coal-derived feedstocks. Carbon products can include precursor materials such as solvent extracted carbon ore (SECO) and synthetic pitch (Synpitch). In addition, derived products include carbon composites, fibers, foams and others.

Key milestones included producing hydrogenated coal in the Hydrotreating Facility for the first time. The facility is now operational, although digital controls have not yet been completely wired.

In addition, ultrasound is being used to investigate enhanced dissolution of coal. Experiments have been carried out.

2.0 Technical

2.1 Isotropic and Mesophase-Based Fibers and Composites

2.1.1 Production of Fibers

No data this reporting period.

2.1.2 Production of Composites

A low cost method for producing reinforced composites was trialed using air-blown Koppers coal tar pitch. Preliminary experiments have been carried out with different fiber and ceramic reinforcements (see also Section 2.4.0).

.

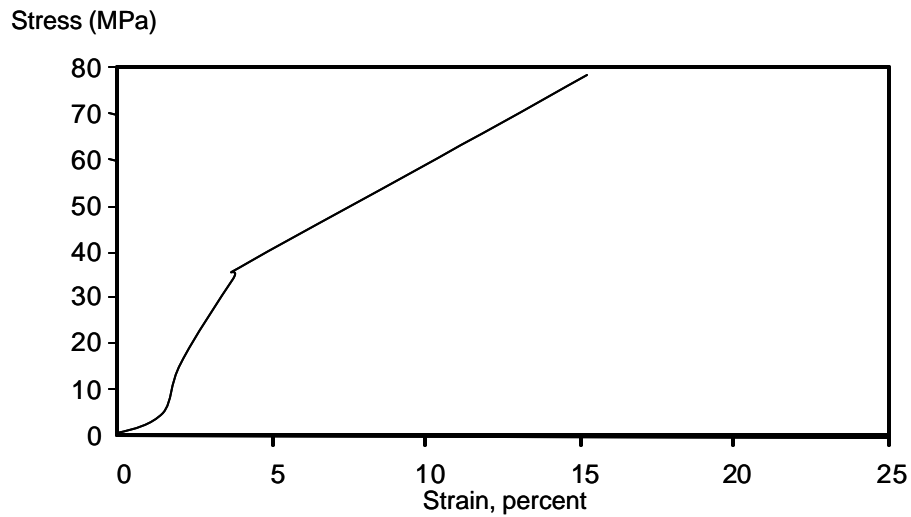


Figure 1. Stress vs. Strain for an uncalcined pitch composite using ceramic reinforcement.

2.1.3 Processing Optimization

No data this reporting period.

2.2 Coal Derived Carbon Foam

2.2.1 Pretreatment on Manufacture of Carbon Foams at Low Pressures

Foam can now be produced at atmospheric pressure with a foaming time of 30 minutes. Previously, only one sample could be fabricated per day in a batch reactor. Continuous samples are now possible. Several carbon foam samples were manufactured using raw coal as well as coal tar pitch and exhibit properties comparable to high pressure foams.

This is done using radiant heat in a nitrogen atmosphere furnace. This enables the use of a continuous process, as described in Section 2.4.0.

2.2.2 Evaluation of Properties of Foams

A stress-strain plot for foam fabricated in only 30 minutes is shown below.

