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COOPERATIVE RESEARCH IN COAL LIQUEFACTION
INFRA TECHNOLOGY AND GENERIC TECHNOLOGY DEVELOPMENT
Final Report for the Period October 1, 1985—December 31, 1986

June 29, 1987

Work Performed Under Contract No. FC22-85PC80009

For
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Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By
University of Kentucky
Lexington, Kentucky

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Final Report on DOE Contract
No. DE-FC22-85PC80009
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Submitted to the
U.S. Department of Energy

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June 29, 1987

Submitted by the University of Kentucky
on behalf of the
Consortium for Fossil Fuel Liquefaction Science

University of Kentucky
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Kentucky Energy Cabinet

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Overview of Research Activities of the
Consortium for Fossil Fuel Liquefaction Science
on DOE Contract No. DE-FC22-85PC80009

Period: Oct. 1, 1985 to Dec. 31, 1986

G.P. Huffman, Director, Consortium for Fossil Fuel Liquefaction Science
L.V.A. Sendlein, Director, Institute for Mining and Minerals Research

Introduction

The Consortium for Fossil Fuel Liquefaction Science is a research consortium that currently includes six universities and a state energy laboratory. The membership includes Auburn University,* the University of Kentucky, the University of Pittsburgh, Syracuse University, the University of Utah, West Virginia University, and the Kentucky Energy Cabinet Laboratory. The Consortium was founded in response to the concern of the faculty and scientists at these institutions over the decline of coal liquefaction research in this country, particularly long range, basic research.

The principal goals and objectives of the Consortium are briefly summarized below.

1. To identify and evaluate new methods of coal liquefaction.
2. To develop high-tech methods of characterizing coal structure for liquefaction potential, and to establish a liquefaction data base for U.S. coals.
3. To provide continued systematic assessment of liquefaction concepts for the potential of future new technology options.
4. To coordinate the activities of some of the nation's outstanding coal research laboratories, scientists and engineers as part of a single research program that is responsive to the needs of both government and industry.
5. To provide the nation with an adequate supply of well-trained young scientists and engineers for future energy research.

*Auburn University was not a member of the Consortium during its first year. Consequently, the current report does not include any research conducted at Auburn.

Currently, over forty faculty and scientists, a similar number of graduate students and postdoctoral students, and a significant number of technical and clerical staff are working on Consortium research projects. Consequently, approximately 100 people participate in the Consortium program.

During our first year of research funding significant progress was made on a number of coal liquefaction research topics. Some specific areas where notable progress was made include integrated molecular structure and liquefaction studies, differential liquefaction processes, maceral separation, analysis, and conversion studies, development and application of sophisticated structural analysis techniques, multivariate computer analysis of spectroscopic and other data, catalysis studies, biodesulfurization and bioprocessing of coal, co-processing of crude oil and coal, in situ microscopy studies of coal conversion at high temperatures and hydrogen pressures, basic studies of bond splitting reactions, innovative coal dissolution studies using supersolvents, assessment of the liquefaction potential of a large number of U.S. coals, and completion of a retrospective technology assessment for direct coal liquefaction. In the remainder of this section, a brief summary of the principal accomplishments in these areas will be given. More detailed discussions are given in the main body of the report.

Integrated Coal Structure/Liquefaction Studies

A variety of techniques was used to characterize the molecular structure of five coals and maceral separates, tars, and extraction products prepared from those coals. The techniques utilized included Fourier transform infrared (FTIR) spectroscopy, photoacoustic (PAS) infrared spectroscopy, cross polarized/magic angle spinning (CP/MAS) C^{13} nuclear magnetic resonance (NMR), proton NMR, and Curie-point pyrolysis mass spectroscopy (PY-MS).

Density gradient centrifugation (DGC) separation techniques were employed to isolate pure maceral specimens from resinite-rich and sporinite-rich coals. CP/MAS C^{13} NMR, FTIR, and PY-MS were used to characterize the molecular structure of the separates. These maceral species are of interest with respect to differential liquefaction techniques that employ tars from low-temperature pyrolysis procedures. Such tars show promise for conversion to high energy density aviation fuels. Additionally, solvent extraction experiments, coupled with a variety of spectroscopic studies, were conducted on the resinite-rich Hiawatha coal and on resinite concentrates obtained by physical separation from the waste stream from the Hiawatha coal washing plant. Samples of catalytically hydrogenated Hiawatha coal and pyrolysis tars from Hiawatha coal were subjected to similar investigations.

Both naphthalenes and phenols were detected in the MS analyses. Knowing these compositions will help in guiding the hydrotreating and other subsequent steps to upgrade the material to be suitable for a high energy density fuel. Currently, high volatile bituminous

coals from the Utah Wattis seam and the Kentucky Elkhorn seam are being prepared by density gradient centrifugation.

The photoacoustic (PAS) IR method is being further developed and compared to diffuse reflectance IR spectroscopy of coal powders. This is important in making PAS a routine procedure for coal analysis which can avoid the problems of KBr pellet and diffuse reflectance measurements.

A detailed study of 13 hydrocarbon subfractions derived from pyrolysis tar from Hiawatha coal was conducted. The experimental techniques used were PY-MS, FTIR spectroscopy, proton NMR, and C^{13} NMR. Canonical correlation methods have been applied to bring into focus all of the techniques that are available to help understand the fundamental processes. These computer programs are critical in the successful determination of the changes that are undergone as coal is subjected to pyrolysis, liquefaction, extraction or gasification work. The chromatographic and spectroscopic data generated from the samples produced by all of these processes are so voluminous as to make it impractical to draw reliable conclusions by direct visual evaluation. Using the multivariate analysis techniques developed by Dr. Willem Windig and others at the University of Utah, it is possible to determine subtle differences in peak height intensity, concentration or behavior of specific components of interest.

Valuable information was gained by correlating the four analytical techniques. For example, mass spectral peaks of samples containing 2 and 3 units of unsaturation, were shown to contain by PMR and CMR double bonds, whereas mass spectral peaks corresponding to molecules containing one unit of unsaturation were found to be cyclic. Since all the techniques showed the predominantly aromatic fractions to be very different from each other when moving to higher fused ring systems, a better understanding of spectral interpretation of aromatic hydrocarbons mixture data appears possible. The data correlation and integration results will be presented at the 1987 ACS meeting in Denver [Hoesterey, B.L., Meuzelaar, H.L.C., Eyring, E.M., Grant, D.M., Pugmire, R.J. "An Integrated Spectroscopic Approach to the Chemical Characterization of Pyrolysis Oils," Fuel Div. ACS, Denver, 1987].

Coal Dissolution Studies

A novel extraction process has been developed that uses a unique solvent/antisolvent system to extract organic material from coal. The solvent is N-methyl-2-pyrrolidone (NMP) and the antisolvent is water. The process is carried out using -70 mesh coal at atmospheric pressure and relatively low temperature (200°C).

Detailed experiments involving solvent extraction of three West Virginia bituminous coals were carried out using the solvent N-methyl-2-pyrrolidone (NMP), followed by recovery of the extracted material as a precipitate on addition of the antisolvent (water). These experiments produced two coal fractions: the first, a solid

residue made up of unextracted organic matter and greater than 99% of the ash in the original coal sample; the second, an almost ash-free organic fraction. The latter fraction demonstrates the preparation of an organic coal-derived product which could be used as an ultra-clean fuel or feedstock for subsequent processing to liquid fuels or chemicals.

It was found that this procedure produces a solid coal fraction characterized by very low ash contents (as low as 0.1%), high energy densities (as high as 15,000 BTU/lb) and complete removal of all pyritic and inorganic sulfur-containing species. The percent recovery of the soluble fraction on a moisture and ash-free basis (MAF) ranged from 36% to 74% and was dependent on the coal seam from which the parent coal was mined. Solvent recovery of up to 97% was achieved in laboratory-scale experiments using a distillation process.

