

# Research on Carbons from Coal

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## Introduction

There are numerous examples of carbon products produced from coal. Included are products such as cokes, activated carbons, carbon blacks, and specialty products such as coal-derived carbon fibers. The processes that produce these products include combustion, gasification, coking, pyrolysis, and related coal-conversion technologies. In most processes to produce carbon materials from coal, there is a need to separate carbon from inherent mineral matter contained in coal. Separation of the carbon is necessary to minimize the amounts of contaminants that will ultimately appear in the products. Separation can be achieved prior to use by physical separation of the mineral matter or by post-processing in coal conversion and coal combustion processes. This paper presents some of the separation and subsequent processing schemes for producing high value products from coal that are being studied.

## Experimental

The 1-L semibatch autoclave reactor employed a flowing gas, batch slurry system (typically 400 g charge). The feed comprised a coal-derived recycle solvent with 30% Pittsburgh No. 8 coal added, with H<sub>2</sub> pressure between 1000 and 1500 psig, temperatures of 350 or 390°C, with a 0.5 h reaction time (0.67 h nominal heat-up time). Following the reaction, the reactor was cooled to ambient temperature (0.5 h nominal cool-down time), the reactor was depressurized, and the products were removed. Procedures and product work-up are described in full elsewhere [Cugini, et al. 1998].

## Results and Discussion

Coal can be used to prepare precursors for carbon fibers. Coal-tar pitch has been used as a precursor to mesophase pitch. A good mesophase pitch for forming carbon fibers is easily stabilized, has a low viscosity and melting point, has high purity, has high coking value, and produces a highly-oriented structure. Although these mesophase pitches contain hundreds of compounds, naphthalene and phenanthrene are present in relatively

large concentration. Coal-tar mesophase is characterized by two significant processing difficulties. First, mesophase pitches from coal tars can have high softening points and can be unreactive to oxygen stabilization [Mochida, et al. 1995]. Second, the yield of mesophase pitch from the precursors is only several weight percent [Song and Schobert, 1993]. During the preparation of mesophase pitches suitable for spinning, lighter molecules are typically driven off rather than condensed into the mesophase, leading to low yields.

Hydrogenation has been proposed as a means of improving the qualities of mesophase pitch. The hydrogenation can be accomplished either catalytically or with a hydrogen donor solvent such as tetrahydroquinoline [Yamada et al. 1981, Mochida, et al. 1985]. This tends to increase the concentration of naphthenic groups in the precursor pitch, some of which remain in the mesophase pitch. These naphthenic groups, along with short-chain alkyl groups, induce a low softening point of the mesophase precursor and are amenable to the stabilization reaction of oxidative condensation [Mochida, 1985]. However, the costs associated with the hydrogenation of the coal can be substantial.

One potential opportunity to make use of hydrogenated coal-derived material in the production of carbon fibers is to take advantage of the asphaltenes. In the conversion of coal to liquid products several fractions are produced. A potential economic advantage might be obtained by optimizing such processes to produce high-value carbon precursors while using the other fractions as by-product transportation fuels. Asphaltenes, defined by their solubility characteristics in certain solvents such as pentane through tetrahydrofuran (THF), are high molecular weight compounds with high aromatic content and are nearly free of mineral matter. Table 1 lists the solid state NMR analyses of a coal-derived asphaltene derived from catalytically hydrogenated coal and the carbonized product from this asphaltene.

As is indicated in the table, the carbon aromaticity of the original asphaltene sample was 0.83 and was increased to >0.95 by carbonization at 750°C in an inert atmosphere for 0.5 h. An optical study of the carbonized sample indicated that the mesophase was observable in the carbonized sample and as carbonization increased (either by increasing the time or temperature) the extent of mesophase fraction increased.

The asphaltenes used in the above study were produced under conditions designed to maximize yields of distillate products (425°C, 2,500 psig, and added catalyst). For the sake of producing mesophase pitch, it would be advantageous to use milder hydrogenation conditions. Table 2 lists the yields of asphaltenes that were produced in tests at milder coal liquefaction conditions with no added catalyst.

Asphaltenes are the intermediates between the conversion of THF insolubles to heptane solubles. The results indicate that the largest yield of this intermediate fraction was found at 390 °C. Further tests are planned to evaluate the trends with temperature and pressure. Currently, softening points and coking values of the asphaltenes produced in these tests are being determined by ASTM methods. These samples are also being prepared for surface inspection and mesophase formation under an optical microscope along with their solubility profiles. These parameters along with the ultimate and proximate analyses will help determine their potential for the production of fibers or other high value products. A search for the optimum conditions needed to obtain asphaltenes for the production of premium carbon products (e.g. temperature, pressure, catalyst) will be conducted. The results in hand indicate that a combination of liquefaction and carbonization technologies holds promise as a synergistic route from coal to high value carbons.

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## Disclaimer

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

## References

1. Cugini, A.V., Rothenberger, K. S., Krastman, D., Ciocco, M.V., Thompson, R. L., McCreary, C., and Gardner, T.J., *Catalysis Today*, 43, 1998, 291-303.
2. Mochida, I., Yoon, S.-H., Korai, Y., Otsuka, H., Sakai, Y., and Komatsu, M., *ChemTech*, 25-6, Feb. 1995, 29-37.
3. Song, C. and Schobert, H., *Fuel Processing Technology*, 34, 1993, 157-196.
4. Yamada, Y., Matsumoto, S., Fukuda, K., and Honda, H., *TANSO*, 107, 1981, 144.
5. Mochida, I., and Korai, J., *J. Fuel Soc. Japan*, 64, 1985, 802.

**Table 1. Carbon Aromaticity of Asphaltenes**

Sample	Carbon Aromaticity	$f_{al}$	$f_{ar}$	$f_{ar}^{CH}$	$f_{ar}^C$
Asphaltene	0.83	0.1871	0.8129	0.5580	0.4420
Carbonized Asphaltene	>0.95				

**Table 2. Effect of Processing Conditions on Asphaltene Yield**

T, °C	P, psi	Coal (wt% in Feed)	%THF Insols <sup>a</sup>	Asphaltene Yield, % <sup>b</sup>
390	1,500	Pittsburgh No. 8 (30)	4	79
350	1,500	Pittsburgh No. 8 (30)	16	51
350	1,000	Pittsburgh No. 8 (30)	16	41

<sup>a</sup> Insolubles are based on total feed.

<sup>b</sup> Based on coal feed.