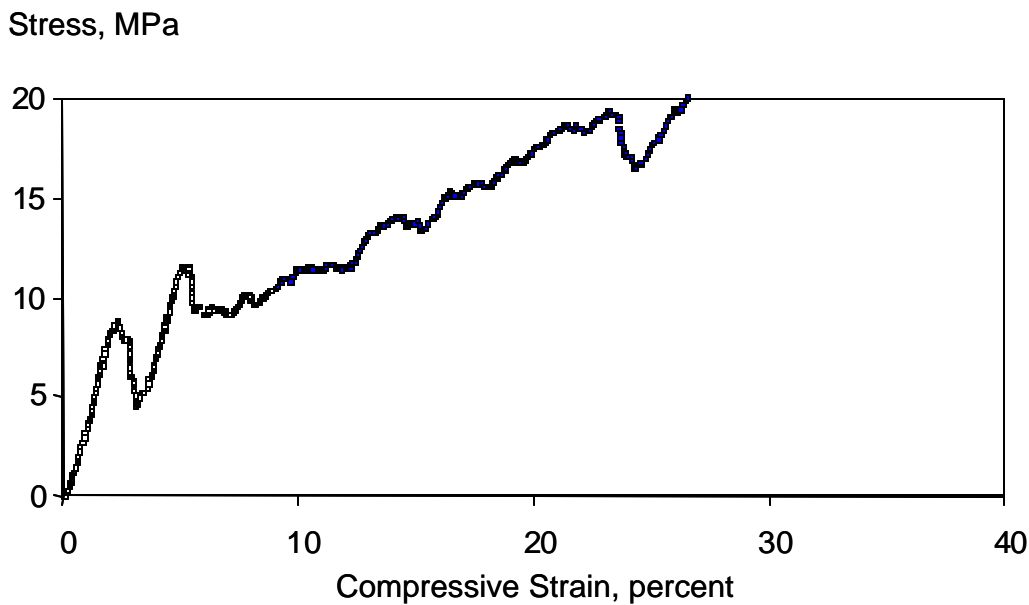


Figure 2. Stress-strain curve for a carbon foam sample fabricated in 30 minutes.

2.3 Production of Coal-Derived Pitches and Cokes

The ultrasound was used to reduce the particle size of solvent extracted coal ore (SECO) that had been ground in the ball mill. The ultrasound significantly decreased the particle size, but the resulting solution was very difficult to filter. While the ultrasound effectively reduced the size of small particles, it did not break up larger particles. The ultrasound was also tested to determine if it can be used for hydrogenation. This was done by exposing a mixture of tetralin and coal to ultrasound for about 24 hours. The initial results indicate that the conversion efficiency of the coal was relatively low.

Utilization of Lower Cost Solvents

Experiments were carried out to show that the donor solvent reaction can be effective when a fraction of the solvent is not hydrogenated. Surprisingly, it was found that the best performance is achieved when only about 25% of the solvent is hydrogenated.

Carbon black base (coal derived solvent) was hydrogenated using Ni - Mo catalyst using a catalyst basket. Ni - Mo catalyst is taken in the oxide form is first sulfided using DMSO (di methyl sulfoxide) and then hydrogenated at 350 °C.

Hydrogenation reactions were accomplished at 500 psi nitrogen overpressure and temperature of 400 °C using the raw CBB and blends of fresh and hydrogenated CBB. A solvent/coal ratio of 5:1 was used.

The results are contained in Table 1.

Table 1. Coal Conversion Results using Solvent Blends

Solvent	Amount of coal used (g)	Amount of coal unconverted (g)	Conversion,%
100% fresh CBB	4.0581	2.7865	33.6 ± 1
50% Hydrogenated CBB 50% fresh CBB	4.0004	2.0931	51.19
50% Hydrogenated CBB 50% fresh CBB	4.0003	2.0467	52.4
25% Hydrogenated CBB 75% fresh CBB	4.1160	1.8632	58.7
25% Hydrogenated CBB 75% fresh CBB	4.0113	1.9035	56.4
25% Hydrogenated CBB 75% fresh CBB	4.1999	2.2185	50.6
25% Hydrogenated CBB 75% fresh CBB	4.0025	1.9822	54.1