Future studies on the NMP coal dissolution process will concentrate on three principal areas. First, it is desirable to thoroughly investigate the structure of the ultra-clean extract from the process, which contains only organic sulfur as an impurity. A number of techniques will be used for this purpose, including ESR and ENDOR studies, ^{13}C NMR, FTIR, and EXAFS spectroscopy measurements on the only remaining impurity in the extracted material, organic sulfur. Second, the conversion of the extracted material to a clean liquid fuel will be investigated. Both hydrogenation of the material in solution in NMP and of the solid extract will be studied. Finally, desulfurization processes to remove the remaining organic sulfur will be explored. Removal of the organic sulfur from the NMP solution by precipitation of metal sulfides will be investigated, as will biological desulfurization of the extract.

Coal Depolymerization and Free Radical Formation

Optical absorption techniques were used to investigate bond cleavage in the model compounds benzyl phenyl ether (BPE), benzyl phenyl sulfide (BPS), and benzyl ether (BE). BPE and BPS contain C-O and C-S bonds typical of what might be found in coal. Both equilibrium constants and reaction rates were measured for a number of charge-transfer reactions. Additionally, a new uv spectrophotometer capable of variable temperature uv-vis spectroscopy was constructed for future experiments of this type.

A microwave cavity furnace was developed for in situ ESR studies of free radical formation during coal pyrolysis. The free radical concentration increases to maxima in two stages, 25 to 300°C, and 450 to 600°C, that correspond to dissociation of weak bonds and depolymerization of the coal matrix, respectively. Activation energies for bond splitting were determined and found to vary significantly with coal type. The addition of ZnCl_2 and SnCl_2 catalysts shifted the stages to significantly lower temperatures.

ENDOR (electron-nuclear double resonance) was also used to

investigate the free radicals in coals and coal pyrolysis samples. ENDOR appears to be a powerful new method of investigating such systems. The technique established the existence and determined the values of two different C-H distances in several coals.

Biological Desulfurization of Coal

Biological processing presents exciting new opportunities for both coal cleaning and coal conversion to liquid or gaseous fuels. The initial Consortium biological processing program has focused primarily on microbial removal of sulfur. In the first year of the program, a 10 liter fermenter system with automated control of pH, %O₂ saturation, temperature, and agitation and air flow rate was installed and tested, and sulfur removal experiments were conducted on two coals with four types of microorganisms. The specific microorganisms investigated included *Thiobacillus* (T.) thiooxidans, T. ferrooxidans, *Sulfolobus brierleyi*, and microorganisms derived from acid mine water. Experiments were conducted to optimize a number of critical parameters, including pH, microorganism concentration, and temperature, in order to achieve maximum desulfurization rates.

It was demonstrated that both T. ferrooxidans and *Sulfolobus brierleyi* remove pyritic sulfur from coal effectively. Removal of nearly all pyrite from two high sulfur coals was achieved using both microorganisms. *Sulfolobus brierleyi* was also shown to be somewhat effective in removal of organic sulfur (10 to 30% reduction), provided the microorganism was first acclimatized on a coal of high organic sulfur content.

Future work will include further acclimatization studies using such growth media as separated coal macerals and solvent extracted coal that contain only organic sulfur. The structure of the sulfur containing compounds will be thoroughly investigated as a function of biological processing. Mossbauer spectroscopy will be used to investigate the biooxidation of pyrite, X-ray absorption fine structure spectroscopy, usually referred to as EXAFS spectroscopy, will be used to study the atomic structure of organic sulfur, and electron microscopy will be applied to determine microstructural changes in sulfur phases and microbe attack mechanisms.

Catalyst Studies

Structural studies of homogeneous catalysts for use in the liquefaction of both untreated and biologically processed coal made excellent progress. The specific compounds investigated included a number of transition metal complexes of thiophene (tp), benzo-thiophene (bp), dibenzothiophene (dbt), and other sulfur-containing ligands. ¹³C and ¹H NMR studies were combined with X-ray diffraction measurements to derive atomic models of these compounds, including bond distances and angles. The results will be refined by Mossbauer and EXAFS measurements in the future.

The catalytic activity of 14 different homogeneous catalysts was

investigated by means of tubing-bomb reactor experiments. Both untreated and bio-treated Kentucky #11 coal were studied. The runs were conducted in tetralin solvent with no added hydrogen. Conversion was measured as a function of catalyst concentration, reaction time, and temperature. Of the 14 homogeneous catalysts studied, nine gave increases in conversion ranging from 5 to 15% over that observed with no added catalysts. The most successful homogeneous catalyst was a molybdenum compound, $C_7H_8Mo(CO)_3$.

A new ESR technique was developed for detecting pentavalent Cr, Mo, and W, which have been suggested as possible active sites in heterogeneous catalysis. The method is based on the significantly different temperature dependence of ESR linewidths exhibited by tetraoxyanions and trioxyanions. Additionally, a new class of model compounds containing Cr(V) was synthesized and structurally investigated by ESR and ENDOR.

Assessment of the Liquefaction Characteristics of U.S. Coals

One of the most important Consortium activities is to assess the liquefaction potential of many U.S. coals by means of a variety of analytical tests and liquefaction conversion experiments. Ultimately, this information will be incorporated into a liquefaction data base that can be accessed by scientists from industry, academia, and government. Such a database will be of significant value in optimizing coal selection for both research and industrial processes.

Over 100 coal samples from 18 locations and 16 seams in Western Kentucky were collected and analyzed by the Kentucky Energy Cabinet Laboratory as part of this program during our first year contract. Analyses performed on the coal samples and on maceral separates prepared by DGC included proximate analysis, ultimate analysis, petrography and reflectance measurements, forms of sulfur, free swelling index, heating values, and mobile component [Brenner, D., Fuel 64, 167 (1984)] extraction. To assess the liquefaction conversion properties of these coals, a microautoclave liquefaction reactor was used. The liquefaction reaction runs utilized tetralin as the solvent (5 g coal, 7.5 g tetralin), H_2 pressures of approximately 2000 psig, temperatures of 385, 427, and 445°C, and a reaction time of 15 minutes. The reaction product was separated into four soluble classes, with percent conversion defined as 100 - percent pyridine insoluble (IOM).

A variety of spectroscopic measurements were made on the reaction products and the coal. These included 1H NMR, molecular weight by vapor phase osmometry, and Curie point PY-MS. The previously mentioned SIGMA program was used for multivariate analysis of the data.

The principal products of the microautoclave process are asphaltenes and preasphaltenes (SRC = asphaltenes + preasphaltenes). The amount of SRC was observed to increase linearly with the total conversion percentage. The amount of mobile component exhibited a systematic variation with coal rank, exhibiting a broad maximum at a

reflectance of approximately 0.6. No other strong correlations between liquefaction product yields and individual coal characteristics have been found at this time. This suggests that more than one coal characteristic influences liquid product yield and a multivariate regression analysis will be required.

The Role of Coal in the Removal of Metals from Heavy Oil During Co-Processing

Co-processing involves the reaction of a (mixture of) coal with a heavy oil. The primary aim of co-processing is to obtain a simpler direct liquefaction process by using the heavy oil as a way to feed coal into the reactor, thus simplifying the conversion of coal to oil by eliminating the need for a recycle system.

Heavy oils contain a considerable amount of metals, chiefly bound in porphyrins and porphyrin degradation products. The main metals found are vanadium (sometimes exceeding 1000 ppm) and nickel (to $\approx$ 100 ppm).

This investigation was aimed at determining some of the factors involved in the demetallization of heavy oils by the addition of coal during thermal co-processing under hydrogen pressure. The work was concerned with the removal of vanadium, the metal present in the largest amounts in heavy oils. A bituminous coal (Illinois No. 6) and two heavy oils, Maya (650 °F+) ATB and whole Boscan crude were used in this co-processing study. It appears that coke (THF-insolubles) is the main agent involved in demetallization.

