

# SOLVENT EXTRACTION OF LOW GRADE COALS FOR CLEAN LIQUID FUELS

*Elliot B. Kennel, Mayuri Mukka, Alfred H. Stiller and John W. Zondlo*  
West Virginia University  
Department of Chemical Engineering  
PO Box 6102 Morgantown WV 26506-6102  
304-293-2111 x2423  
[Elliot.kennel@mail.wvu.edu](mailto:Elliot.kennel@mail.wvu.edu)

## Abstract

Solvent extraction of bituminous coals has been used as a means of coproducing clean liquid transportation fuels as well as solid fuels for gasification. Coal solvents are created by first hydrogenating coal tar distillate fractions to the level of a fraction of a percent and then simply dissolving the coal in the hydrogenated solvent. This enables bituminous coal to enter the liquid phase under conditions of high temperature (above 400 °C). The pressure is controlled by the vapor pressure of the solvent and the cracked coal. Once liquefied, mineral matter can be removed via centrifugation, and the resultant superheavy crude can be processed to make pitches, cokes and lighter products.

Lower rank coals such as sub-bituminous coal and lignite are desirable feedstocks for this process due to their low cost and high aliphatic character, which can result in superior transportation fuels. However, these advantages are partially offset by the disadvantages of high moisture content and high ash content which typically accompany lignite and sub-bituminous coals.<sup>1</sup> In particular, ash content of approximately 20% is problematic because centrifugation might not succeed in decreasing the ash content of the extract. Much of the liquid product would be contained in the nominal tails rather than in the separated liquid centrate.

In order to overcome this, a more complete liquid separation can be accomplished by vacuum distillation. Mineral matter is further heat treated to produce a value-added slag product. Solids separation can be over 90% effective using this technique depending upon the degree to which coal molecules are broken down during the solvent extraction process.

## Concept

Solvent extraction is an evolutionary way by which criteria emissions can be reduced during the production process while replacing processes such as co-production of coal tar from metallurgical grade coke production, as a means of obtaining liquid products from coal. Coal tar results from the condensation of vapors emitted from coal as it is coked in a metallurgical coke oven. However, non-recovery ovens, in which the coal tar is consumed in order to fuel the metallurgical grade cokemaking, offer superior environmental performance, and thus receive additional consideration as the process of choice in the modern environmentally conscious era. Hence, supplies of coal tar are decreasing even as demand for it is increasing.<sup>2</sup>

Because coal tar is an aromatic liquid, aromatic chemicals from it are more easily produced rather than aliphatic chemicals preferred for transportation fuels and the like. This is not to say, however, that coal liquids are inherently useless for fuels. Other aromatic heavy liquids, such as Athabasca Oil Sands crudes and Venezuelan Orinoco crudes, might have

been considered unacceptable for the fuels industry a generation ago, but are now routinely handled in state-of-the-art North American refineries.<sup>3</sup> Were it not for the fact that established markets exist for chemicals derived from coal tars, no doubt coal tar would be increasingly utilized as a feedstock for transportation fuels, as the technology certainly exists to upgrade such hydrocarbons.

In the case of solvent extraction processes, the present authors advocate the creation of heavy aromatic coal-derived crudes from coal as a simpler and less expensive process than the creation of synthetic sweet light crudes.

This process involves dissolving coal in a commodity solvent such as decant oil or coal tar distillate, usually with the addition of hydrogen-rich diluent in order to increase the total solubility of the coal, and to decrease the viscosity. The total amount of hydrogenation in the solution can be as low as a fraction of a percent by mass, compared to the level obtained in commodity solvents (e.g., coal tar distillate).

In this way, it is possible to dissolve up to about 90% of the coal feedstock as determined on a dry ash-free basis. Both bituminous as well as sub-bituminous rank coals have been successfully trialed in this way. The result is slurry containing dissolved coal as well as undissolved mineral matter and fixed carbon. The solid phase is then removed via centrifugation, resulting in a heavy, aromatic synthetic hydrocarbon liquid.