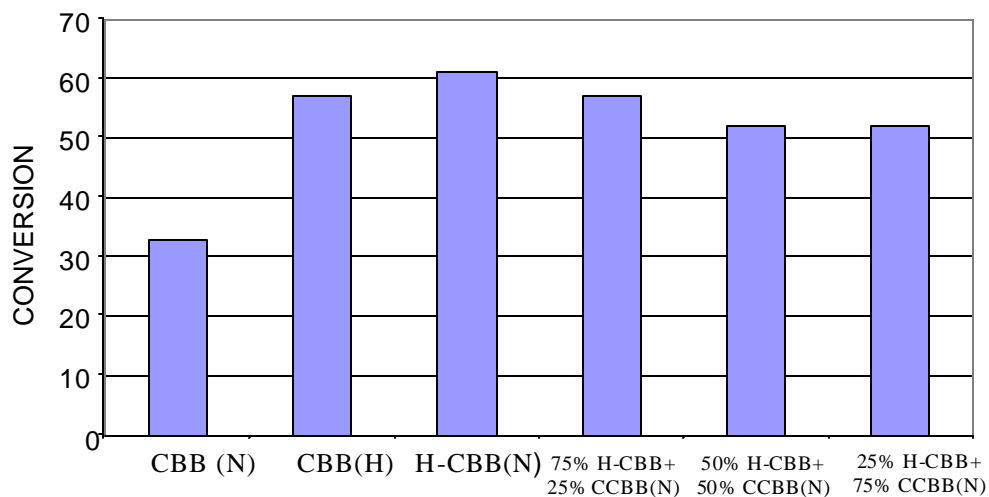


Figure 3. Coal Conversion Results.

Analysis of Carbon Black Base (CBB) samples send to Koppers Industries have been reported on the basis of Polyaromatic Hydrocarbons (PAH). Table 2 shows the PAH content of raw and recovered CBB obtained at varying degrees of temperature and hydrogen pressure.

Table 2. PAH Species in Fresh and Recovered CBB at Various Conditions of Temperature and Reaction Atmosphere.

Sample	Fresh (%)	Recovered at 350 °C (%)	Recovered at 400 °C (%)	Recovered at 450 °C (%)	Recovered at 400 °C & N ₂ (%)
Naphthalene	2.53	3.79	5.75	7.07	5.47
Acenaphthylene	0.04	0.17	0.37	0.5	0.31
Acenaphthene	4.57	4.22	4.61	4.89	4.32
Phenanthrene	14.63	15.45	15.82	16.05	15.56
Anthracene	1.07	1.09	1.45	1.49	1.15

There is probably a hydrogen shuttling effect which results in higher conversion from the recovered (R) solvents than with fresh solvents. The primary PAH components responsible for shuttling are naphthalene, phenanthrene and anthracene. The concentration of naphthalene, phenanthrene and anthracene is observed to increase in recovered CBB compared to fresh CBB, especially at higher temperatures, while other chemicals likely remain in the product and are not recovered with the solvent. This result supports the otherwise surprising contention the strength of the solvent actually improves after each recycling.

The overall mass balance using the recovered solvents is shown in Table 3. The mass loss percentage using the recovered solvents is about 12% whereas for fresh solvents the mass loss figure is around 7%. This suggests that some part of the solvent, especially heavy compounds, are left in the pitch product and not recovered. The process mass balance must then correct for this effect.

Table 3. Overall Mass Balances of Coal Hydrogenation Reactions with Recovered Solvents.

Run	Trial	In Coal (g)	In Solvent (g)	Total In (g)	Out Pitch (g)	Out THF Ins. (g)	Out Rec. Solv. (g)	Total Out (g)	In - Out (g)	Loss (%)
CBB	A	4.001	20.1	24.101	2.988	2.3014	16.125	21.4094	2.6916	11.2
CBB	B	4.0021	20.4	24.4021	3.1088	2.3708	15.58	21.0596	3.3425	13.7
HCO	A	4.0012	20.2	24.2012	3.2931	2.3431	15.49	21.1262	3.075	12.7
HCO	B	4.0036	20.1	24.1036	2.656	2.405	16.36	21.421	2.6826	11.2
RCO	A	4.0026	20.4	24.4026	2.6822	2.6991	15.98	21.3613	3.0413	12.4
RCO	B	4.0001	19.9	23.9001	3.2612	2.7691	15.14	21.1703	2.7298	11.4

In the hydrotreatment of coal the nature of the products of hydrogenation changes progressively as the amount of hydrogen addition increases. One of the most important effects of hydrogenation is a reduction in the molecular weight of the products. In particular, this is reflected in their boiling range or the softening point of the product pitch. As hydrogen addition progresses, the yield of distillates increases and the yield of

distillation residue is correspondingly reduced. Furthermore, the distillates become lighter in character so that a greater proportion of the product slate occurs in the lower boiling fractions.