The effects of coal to heavy oil ratios, temperature, residence time and coke formation on demetallization were studied. Good yields (68 wt%) of pentane-solubles (oils) containing 2.2 % of the vanadium initially present in the feed were obtained from the co-processing of 25 wt% Illinois No. 6 with 75 wt% Maya Oil. A 55 wt% of pentane-solubles with 5.3 % of the vanadium initially present in the feed were obtained using whole Boscan crude as the host oil at the same ratio. Preliminary experimental results indicate that EXAFS spectroscopy will be useful in following the changes in the atomic structure of vanadium that occur during co-processing.

An artificial coal-like char made from cellulose (containing only traces of inorganics) also served as a demetallizing agent. In addition, a granular active carbon, which did not liquefy, also served as a demetallizing agent.

Significant desulfurization ($\approx$ 40 %) and some removal of nitrogen accompanied demetallization.

Retrospective Technology Assessment

As part of the first year Consortium program, researchers in the Technology and Information Policy Program at Syracuse University

conducted a retrospective technology assessment of the historical, political, and economic factors that have shaped the development of direct coal liquefaction (DCL) technology. This highly comprehensive study has resulted in a ten chapter, 250 page volume that should serve as a guide for future U.S. energy policy makers. The complete Syracuse report is available as a supplementary volume to the current document, which is a report of the Consortium technical research activity.

Only one chapter of the Syracuse report has been included as a part of this report. That chapter presents the principal conclusions of the retrospective DCL technology assessment, which may be briefly summarized as follows.

1. Pioneering Processes Cannot be Addressed Like Conventional Technologies. Problems in management of plants, in engineering, in equipment maintenance have been viewed as extraordinary, but in fact they should be expected and accepted as routine. Standards of technical efficiency applied to pioneering processes and plants require different standards.

2. DCL is Best Viewed as Government Sheltered High Technology Development (not industry development). DCL development policy has been premised on government-business partnership and the building up of DCL as market-competitive industry. DCL should be developed whether or not industry is interested and should be rationalized in national security/energy security terms. Short or intermediate-term competitiveness with the price of oil should be a less relevant consideration. Policies should be similar to those used to build the computer industry: overspecification of performance at cost-plus, guaranteed purchase for government stockpiles, procurement-based incentives.

3. Information Management Should be Improved. Currently many technologies are viable and the likelihood of an economic magic bullet seems remote at existing budget levels. One key is to use current information more effectively and to encourage cross-fertilization among DCL researchers and others working on separate but potentially relevant problems.

4. Resources have been Spread too Thin: Small Increments Spread Out Over Multiple Projects. Limited resources have been spread too thin. The result is that not enough attention has been given to sustained development of the strongest candidate technologies.

5. Invest in Contingency Planning. DCL policy has typically been developed in the context of the immediate events -- current crisis, current energy availability, current federal budgetary climate. DCL and synfuels generally require longer-range thinking and contingency planning.

Overarching Theme: The Hiatus Effect. The constant changing of policy and the on-again-off-again nature of support for DCL have undermined development efforts. DCL development requires some long-run, sustained development activity. The DCL effort in the

U.S. has failed because of the inability of the political system to invest in a long term research and development program.

Conclusion

During the first year of its research program, the Consortium for Fossil Fuel Liquefaction Science has made significant progress in many areas of coal liquefaction and coal structure research. As summarized briefly above, research topics for which substantial progress has been made include integrated coal structure and liquefaction studies, investigation of differential liquefaction processes, development and application of sophisticated techniques for structural analysis, computer analysis of multivariate data, biodesulfurization of coal, catalysis studies, co-processing of coal and crude oil, coal dissolution and extraction processes, coal depolymerization, determination of the liquefaction characteristics of many U.S. coals for use in a liquefaction database, and completion of a retrospective technology assessment for direct coal liquefaction. These and related topics are discussed in considerably more detail in the remainder of this report.

BIOLOGICALLY IMPROVED COAL STRUCTURE FOR
BETTER LIQUEFACTION OF COAL

October 1, 1985 - December 31, 1986

University of Kentucky

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Title: Task I. Biologically Improved Coal Structure for Better Liquefaction of Coal

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Objectives

- I.1 To identify and quantify those factors which are responsible for the rate and extent of microbial removal of inorganic and organic sulfur in coal, to establish the potential liquefaction characteristics of the coal after being subjected to low pH microbial treatment, and to identify a microorganism which is capable of removing nitrogen heteroatoms from coal.
- I.2 To synthesize a labile p-xylene complex and several derivatives for evaluation as coal liquefaction catalysts, to characterize the above compounds, and to compare homogeneous coal liquefaction catalysts in tubing bomb experiments.

Scopes

- I.1 Sufficient quantities of four microorganisms to be used in the desulfurization study will be grown. A series of runs using model organic sulfur compounds will be carried out. The effect of variables such as pH, temperature, slurry composition, etc., on coal desulfurization using both shaker flasks and the large scale fermenter will be studied. Particular emphasis will be on organic sulfur removal. An understanding of the extent of demineralization as a function of variables such as pH and temperature will be sought, and then applied to biological activity in desulfurization. Measurements of the surface area and pore volume distributions in coal particles as a function of pH, and extent of desulfurization will be made, and various well characterized coal samples for liquefaction studies will be submitted for use in I.2. A test of at least one promising microorganism for potential nitrogen removal will be made.

- I.2. Based on literature results, the complex $[\text{Fe}(\text{xylene})(\text{Cp})](\text{PF}_6)$ is thought to be potentially active. Micro-analysis, spectroscopy (multinuclear NMR, IR, and mass) and x-ray diffraction characterization will be carried out as appropriate for the complexes synthesized. Baseline data for coal liquefaction using iron pentacarbonyl and iron pentacarbonyl/molybdenum hexacarbonyl mixtures as homogeneous catalysts for a bituminous coal will be established. Comparisons of these results with the synthesized catalysts and with biologically treated coal from Task I.1 will be made.

Final Report

I.1 BIOLOGICALLY ENHANCED COAL LIQUEFACTION

I.1.1 Abstract

The main result of this study is that both Thiobacillus ferrooxidans and Sulfolobus brierleyi are capable of removing pyritic sulfur from coal effectively. Removal of organic sulfur requires growth of Sulfolobus brierleyi on coal for the development of sulfur metabolizing enzymes in the organism and thus this organism appears to be superior in this respect as compared with Thiobacillus ferrooxidans. The results have also indicated that during the heterotrophic metabolism of organic sulfur by Sulfolobus brierleyi the autotrophic enzyme systems are depressed and thus there is a switchover mechanism between the heterotrophy and autotrophy with respect to the organic and inorganic sulfur transformations by the archaebacterium Sulfolobus.

I.1.2 Introduction

The overall objective of this project was to produce low sulfur, biologically treated coals which have favorable liquefaction characteristics. Studies included both mesophilic and thermophilic microorganisms and coals with two different sulfur contents. The variables studied included: temperature, pH, aeration rate, nutrient level, and residence time. The results are analyzed in terms of total sulfur, pyritic sulfur, ash content, liquid phase $\text{Fe}^{2+} - \text{Fe}^{3+}$, and selected heavy metals. Leaching runs (without microorganisms) were also conducted for comparison.