The role of hydrogen was historically viewed as being “donated” to solid molecules in the coal in order to create lower molecular weight species and render them more fluid.<sup>4</sup> In the current application, however, it is recognized that the amount of hydrogen is insufficient to cause fluidity by transfer to molecules in the coal structure. Rather, hydrogen is seen as an agent that causes the breakup of polymerized molecules in the coal. Hence a single hydrogen atom can break up many hydrocarbon molecules. This somewhat surprising issue is supported by examination of Tables 1-3, in which it is seen that the mass ratio of hydrogen to carbon is actually lower for binder pitch (i.e., the product), than either the coal or coal tar distillate solvent.

**Table 1. Elemental Analysis of Bituminous Coal (Kittanning).**

| <b>Element</b> | <b>Average</b> | <b>% Rel. S. D.</b> |
|----------------|----------------|---------------------|
| Nitrogen%      | 1.7            | 2.2                 |
| Carbon%        | 77.9           | 1.1                 |
| Hydrogen%      | 5.3            | 1.0                 |
| Sulfur%        | 1.8            | 22.9                |
| H/C ratio      | 0.07           |                     |

**Table 2. Elemental Analysis of Coal Tar Distillate (Solvent/Diluent).**

| Component Name | Average | % Rel. S. D. |
|----------------|---------|--------------|
| Nitrogen %     | 1.1     | 1.2          |
| Carbon %       | 92.7    | 0.2          |
| Hydrogen %     | 6.2     | 0.05         |
| Sulfur %       | 0.3     | 6.4          |
| H/C ratio      | 0.07    |              |

**Table 3. Elemental Analysis of Binder Pitch (110 °C Softening Point).**

| Component Name | Average | % Rel. S. D. |
|----------------|---------|--------------|
| Nitrogen%      | 1.2     | 3.8          |
| Carbon%        | 93.3    | 0.05         |
| Hydrogen%      | 4.3     | 0.6          |
| Sulfur%        | 0.3     | 2.5          |
| H/C            | 0.05    |              |

Thus basic principles suggest that additional hydrogen is not needed to convert coal to binder pitch, but in fact a small amount of excess hydrogen might be generated. In practice, however, a certain amount of hydrogen is lost due to methane generation or entrainment of liquid products in the centrifuge tails, requiring that coal feedstocks be supplemented by addition of a makeup solvent/diluent. The environmental consequence is that hydrogen is consumed only in small amounts (less than one mass percent of the product) to generate a pitch product, implying that carbon generation during hydrogen production is also very small. A zero-hydrogen process is also potentially achievable.

Generation of thermal energy for processing is another requirement that could be associated with generation of carbon dioxide. This would have to be evaluated on a case-by-case basis depending on the particular method used to generate thermal energy, and the associated capture and sequestration strategy associated with each case.

The refining process of the resultant coal extract solution would presumably be conceptually similar to the processes used for upgrading petroleum-based crudes such as Orinoco Venezuelan or Athabasca Oil Sands. Extensive hydrotreating would be necessary in order to remove sulfur and nitrogen compounds, as well as to enhance aliphatic content and to lower the molecular weight distribution.

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<sup>®</sup>). Thus hydrogen is added to the system in an aliphatic state, as shown in the figures below.

The ratio of the aromatic peak area to the 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<sup>®</sup>, the donor solvent reaction may take place in several aliphatic compounds and not just in Tetralin<sup>®</sup>. 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 FTIR peak areas corresponding to aromatic hydrogen and to aliphatic hydrogen. The basic technique is to define a peak area by truncating the peak, and subtracting the background as illustrated by the calculations below.