The species formed as coal is hydrogenated to produce distillate fuels may also be classified by their solubility in various solvents. Materials soluble in hexane are generally referred to as oils and materials insoluble in hexane but soluble in benzene are generally referred to as asphaltenes. The terminology for materials insoluble in benzene is preasphaltenes. The increasing solubility of the products is a further reflection of the reduction in molecular weight with hydrogen addition. Initially, the main product of extraction is preasphaltenes but, as hydrogenation progresses, these are broken down into asphaltenes and oils.

Accordingly, a hydrotreatment run was performed to see reduction in softening point with progressive hydrogenation. A run was performed wherein a solvent (CBB) to coal ratio of 3:1 was used. The product pitch was isolated after separation from the solvent by vacuum distillation. Softening point analysis was performed on this product pitch. Note that the softening point was done under nitrogen to avoid smoking of the sample in air at higher temperatures. Then the pitch obtained was further hydrotreated under the same hydrogenation conditions as with the parent coal. The second product pitch was isolated from this run by separating the solvent by vacuum distillation. Again a softening point was carried out on this pitch to see for differences in the molecular weights or the boiling points of these two pitches. Note here the temperature at which the vacuum distillation was cut off was kept the same for both runs, i.e. 250 °C to avoid any variation in molecular weight of the two pitches obtained. The results are summarized in Table 4.

Table 4. Softening point for products obtained via progressive hydrogenation.

	Trial 1 oC	Trial 2 oC
Softening Point of pitch from coal	158.5	159.9
Softening Point of pitch from first pitch	122.7	124.1

The above differences in softening point suggest that there is progressive hydrogen addition going on in the product pitches with each hydrotreatment run.

2.3.1 Measurement of Multi-Component Solvents

A Chromatography column was set up for analysis of hydrocarbon liquids, tars and extracts. Three other columns are in the process of being setup for analysis of Lower Powellton Coal extract. Figure 4 is a picture of the chromatography column setup.



Figure 4. Chromatography Column(s)

The first attempt at packing the column was a failure. The alumina was not packed tight enough and there was severe channeling of the solvents and solute. To solve this problem, a vibrator was used to pack the alumina more tightly. The vibrator appeared to have made a significant difference. In a four-foot column, the alumina dropped about half a foot from vibration.

The column will produce bands that can be seen under both visible light and black light. The column contents will be removed and analyzed by both UV-Visible spectroscopy and mass spectrometry. Some of these coal extract components will also be taken to foaming temperature to see which ones turn liquid and which ones do not. This will be our attempt to isolate the “Coking Principle.”

Additional coal dissolution data was taken for Lower Powellton coal. Comparatively little coal dissolution occurred at 170°C, although a significant increase in the coal solubility occurs between 170°C and 202°C. A new model is being formulated to describe this behavior. Figure 5 illustrates this trend.