I.1.3 Coal Samples

Most experiments were conducted with 200 mesh Kentucky #11 medium sulfur (#91182) coal, unless otherwise indicated. A few experiments were also conducted with a higher sulfur coal (#85098). Analytical data for both coals are shown in Table 1. In addition,

Table 1. Coal Analysis (KY #11)

	Medium Sulfur* Coal (#91182)	High Sulfur Coal (#85098)
Volatile Matter	39.1 + 0.2	35.5 + 0.2
Ash	7.83 ± 0.07	18.7 ± 0.19
Total Sulfur	3.18 ± 0.02	5.81 ± 0.06
Pyritic Sulfur	1.03	2.92
Sulfate Sulfur	0.1	0.12
Organic Sulfur	2.05	2.77
Carbon	70.69 ± 0.22	63.22
Hydrogen	4.95 ± 0.01	4.35
Nitrogen	1.50 ± 0.03	1.28
Total Fe	1.03	4.00

*Most experiments were conducted with this coal.

macro- and meso-pore analysis of the medium sulfur coal were conducted. Nitrogen adsorption techniques indicated very low values of surface area ($SA = 9.4 \text{ m}^2/\text{g}$) and the pore volume ($pv = 0.015 \text{ cm}^3/\text{g}$). Carbon dioxide adsorption analysis showed an extensive microporous structure with $SA = 140 \text{ m}^2/\text{g}$.

I.1.4 Analytical Procedure

Proximate analysis of all samples were determined using a Leco Model MAC 400 Proximate Analysis Determinator. Proximate analysis was the determination, by prescribed methods, of moisture, volatile matter, ash and fixed carbon (by difference). The MAC 400 is a single oven-furnace unit consisting of a 20 position turntable for sample crucibles and an internal balance for weighing the sample during the analysis.

A Leco Model CHN-600 Elemental Analyzer was used for the ultimate analysis. The Model CHN-600 is a microprocessor-controlled unit for the simultaneous determination of carbon, hydrogen, and nitrogen.

Total sulfur was determined with the Leco Sulfur Analyzer Model SC-132. The Model SC-132 used the absorption of infrared (IR) radiation method of measuring the sulfur dioxide in the combustion gases. The IR radiation absorbed during combustion of the sample is proportional to the sulfur dioxide in the combustion gases and hence to the sulfur in the sample.

Sulfate sulfur was determined by extracting a weighed sample of coal with dilute hydrochloric acid. The oxidized sulfur was precipitated from solution with barium chloride and weighted as barium sulfate.

Pyritic sulfur was determined by first extracting a weighed sample with dilute hydrochloric acid, and boiling the mixture for thirty minutes. After filtering and washing, the coal residue was ashed at 800°C overnight. Total iron was then determined in the extracted ash (hot dilute hydrochloric acid) by atomic absorption, the iron in the ash sample representing the pyritic iron in the sample. The pyritic sulfur is then calculated using the following expression:

$$\% \text{ Pyritic sulfur} = \% \text{ Pyritic iron} \times 1.4181$$

where 1.4181 is the ratio of sulfur to iron in pyrite.

Organic sulfur was taken as the difference between total sulfur and the sum of the sulfate and pyritic sulfur.

I.1.5 Propagation of Microbial Cultures

The following bacterial cultures were propagated to obtain reasonable amounts of cells for inoculation into the coal samples for desulfurization studies.

- 1- Thiobacillus thiooxidans. (Sulfur Oxidizer).
- 2- Thiobacillus ferrooxidans. (Sulfur/Ferrous Oxidizer).
- 3- Sulfolobus brierleyi. (Thermophilic, Sulfur/Ferrous Oxidizer).

Thiobacillus thiooxidans was successfully cultivated autotrophically in large vessels of 10 liters capacity. Elemental sulfur was provided as the energy source for growth and pH and temperature were controlled at 4.5 and 30°C respectively. After completion of the logarithmic growth phase the cells were harvested by centrifugation at 10,000 x G and the cell pellet was resuspended in the Basal Salt Solution and standardized by determining its protein contents. This standardized cell suspension was utilized during other investigations.

Thiobacillus ferrooxidans was also cultivated autotrophically using ferrous sulfate as the energy source in a 10 liter fermenter fitted with pH and temperature controlling devices. Cells were harvested during the active growth phase by centrifugation at 10,000 x G. Cells were resuspended in the Basal Salt Solution (pH 2.5) and stored at 4°C for future use.

Sulfolobus brierleyi, a thermophilic, facultatively autotrophic bacterium was first grown in the shake flasks with elemental sulfur as the sole energy source at 70°C. For large quantities of cells, the bacterium were also cultivated in a 10 liter fermenter.

Isolations of microbial populations from two coal mine waters were screened for the presence of autotrophic sulfur oxidizing bacteria and for the presence of other bacteria which may be able to remove organic sulfur from the coal. The presence of Thiobacillus ferrooxidans and Thiobacillus thiooxidans was indicated but no thermophilic bacterium mainly associated with the coal mines (such as Thermoplasma) were detected.

I.1.6 Optimization of Desulfurization Parameters

The following parameters governing the desulfurization of coal by bacterial suspensions were also determined:

Pulp Density:

In solid substrate fermentations, the substrate levels are controlled by the pulp density which is related to the contact surface area that is available for bacterial action. Rate of oxygen uptake by slurries of different pulp densities in the presence of bacteria was measured, and results are shown in Figure 1. As indicated from these results the rate of oxygen uptake in the presence of bacteria was directly related to the pulp density of coal suspension. The data also indicated an exponential trend in the lower concentrations (between 1-25%). At higher pulp densities various other factors start affecting the kinetics and this is perhaps why the trend has deviated from exponential to linear regression. However, the results indicated that a pulp density of 25% should yield significantly higher oxidation rates as compared with 10% pulp density.

Optimization of pH:

Another important parameter controlling the activities of bacteria is the pH. Different bacteria have different pH optima for growth on different substrates. Attempts were made to determine the pH optima for oxidation of coal slurries by Thiobacillus ferrooxidans and Thiobacillus thiooxidans. Figures 2 & 3 present the results of these experiments. pH profiles for Thiobacillus thiooxidans on coal and elemental sulfur show a markedly different trend (Fig. 2). When this microorganism is grown on sulfur its tolerance to pH is very high; it can oxidize elemental sulfur from pH 1 to 9. But when coal is provided as the sole source of energy (i.e., pyrite present in the coal) there is a very sharp pH optima and the oxidative activities are also limited between pH values of 1 and 7. Interestingly the pH optima for both substrates is same, i.e., 4.5. Thiobacillus ferrooxidans, however, exhibited a markedly different pH optima for oxidation of coal slurries from oxidation of ferrous sulfate (Fig. 3). This difference in pH optima may be due to the different nature of substrates as coal is an insoluble substrate while ferrous sulfate is soluble and hence easily accessible to the bacteria. The trend of pH profiles for coal is similar with both microorganisms. pH optima were found to be very sharp and sensitive to pH changes. pH 1.5 inhibited 66% rate of oxidation of coal while pH 2.1 lowered the oxidation rate by 60% in the presence of the same concentration of T. ferrooxidans; similarly an increase of 0.5 unit of pH (from 4.0 to 4.5) resulted in three times higher oxidation rates of coal by Thiobacillus thiooxidans.

Substrate Concentrations:

Oxidation rates in the presence of different substrate concentrations were also investigated in order to determine the optimum concentrations for growing these bacteria for cell mass productions. Fig. 4 presents oxygen uptake rates by T. thiooxidans in the presence of elemental sulfur and thiosulfate. As indicated the optimum concentration of elemental sulfur is approximately 150 mMoles as compared to 250 mMoles of sodium thiosulfate.

I.1.7 Fermenter Description

The Biostat E fermenter (Braun Biostat ER10) is equipped with a 10-liter reactor vessel. The fermenter working vessel is made of a cylindrical heavy-wall borosilicate glass and all metal parts that come in contact with the liquid medium are made of acid-resistant steel. The system is totally automated, allowing the operating conditions to be precisely controlled. Three electrodes, located in the bottom of the reactor vessel, relay information back to the main module on pH, %O₂ saturation, and temperature. Controllers in this module allow the operator to maintain the exact conditions necessary for operation. Temperature is controlled by thermostats, heaters, and cooling water. Prepared solutions of acid and alkali are added as needed, via pumps and tubes, to correct the pH. The percent O₂ saturation can be controlled either by changing the air flow rate or the stirrer speed. The stirrer in the reactor vessel can be regulated from 100 rpm to 650 rpm.