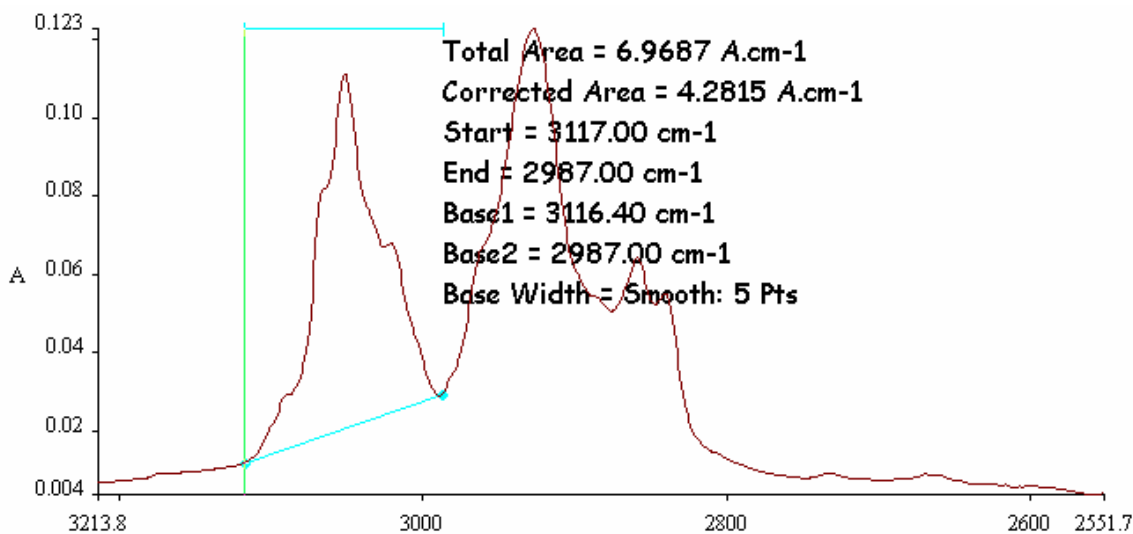


Figure 1. FTIR Aromatic Peak Measurement Algorithm.

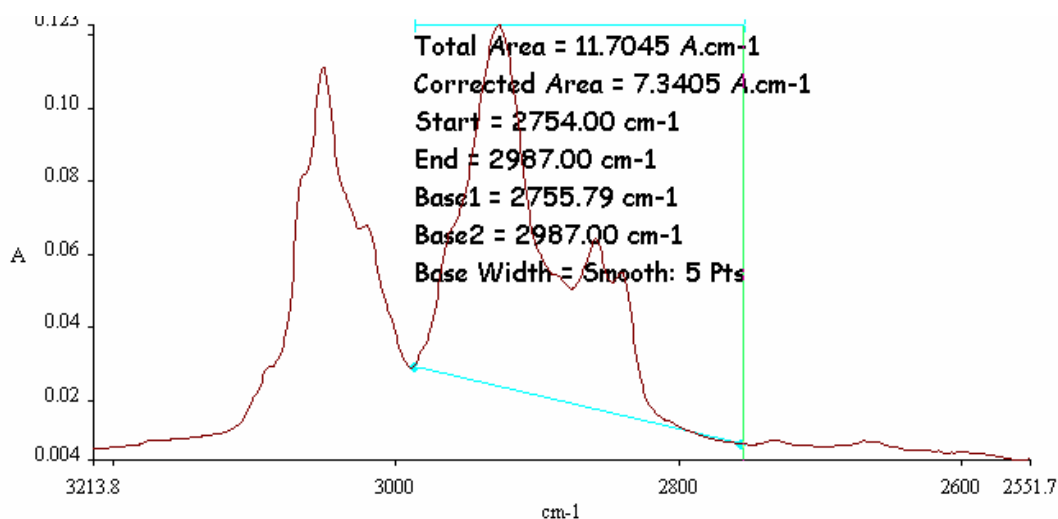


Figure 2. Sample FTIR Aliphatic Peak Measurement Calculation.

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 FTIR machines, different calibration standards were examined using both instruments and compared. Typical values for aromatic to aliphatic ratio are about 2.0 before the reaction and 0.5 to 1.0 after the reaction is carried out as estimated by FTIR, consistent with the notion that aromatic content is decreased as the reaction is carried out. Again however, this does not prove that hydrogen donation is actually the primary reaction that causes a phase transition. Depolymerization may be at least as significant in many processes.

FTIR studies verify that the digestion process tends to result in reduced aromatic content, although coal derived fuels are still higher in aromatic content than desired by fuels producers, suggesting that blends with highly aliphatic liquids may be desirable.