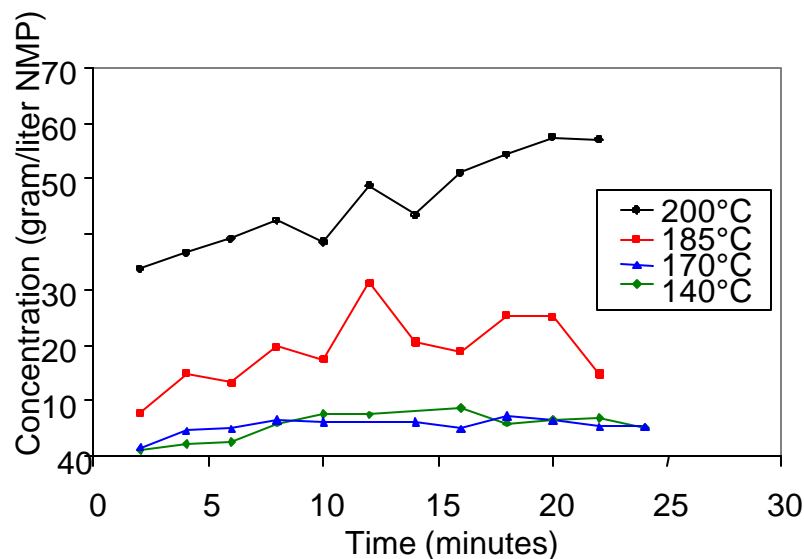


Figure 5. Concentration of Small Coal (less than 106 microns) in solution as a function of time.

Lower Powellton coal was used in a 22 factorial experiment. The two levels of high and low for temperature are 202°C and 170°C respectively. The low and high levels for time are 5 minutes and 60 minutes respectively. Large coal (48 x 65 US Tyler Mesh) was used for all extraction runs, so better time control could be established; i.e., because the dissolution rate is lower for large coal, resulting in larger time periods for the low-level time in the 2n factorial experiment.

Solvents of increasing polarity will be passed through the chromatography columns so that the classes of compounds present in the coal extract will separate into distinct bands. Solvents of increasing polarity will be used according to Table 5.

Table 5. Solvent Protocols.

Desired Elution Strength (on Al₂O₃)	Mixing Proportions
0.01	500 ml of Hexane and 0 ml of Toluene
0.06	425 ml of Hexane and 75 ml of Toluene
0.11	345 ml of Hexane and 155 ml of Toluene
0.16	259 ml of Hexane and 241 ml of Toluene
0.21	166 ml of Hexane and 334 ml of Toluene
0.26	65 ml of Hexane and 435 ml of Toluene
0.31	451 ml of Toluene and 49 ml of THF
0.36	313 ml of Toluene and 187 ml of THF
0.41	152 ml of Toluene and 348 ml of THF
0.46	474 ml of THF and 26 ml of DMSO
0.51	338 ml of THF and 162 ml of DMSO
0.56	192 ml of THF and 308 ml of DMSO
0.61	33 ml of THF and 467 ml of DMSO
0.66	322 ml of DMSO and 178 ml of Methoxyethanol
0.71	116 ml of DMSO and 384 ml of Methoxyethanol
0.76	445 ml of Methoxyethanol and 55 ml of Ethanol
0.81	287 ml of Methoxyethanol and 213 ml of Ethanol
0.86	92 ml of Methoxyethanol and 408 ml of Ethanol
0.88	0 ml of Methoxyethanol and 500 ml of Ethanol

2.3.1 Construction of a Continuous Green Coker

Two cokers were constructed during this reporting period. Coking occurs in a ram-fed pipe, which is heated by a clamshell heater. In the initial attempt to test the coking performance of the unit, the clamshell temperature reached over 1000 °C which caused the pipe to deform.

The design was modified slightly to permit a rotary feed mechanism, and used to produce anisotropic coke.



Figure 6. The initial design failed because the temperature was allowed to rise too quickly.

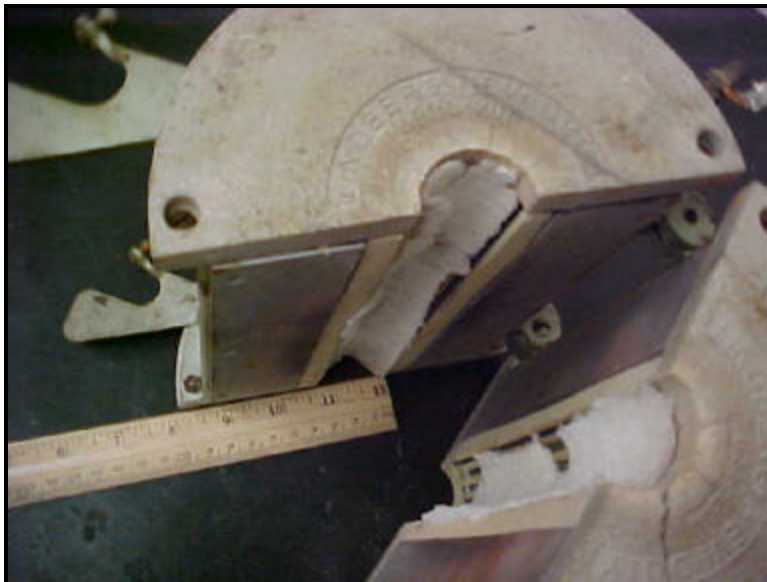


Figure 7. A clamshell heater is used to heat a steel tube through which a coke precursor is fed.