I.1.8 Acid Leaching of Coal With and Without Microorganisms

The leaching studies of metals were conducted in the fermenter with solutions of 5% coal slurry. At temperature = 30°C, and pH = 2.5, about 50% of Ni, Cu and Zn were leached after 5 days. Iron concentration of 31.4 mg/l (5% leached) also resulted. At high temperature (T = 70°C), the acid leached concentration of Fe was 228 mg/l (38.5% leached). These results were summarized in Table 2.

Table 2. Acid Leaching of Selected Metals in a 5% Coal Slurry with pH = 2.5, Stirring Speed = 300 rpm

Temperature Days	Low (30°C)		High (70°C)	
	<u>3</u>	<u>6</u>	<u>3</u>	<u>5</u>
Fe (ppm)	21.6	31.4	150	228
Ni (ppm)	0.34	0.40	0.42	0.54
Cu (ppm)	0.40	0.45	0.29	0.32
Zn (ppm)	1.0	1.0	0.62	0.82

Acid leaching of coal slurry at pH = 2.5 in the presence of sulfur removal microorganisms, increased Fe concentration. This resulted from the biological action on pyrite. Some results are shown in Table 3.

Table 3. Leaching of Selected Metals in the Presence of Microbes with pH = 2.5, Stirring Speed = 300 rpm, Coal = 5% Slurry

Temperature Microbe	Low (30°C)		High (70°C)	
	<u>T. Ferrooxidans</u>		<u>S. brierleyi</u>	
Days	<u>1</u>	<u>8</u>	<u>2</u>	<u>5</u>
Fe (ppm)	3.2	45.0	210	350
Ni (ppm)	0.28	0.28	0.5	0.45
Cu (ppm)	0.13	0.26	0.4	0.4
Zn (ppm)	0.2	0.43	0.7	0.85

The effect of pH on coal leaching was also studied in shaker flasks. A 5% coal slurry in a pH range from 1.7 to 3.8 was put in a shaker for 5 days. Table 4 shows increased leaching of iron at the low pH conditions. This caused a slight lowering of sulfur content as the pyrite was chemically oxidized.

Table 4. Effect of pH on Leaching (at 25°C)

<u>Flask</u>	<u>Initial pH</u>	<u>Final pH</u>	<u>% Sulfur (dry basis)</u>	<u>Fe(ppm)</u>
1	1.70	1.70	2.68	41.9
2	1.90	1.90	2.90	54.7
3	2.50	2.50	3.0	27.3
4	3.80	6.65	2.94	0

I. 1.9 Microbial Desulfurization of Coal by Thiobacillus thiooxidans

Two separate coal samples were treated with T. thiooxidans in the absence and in the presence of nutrients. These two runs were aimed at determining the effect of nutrient addition on the bacteria's effectiveness. Also, working in the optimum pH range of 2-3 presents a problem of corrosion in an industrial situation. It was desired to see if pyrite reduction could be achieved at the high end of the pH range (pH = 4.5). For the first run, no nutrients were introduced with the bacteria. The pH of the 5% coal slurry was maintained at 4.4 for the 7 day run, and temperature was kept constant at 30°C. The stirrer speed started out at 300 rpm, but was reduced to 100 rpm when the bacteria were introduced on the second day. Coal slurry samples were taken daily and analyzed in the manner previously described. Virtually no pyritic sulfur removal was obtained. The % sulfur and ash content remained constant.

The second run was carried out at the same conditions as the first, with the bacteria being introduced on the third day. The following nutrient was added with the culture: KH_2PO_4 (3.0g/l); $(\text{NH}_4)_2\text{SO}_4$ (.2g/l); FeSO_4 (.005g/l); $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (.5g/l); and CaCl_2 (.25g/l). There was a lag of about 6 days before the sulfur content started to decrease. During 17 days the percent ash (dry basis) dropped from 7.85% to 4.96% and the percent sulfur (dry basis) dropped from 3.48% to 2.69%. It was assumed that the only sulfur removed was pyritic. Figure 5 gives the percent pyrite removed versus time in days. From these two runs it was concluded that nutrient addition is important for T. thiooxidans oxidation of pyrite. Also, the reduction of pyrite can be obtained at the upper limit of the pH range with some loss in effectiveness.

I.1.10 Coal Treatment with T. ferrooxidans

T. ferrooxidans was also used in the treatment of 5% slurry of coal. An 18 ml suspension of these bacteria was used as inocula which provided 3 mg. protein per liter (approximately 10^9 cells/liter). The conditions for this run (in the presence of nutrients) were as follows: pH = 2.4, temperature = 30°C, air flow rate = 1.3 liter/min., mixing speed = 150 rpm, microorganisms concentration (as protein) = 3 mg protein/liter. At the end of nine days the percent total sulfur (dry basis) had dropped to 2.33%. Figure 6 shows that after about 16 days 90% of the pyritic sulfur had been removed. At the end of this run the coal slurry containing primarily organic sulfur was inoculated with Thiobacillus thiooxidans (3 mg protein per liter). At the end of five days, coal sample analysis showed no additional removal of sulfur.

Concentrations of leached total iron and ferrous ions were measured by atomic absorption and standard phenanthroline method. From the result of the oxidation of ferrous ion by T. ferrooxidans, all the iron leached out was in the ferric form as shown in Figure 7. The resultant concentration of iron was about 230 mg/l after 16 days. This corresponds to 90% pyritic sulfur removal as shown in Figure 6.

The optimal pH for desulfurization with T. ferrooxidans was studied in a shake flask in the pH range from 1.0 - 3.0. The maximum desulfurization of pyritic sulfur was found to be at pH 2.5. Table 5 shows the pH effect on pyritic sulfur removal.

Table 5. Effect of pH on Pyrite Removal from Coal by T. ferrooxidans at 10 days

Coal: 5% Slurry, Temperature: 30°C

pH	Removal at a given pH Removal at optimum pH
1.0	0.43
2.0	0.55
2.5	1.0
3.0	0.19

A run was conducted with the thermophillic microorganism Sulfolobus brierleyi in the controlled 10-liter fermenter. Operating conditions were: 5% coal slurry, pH = 2.5, air flow = 2.0 liters/min., stirring rate = 150 rpm, and temperature = 70°C. Figure 9 shows the removal of total sulfur, pyritic sulfur and ash content. As expected, at 70°C with Sulfolobus brierleyi 50% of pyritic sulfur was removed within five days. Eventually, about 22% total sulfur and 90% of pyritic sulfur removal were achieved in less than 2 weeks. The organic sulfur removal was calculated from the difference of total and pyritic sulfur removed and it showed no removal after 7 weeks. Total iron and ferrous iron (Fe^{2+}) in the liquid phase were also analyzed. Figure 10 shows the concentrations of total Fe and Fe^{2+} . In this case all iron is present as Fe^{2+} , whereas in the case of T. ferrooxidans most of the iron was present as Fe^{3+} .

A high sulfur coal (Ky #11, 85098) was also treated with S. brierleyi at $T = 70^\circ\text{C}$ and $\text{pH} = 2.5$. This coal contained 5.8% total sulfur and 2.92% pyritic sulfur. After 18 days, 49% of total sulfur and 82% of pyritic sulfur were removed as shown in Figure 11. The initial rate of desulfurization is 0.50%/day. When comparing with the initial rate of previous low sulfur coal (3.3% total sulfur and 1.1% of pyritic sulfur), which is 0.155%/day, a 3.22 times rate increase is obtained. This value is comparable to the increase of pyritic sulfur content (2.65 times) in the high sulfur coal.