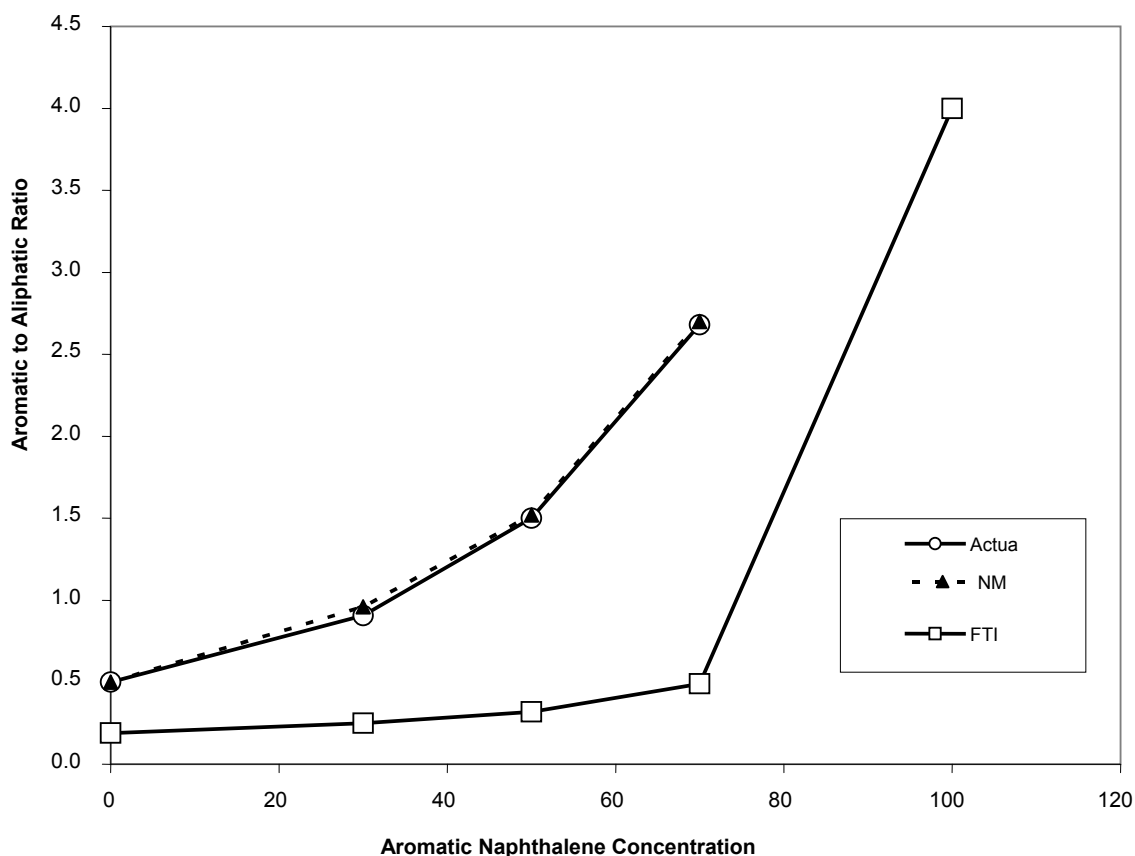


Figure 3. Aromatic to aliphatic ratio as estimated by FTIR and NMR in a solution of naphthalene and tetralin.

A logical extension of this effort would be to create extracts from lower rank coals from the western US and Canada. One reason is that lower rank coals may offer enhanced aliphatic content and reduced aromatic content. This may be a disadvantage from the standpoint of commercial pitch production since pitches require aromaticity in order to create well-ordered structural carbon for use in the metals smelting industry. However, from the standpoint of fuels production, lower aromatic content is an advantage from the standpoints of handling, combustion rate kinetics, etc.

Blends of coal-derived liquids with other fuels such as biofuels may be desirable in order to achieve proposed standards on carbon footprint. In addition, other parameters such as aromatic-to-aliphatic ratio, combustion rate constant, specific enthalpy content, lubricity, cold viscosity etc. might be effectively modified by combining coal derived fuels with other fuels having desirable environmental characteristics. As an example, a blend of 85% ethanol with 15% coal derived liquids of the appropriate molecular weight would likely combust cleanly since the aromatic content of the coal derived liquids would be outweighed by the nonaromatic ethanol. At the present time, an agreed-upon carbon accounting methodology has not yet been developed, however.

## Summary

The results suggest that fuels produced from solvent extraction of coal can be “greener” than conventional fuels if not perfectly so. Direct liquefaction processes do not produce CO<sub>2</sub> directly although anytime energy or hydrogen is consumed, the processes used to generate those commodities need to be considered for their environmental footprint. Combinations of coal-derived fuels with fuels with exceptional environmental characteristics such as biofuels may offer the best overall combination of environmental and other performance metrics.

## Acknowledgement

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