Figure 8. Bench scale coking experiment.

2.3.2 Effects of Green Coking and Calcining Conditions

Data on coking is being accumulated using the modified coker.

2.3.3 Development of Matrix and Mesophase Pitches

A variety of lab scale tests were conducted to determine the optimum solvent type and the degree to which the solvent is hydrotreated. These reactions were carried out in tube bomb reactors in which approximately 4.0 grams of coal were mixed with approximately 20.0 milliliters of solvent. The reactions were carried out at 400°C in a nitrogen atmosphere at atmospheric pressure and 500 pounds of pressure.

The first set of experiments was conducted using five different solvents: carbon black base, anthracene oil, marflax oil, slurry oil, and tetralin. Tetralin, a traditional coal extraction solvent, was used as a control case to analyze the effectiveness of the other four solvents which are significantly cheaper than tetralin. The results are shown in Figure 9. Tetralin is clearly the best solvent. However, the other solvents perform reasonably well, particularly the carbon black oil and the slurry oil.

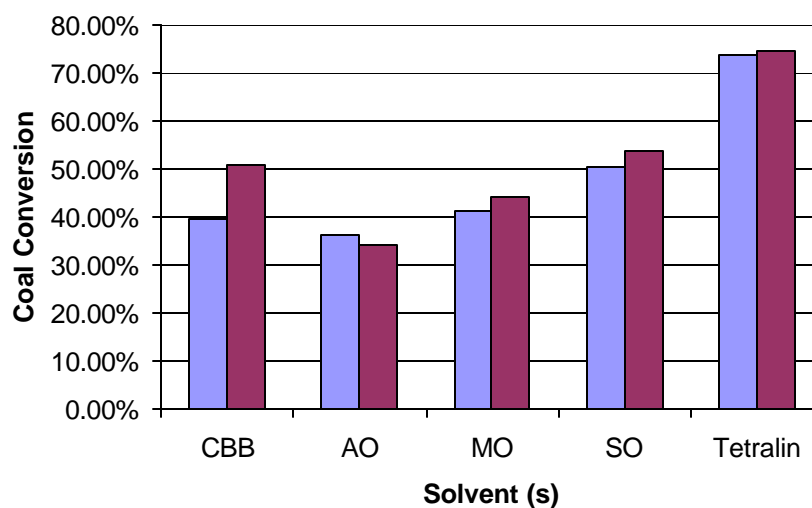


Figure 9: Coal conversion efficiency for various solvents at 0 pounds (blue) and 500 pounds (purple) of nitrogen pressure. Solvents include carbon black base (CBB), anthracene oil (AO), marflax oil (MO), slurry oil (SO), and tetralin.

The second set of experiments was carried out to determine the effect of hydrotreatment on the effectiveness of the solvent. Carbon black base was mildly and severely hydrogenated and the results were compared to non-hydrogenated carbon black base. The results are shown in Figure 10. It is clear that hydrotreating the solvent increases the coal conversion efficiency.