I.1.11 Microbial desulfurization of Coal by Sulfolobus Brierleyi

Sulfolobus brierleyi, a thermophilic, facultative autotrophic bacterium was grown in a 10 liter fermenter at 70°C with elemental sulfur. Figure 8 presents a typical growth curve for this bacterium. The growth was measured by determining the turbidity of the culture and pH was also monitored. The pH of the culture decreases concomitantly with the increase of turbidity of the

culture. After 66 hours the cells were harvested by centrifugation and used for further desulfurization studies. S. brierleyi was also grown on coal in shake flasks with 10% coal slurry. Initially pH was adjusted to 2.5 and monitored at regular intervals. It was found that after 4 weeks pH dropped to 1.4. At this point the coal sample was washed and dried and submitted for analysis. The coal sample contained volatile matter 38.5%; ash 6.81%; total sulfur (DMB) 2.6%; Pyritic sulfur 0.29%. Therefore S. brierleyi was capable of removing approximately 75% of Pyritic Sulfur from the coal and it removed approximately 25% of the total sulfur. But it did not remove any organic sulfur present in the coal.

I.1.12 Acclimatization of Sulfolobus Brierleyi on Coals

In order to obtain a strain of S. brierleyi which is capable of removing organic sulfur from the coals, it was acclimatized onto the coal in mineral medium in shake flask cultures. 20% coal slurry was used and pH of the shake-culture was monitored and maintained at pH 2.5 by manual addition of acid/alkali.

When first generation of acclimatized cells was inoculated into the shake flask, pH rose to 5.5 initially and was adjusted to 2.5 using sterile acid; 2nd generation, however, did not require any acid and pH was dropped to 2.5 within fortnight (Fig. 12). When pH was stabilized in these flasks they were removed from the shaker and the coal was filtered off and washed with distilled water (pH 2.5) and dried under vacuum. The dried coal samples were submitted for analysis of residual sulfur contents. The filtrate was centrifuged aseptically at 10,000 x G for 15 minutes and cell pellet re-inoculated into fresh coal suspensions for further acclimatization. Results of these acclimatization are shown in Table 6.

Table 6. Effect of Acclimatization on Sulfur Removal by S. Brierleyi

	Transfer #1	Transfer #2	Transfer #3	Transfer #4
Ash	6.91%	6.95%	7.10%	7.11%
Total S	2.96%	2.94%	3.08%	3.03%
Pyritic S	0.96%	0.97%	0.98%	0.90%
Total S Removed	14.50%	15.50%	11.50%	12.90%
Pyritic S Removed	11.10%	10.20	9.30%	16.70%
Organic S Removed	13.80%	15.10	9.50%	8.20%

These results indicate that the 2nd generation showed the maximum capability of removing organic sulfur and perhaps an inverse relationship between removal of pyritic sulfur and organic sulfur existed; the cells capable of removing organic sulfur had comparatively less capability of removing pyritic sulfur.

Microbial Desulfurization of high-sulfur coal [KY#11, No: 85098] was carried out in shake flasks, containing 20% pulp densities and mineral salt medium for the acclimatized Sulfolobus brierleyi strain. Experiment was carried out at 70°C for four weeks. A control experiment without bacterial suspension was also run at similar conditions. Flasks were removed from the shaker after 2, 3 and 4 weeks and coal was filtered, dried under vacuum for 2 hours and submitted for analysis for total and pyritic sulfur contents. Organic sulfur was calculated by difference method. Results are shown in Table 7.

Table 7. Desulfurization of coal [KY #11, No. 85098] by Sulfolobus Brierleyi

Time	% Sulfur Removed		
[Weeks]	Total Sulfur	Pyritic Sulfur	Organic Sulfur
2-	19.3	10.3	29.16
3-	15.3	2.8	29.80
4-	18.0	7.6	29.17
Control (4- weeks)	1.3	1.3	Negligible

As is apparent from these results acclimatization was much better on the coal which contains high sulfur contents. Further work is being carried out using this high sulfur coal.

Further experiments with acclimatized cells are also being carried out.

Cell cultures of Sulfolobus Brierleyi, Thiobacillus ferrooxidans and Thiobacillus thiooxidans were also maintained.

I.1.13 Coal Treatment with Microbes from Acid Mine Drainage

An acid mine water of pH 2.7 was obtained from Pleasant Valley Gob in Hopkins County, Kentucky. The pH of acid mine water was adjusted to 2.5 and microorganisms were first grown in a medium containing thiophene = 0.25g/l, $(\text{NH}_4)_2 \text{SO}_4$ = 0.4 g/l, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ = 9.5 g/l, KH_2PO_4 = 3 g/l, CaCl_2 = 0.25 g/l, and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ =

0.5 g/l. The fermenter was operated at 1.7 liter/min air flow rate, temperature = 30°C, and mixing speed = 150 rpm. At the end of 21 days the optical density increased 2.5 times indicating significant biological growth. At this point a 5% coal slurry was added. The results from an assay after 36 days are presented on Figure 13. Total sulfur content decreased from 3.30% to 2.49% (24.5% removed) and pyrite content decreased from 1.19% to 0.50% (58.0% removed). Removal of organic sulfur was calculated by difference from the remaining total pyrite sulfur. Figure 13 shows that some organic sulfur was removed, although its rate was low. The concentration of the selected metals Cu, Ni, Zn and Fe were also analyzed. The leachate amount of Cu was 0.13 ppm (20% removal), of Ni 0.4 ppm (50% removal), of Zn 0.34 ppm (19% removal) and 1.25 ppm (0.2% removal) for Fe. The low concentration of Fe was surprising, but might be due to precipitate formation.

I.1.14 Pore Size Analysis of Biologically Treated and Untreated Coal

Surface areas and pore volumes of the Ky. #11 coal used in the studies were evaluated in the raw, acid leached and biologically treated states by reduction of N₂ and CO₂ adsorption isotherm data at 77°K and 219°K, respectively. Results are summarized in Table 6. Noted variations in the N₂/BET SA's are not statistically significant; however, the 40% increase in the CO₂/BET SA's can be ascribed to prolonged leaching over 45 days at pH = 2.5. Coal swelling cannot account for this alone. The simultaneous increase in the surface area and pore volume indicates a significant alteration of the coal's internal structure, probably as a result of removal of the mineral phases in the coal. The lower increase in the CO₂ micro surface area and pore volume would support this premise. The microstructure can be associated with the organic phase.

FIG. 1

FIG. 2

FIG. 3

pH-OPTIMA OF *T. FERROOXIDANS*

FIG. 4

OXYGEN UPTAKE BY *T. THIOOXIDANS* WITH DIFFERENT SUBSTRATES

Figure 5. Pyritic Sulfur Removal with T. thiooxidans in the Presence of Nutrients at pH 4.4

Figure 6. Sulfur and Ash Removal with T. ferrooxidans

Figure 7. Liquid Phase Concentration of Total and Ferrous Iron for Coal Desulfurization with T. ferrooxidans

FIG. 8
SULFOLOBUS BRIERLEYI GROWTH IN 10 L. FERMENTOR

Figure 9. Sulfur and Ash Removal with Sulfolobus brierleyi at 70°C

Figure 10. Liquid Phase Concentration of Total and Ferrous Iron for Coal Desulfurization with *S. brierleyi* at 70°C

Figure 11. Biological Desulfurization of High Sulfur Coal (No. 85098) with S. brierleyi at 70°C

FIG. 12

ACCLIMATIZATION OF S. BRIERLEYI ON COAL

Figure 13. Inorganic and Organic Sulfur Removal with Acid Mine Water Culture

I.2 COAL LIQUEFACTION BY HOMOGENEOUS CATALYSTS

I.2.1 Abstract

We have initiated a study of transition metal complexes of thiophene (tp), benzothiophene (bp), dibenzothiophene (dbt) and other sulfur-containing ligands. These sulfur ligands closely model the organically bound sulfur in coal and coal liquids. By studying their transition metal complexes, we have learned more about how metallic hydroliquefaction (HDL) and hydrodesulfurization (HDS) catalysts function. We believe that the complexes are good models for species formed in the initial states of hydrodesulfurization. We have expanded our understanding of the complexes' structures, and learned about the geometry of the sulfur-catalyst interaction. By studying their spectroscopic characteristics, we have learned about the electronic nature of the metal-sulfur interaction, about changes in both the catalyst and substrate upon coordination, and about the mobility of substrates on the catalyst surface. By studying their reactivity, we learn about possible subsequent steps in the hydrodesulfurization process. As new compounds were prepared they were submitted for catalysts testing under actual liquefaction conditions.

We measured the liquefaction of KY #11 and biotreated coals, and catalytic activities were compared by the solid conversions. Runs were carried out using tetralin solvent in the absence of hydrogen. The effects of the reaction time, the amount of catalyst, and the reaction temperature were studied. All the experiments were conducted in stainless steel tubing-bomb reactors.

Nine homogeneous catalysts were found to give significantly higher conversions of KY #11 coal at 425°C in tetralin for 20 minutes. The absolute increase ranged from 3.3% for $\text{Fe}_2(\text{CO})_9$ to 9.7% for $\text{C}_7\text{H}_8\text{Mo}(\text{CO})_3$. Five catalysts were found to decrease conversion by 2% when compared to the non-catalyst conversion of 66.3% at the above conditions. For $\text{Fe}(\text{CO})_5$ the conversion increased from 77.8% for 1 wt percent metal on coal to 82.7% for 3% catalysts at 425°C and 60 minutes. Catalytic effects of $\text{Fe}(\text{CO})_5$ at 40 and 60 minutes were negligible. Biotreatment of coal raised conversion levels of liquefaction about 2% above untreated KY #11 values without catalyst. Mixed results were obtained with catalysts: $\text{Fe}(\text{CO})_5$ gave increased conversion of BT-1 over untreated coal but gave decreased conversion of BT-2; $\text{Mo}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$, $[\text{Fe}(\text{CO})_2\text{Cp}]^2$ and $\text{Cp}(\text{CO})_2\text{FeMo}(\text{CO})_3\text{Cp}$ gave increased conversions but $\text{W}(\text{CO})_6$ gave a smaller conversion with BT-2 than with raw KY #11 coal.

I.2.2 Introduction

Japanese researchers have published a series of five papers on the use of iron complexes, iron carbonyl complexes - sulfur and metal carbonyls, as homogeneous catalysts for coal liquefaction in the presence of hydrogen. In the first paper,¹ $\text{Fe}(\text{CO})_5$ showed the highest catalytic activity among various iron complexes for hydroliquefaction of two Japanese coals. In the second paper,² hydroliquefaction of two Japanese, one Australian and one American

coal was carried out using $\text{Fe}(\text{CO})_5$ in a non-hydrogen donating solvent. With the addition of $\text{Fe}(\text{CO})_5$ coal conversion increased substantially for all of the coals used. High conversions were achieved in the liquefaction of Illinois No. 6 coal at 480°C for an even shorter reaction time of 10 min.³ Little dependence of coal conversion upon temperature was observed. Hydroliquefaction of two low-sulfur Australian coals was studied in the fourth paper.⁴ When molecular sulfur was added to iron carbonyls ($\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, or $\text{Fe}_3(\text{CO})_{12}$, higher coal conversions were obtained. In the last paper,⁵ the catalytic activity of various metal carbonyl complexes in the liquefaction of two Japanese and one American coal was investigated. The carbonyl compounds of Mo, W, Fe, Co and Ni were highly active catalysts for the liquefaction of Illinois No. 6 coal.

I.2.3 Iron Thiophene Complexes

Our most successful studies have been with iron thiophene complexes. The reaction of $[\text{FeI}(\text{CO})_2(\text{Cp})]$ with AgBF_4 ⁶ followed by dibenzothiophene (dbt) in dichloromethane produced $[\text{Fe}(\text{dbt})(\text{CO})_2(\text{Cp})][\text{BF}_4]$ (1) in low (ca. 10%) yield and fair purity. The crystal structure of 1 was solved and refined to $R = 4.8\%$, $R_w = 5.7\%$ in centrosymmetric space group $P\bar{1}$ (Figures 1 and 2). The most important structural feature is the 2.289 (1) Å long iron-sulfur bond, slightly shorter than the sum of the covalent radii (2.38 Å). Fe-S distances in similar Fp-S (Fp = $[\text{Fe}(\text{CO})_2(\text{Cp})]$) compounds range from 2.109(2) Å in $[\text{Fe}(\text{SO}_2)(\text{CO})_2(\text{Cp})]^+$ to 2.35(1) Å in $[(\text{Cp})(\text{CO})\text{FeSC}(\text{Fp})\text{SCS}(\text{Fp})][\text{SO}_3\text{CF}_3]$.⁷ In general, the higher the sulfur oxidation state, the shorter the Fp-S bond. The dbt ligand in 1 is oriented *anti* to the cyclopentadienyl ligand, presumably minimizing steric contacts, with a Cp(centroid)-Fe-S-Tp torsional angle of -156.8° (Tp is the midpoint of the C8-C9 bond). The dbt ligand is tipped away from iron with pyramidal geometry at sulfur and a Fe-S-Tp angle of 119.4° . The dbt dimensions are very similar to those in free dbt, with a more acute C-S-C angle,

Figure 1.

Figure 2.

slightly longer C-S distances, and slightly more bowing of the benzo rings from the plane of the thiophene ring.⁸ To our knowledge, this is the first S-bonded dibenzothiophene complex in which the dbt group is not part of a chelating ligand. A major improvement in the synthesis of $[\text{Fe}(\text{dbt})(\text{CO})_2(\text{Cp})][\text{BF}_4]$ was the use of $[\text{Fe}(\eta^2\text{-H}_2\text{C=CMe}_2)(\text{CO})_2(\text{Cp})][\text{BF}_4]$,⁹ which raised the yield of 1 to 94% using dibenzothiophene in refluxing dichloromethane. Very pure dbt complex 1 prepared in this way is much more robust than contaminated samples prepared by the other methods.

A possible reason for the improved performance of $[\text{Fe}(\eta^2\text{-H}_2\text{C=CMe}_2)(\text{CO})_2(\text{Cp})]^+$ salts over $[\text{Fe}(\text{thf})(\text{CO})_2(\text{Cp})][\text{BF}_4]$ and $[\text{Fe}(\text{BF}_4)(\text{CO})_2(\text{Cp})]^+$ may be that the latter two complexes are so strongly electrophilic that they attack the electron-rich thiophene and benzothiophene aromatic rings in a Friedel-Crafts sense, forming neutral products with iron-carbon bonds rather than cationic iron-sulfur bonded complexes. The formation of red, ethyl ether-soluble byproducts supports this suggestion, and we hope to investigate it more fully.

Attempts to prepare $[\text{Fe}(\eta^1\text{-thiophene})(\text{CO})_2(\text{Cp})][\text{BF}_4]$ (2) by the reported method, displacement of coordinated tetrahydrofuran (tnf) from $[\text{Fe}(\text{thf})(\text{CO})_2(\text{Cp})]\text{BF}_4$ by thiophene,¹⁰ were unsuccessful. However, the reaction of $[\text{FeI}(\text{CO})_2(\text{Cp})]\text{BF}_4$ with carefully dried AgBF_4 in neat, purified thiophene does produce the desired complex in modest yield and purity. A still better method is the reaction of $[\text{Fe}(\eta^2\text{-H}_2\text{C=CMe}_2)(\text{CO})_2(\text{Cp})][\text{BF}_4]$ with thiophene in refluxing dichloromethane which proceeds in 48% yield. Under similar conditions, $[\text{Fe}(\eta^1\text{-S-2,5-dimethylthiophene})(\text{CO})_2(\text{Cp})][\text{BF}_4]$ was obtained in 59% yield. Our efforts to grow single crystals of these two thiophene complexes suitable for a single crystal X-ray diffraction studies have been unsuccessful so far, because of their lability in solution.