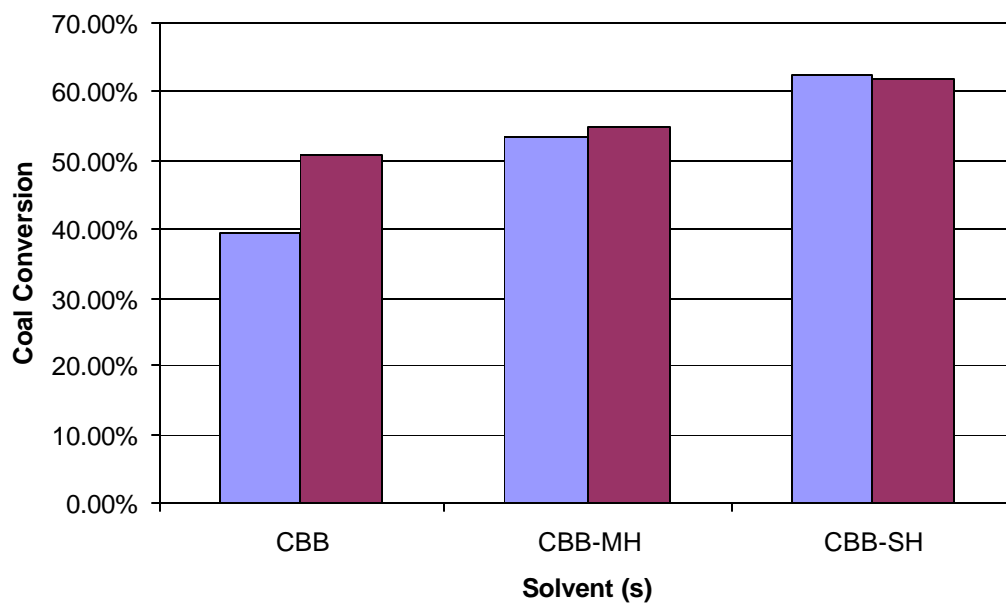


Figure 10. Coal conversion efficiency for various solvents at 0 pounds (blue) and 500 pounds (purple) of nitrogen pressure. The solvents were carbon black base (CBB) and carbon black base that had been mildly hydrogenated (MH) or severely hydrogenated (SH).

The next step in the progression from laboratory scale tests to tests on an industrial level is to perform similar reactions in a one gallon autoclave. In these tests, hydrogenated carbon black oil will be used as the solvent.

2.4. Technology Transfer

The attached presentation is prepared as a summary of carbon foam manufacturing capabilities using low pressure processes.

Low Cost Processing of Carbon Foam

Elliot Kennel, Philip Biedler, Steve
Carpenter, Chong Chen, Pete
Stansberry, Al Stiller, John Zondlo
Chemical Engineering Department
West Virginia University
PO Box 6102
Morgantown WV 26506-6102



Overview

Introduction
Foaming SOTA
Recent Developments
Technical Challenges
Summary



Definitions

Feedstock - a material used as an input stream to a chemical process.

Hydrogenation - adding hydrogen to the coal matrix to improve its properties. Typically only a few percent addition is required.

Pitch - a carbon based material which is a solid at room temperature but becomes fluid-like under elevated temperature processing operations.

Solvent Extracted Carbon Ore (SECO) —organic coal solid extracted using a solvent. SECO devolatilizes but does not melt when heated.

Synpitch — A *synthetic pitch*, or hydrogenated coal extract material which can be melted to form a liquid.



Carbon Foam at WVU circa 2000

Originally based on controlled coking of coal extract and hydrogenated coal (synthetic pitch).

Process occurs at temperatures of 400-500 °C and pressure of 500 psi.

Slow ramp to temperature.

Overnight cooldown.

Capacity = 1 batch per 8 hour day.

Scaleup limited by use of non-commercial feedstocks.



Carbon Foam Focus

Decrease materials cost by using commodity feedstocks

Coal Tar Pitch

Treated Coal

Petroleum Pitch + blends

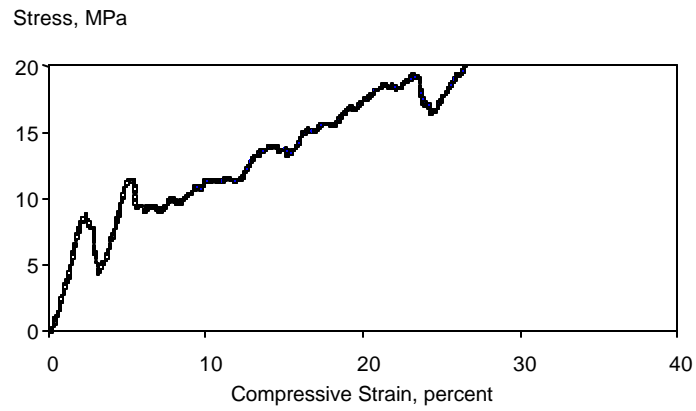
Develop low-cost, mild processing conditions

Modify pitches to produce foam at atmospheric pressure, decrease production time to 30 minutes, improve thermal stability.

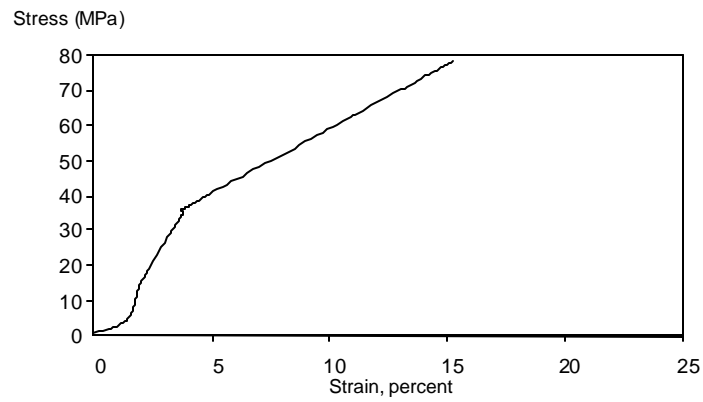
Enables Low-Cost Continuous 1 atm production!



1-Atm 30 Minute Foam Strength (Calcined) Preliminary Data



Compressive Strength of High Density Carbon Foam (uncalcined) Preliminary Data



Treatments to Modify Pitch Properties

Air Blowing: Cross-link and elevate softening temperature.

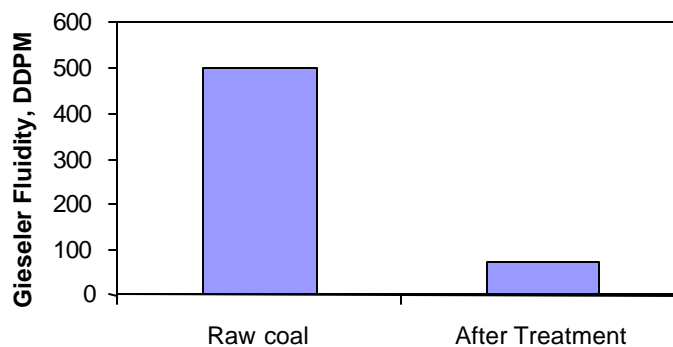
Vacuum outgassing: remove light hydrocarbons.

Partial distillation: remove light hydrocarbons.

Other treatments to modify molecular weight distribution, aromatic content and fluidity.



Oxidation, Cross-linking and Devolatilization Controls Fluidity



Continuous Belt Furnace



Standard Industrial Device

Operates at up to 1600 °C

Nitrogen Atmosphere

Incineration of Volatiles



Belt Furnace Production Capacity

Assumptions:

Foam sheets 1 meter wide
2 cm high
Density = 0.5 g/cm^3
Furnace Active Zone: 5 meters
Residence time: 30 minutes
Feed rate: 10 meters/hour

Production rate: 100 kg/hour

Output is continuous, not batch



West Virginia University

Status

Trial production will likely occur in 2004 using a rented furnace.

1100 C temperature capability
Nitrogen atmosphere
Volatiles handling capability

Trial production rate of ~800 kg/shift.



West Virginia University

Conclusions

SOTA batch process is high pressure and high temperature. Dubious potential for low cost.

New process is continuous mode, ambient pressure. Likely to have excellent potential for low cost.

Current focus is on structural foams with feedstock cost of \$200 per ton.

Both a producer and a customer have been identified. Trial production will likely occur later this year.

Thermally conductive foams are also possible.



West Virginia University

3.0 References.

None