The complex $[\text{Fe}(\eta^1\text{-benzothiophene})(\text{CO})_2(\text{Cp})][\text{PF}_6]$ (3) is prepared in 91% yield from $[\text{Fe}(\eta^2\text{-H}_2\text{C=CMe}_2)(\text{CO})_2(\text{Cp})][\text{PF}_6]$ and 2,3-benzothiophene (benzo[b]thiophene) in refluxing dichloromethane. Surprisingly, this complex is more labile than either the thiophene or dibenzothiophene complex. Slow recrystallization attempts inevitably lead to $[\text{Fe}(\text{CO})_3(\text{Cp})][\text{PF}_6]$ as the principal recovered product.

A number of related reactions were less successful. Reactions of $[\text{Fe}(\eta^2\text{-H}_2\text{C=CMe}_2)(\text{CO})_2(\text{Cp})]^+$ salts with dibenzofuran (a model for organic oxygen in coal), tetraphenylthiophene and hydrogen sulfide gave no tractable products. Reaction of $[\text{Fe}(\eta^2\text{-H}_2\text{C=CMe}_2)(\text{CO})_2(\text{Cp})][\text{BF}_4]$ with one-third equivalent of s-trithiane (thioformaldehyde trimer) led to an insoluble yellow product which is under study. After we began this work, $[\text{Fe}(\text{CO})_2(\text{Cp})]^+$ complexes of s-trithiane were reported by Kuhn and coworkers.¹¹

We sought to improve the stability of iron thiophene complexes by utilizing the $[\text{Fe}(\text{PR}_3)(\text{CO})(\text{Cp})]^+$ group instead of the $[\text{Fe}(\text{CO})_2(\text{Cp})]^+$ group. The reaction of $[\text{Fe}(\text{PPh}_3)(\text{CO})_2(\text{Cp})][\text{BF}_4]$ with trimethylamine-N-oxide (which removes a CO as CO_2) in neat thiophene leads mainly to recovered starting material. Similarly,

$[\text{FeBr}(\text{PPh}_3)(\text{CO})(\text{Cp})]$ reacts with AgBF_4 in neat thiophene to give a green complex, perhaps $[\text{Fe}(\text{thiophene})(\text{PPh}_3)(\text{CO})(\text{Cp})][\text{BF}_4]$, which decomposed during workup. These preliminary results suggested that phosphine substitution actually destabilized the thiophene complexes, and efforts in this direction have been abandoned.

^1H - and ^{13}C -NMR spectra have been obtained for the new complexes. Dynamic NMR spectroscopy was used to study the mobility of thiophene ligands on iron, as a model for catalyst-bound thiophenes. The ^{13}C NMR spectrum of benzothiophene complex **3** shows a singlet at room temperature for the two diastereotopic carbonyl ligands, but two separate signals at low temperature (-90°C), with $\Delta G^\ddagger = 37 \text{ kJ/mol}$. Similarly, the carbonyl ligands of $[\text{Fe}(\text{PhSMe})(\text{CO})_2(\text{Cp})][\text{BF}_4]$ are frozen out at a somewhat higher temperature, with $\Delta G^\ddagger = 50 \text{ kJ/mol}$. These results show that inversion at pyramidal sulfur can be frozen out in these iron-sulfur complexes,¹² further suggesting that the aromaticity of thiophenes results in their increased mobility on catalyst surfaces. In order to measure the barrier to sulfur inversion in $[\text{Fe}(\text{tp})(\text{CO})_2(\text{Cp})]^+$ or $[\text{Fe}(\text{dbt})(\text{CO})_2(\text{Cp})]^+$, it is necessary to lower the symmetry of the complex. Bromination of the 3-position of one of the benzo rings of dibenzothiophene, followed by reaction with $[\text{Fe}(\eta^2\text{-H}_2\text{C=CMe}_2)(\text{CO})_2(\text{Cp})]^+$ in refluxing dichloromethane produced new $[\text{Fe}(\eta^1\text{-S-3-bromodibenzothiophene})(\text{CO})_2(\text{Cp})]^+$ (**4**) as both its $[\text{BF}_4]^-$ and $[\text{PF}_6]^-$ salts. Unfortunately, both were too insoluble to permit detection of the carbonyl ligands by ^{13}C NMR in any available NMR solvents except for CD_3NO_2 , and the freezing point of CD_3NO_2 (-29°C) is too high to achieve separation of the diastereotopic CO signals. $[\text{Fe}(\text{CO})_2(\text{Cp})]^+$ complexes of thiophene and dibenzothiophene with appropriately situated chloromethyl or isopropyl substituents would enable us to detect sulfur inversion using more sensitive ^1H NMR methods. Efforts to prepare such complexes are ongoing.

The reaction chemistry of these iron thiophene complexes is dominated by the lability of the thiophene ligands. In general, monitoring by NMR spectroscopy shows clean release of the thiophene ligand from the complex upon addition of a competing ligand. The dbt ligand of pure **1** is displaced over about one week by ca. two equivalents of water or acetonitrile in CD_3NO_2 solution at room temperature. In contrast, the thiophene ligand of **2** is quantitatively displaced by CD_3NO_2 in ca. three hours at room temperature, and it is very rapidly displaced by acetone, acetonitrile or traces of water. In fact, the previously reported ^1H NMR spectrum of **2** was actually a spectrum of $[\text{Fe}(\text{acetone})(\text{CO})_2(\text{Cp})][\text{BF}_4]$ and free thiophene in d^6 -acetone.¹⁰ The benzothiophene ligand of **3** is rapidly displaced by traces of water, and more slowly by CD_3NO_2 .

We have attempted to convert η^1 -thiophene ligands to η^5 -thiophene or η^6 -arene ligands by elimination of two carbonyls. Ultraviolet photolysis of **1** does not appear (by NMR) to give the desired $[\text{Fe}(\eta^6\text{-dbt})(\text{Cp})][\text{BF}_4]$; instead, free dbt and an unidentified, new cyclopentadienyl iron cation are observed. Thermolysis of **1** at 1300°C in decalin resulted in intractable, nonorganometallic iron salts together with ca. 5% each of $[\text{Fe}(\text{CO})_3(\text{Cp})]^+$ and recovered **1**.

Similarly, attempts to prepare $[\text{Fe}(\eta^6\text{-dbt})(\text{Cp})][\text{BF}_4]$ by photolysis of $[\text{Fe}(\eta^6\text{-p-xylene})(\text{Cp})][\text{BF}_4]$ in the presence of dbt at ambient temperature have been unsuccessful. Ultraviolet irradiation of 2 in thiophene/dichloromethane leads to $[\text{Fe}(\eta^5\text{-thiophene})(\text{Cp})][\text{BF}_4]$. Its proton NMR spectrum in CD_2Cl_2 shows a cyclopentadienyl resonance at δ 5.2, and coordinated thiophene at δ 6.2, 6.4; its infrared spectrum shows no carbonyl absorptions. Attempts to isolate larger than spectroscopic amounts of $[\text{Fe}(\eta^5\text{-thiophene})(\text{Cp})][\text{BF}_4]$ by this method have been unsuccessful.

With some difficulty, 2,3,4,5-tetramethylthiophene was prepared.¹³ Attempts to convert this material to $[\text{Fe}(\eta^5\text{-SMe}_4\text{C}_4)_2][\text{PF}_6]_2$ (the only known bis(thiophene) sandwich complex) using the published procedure¹⁴ and modifications (use of $\text{FeI}_2 + \text{TiPF}_6$) failed to give the desired material.

I.2.4 Ruthenium-Thiophene Complexes

Since two other groups have reported the synthesis of $[\text{Ru}(\eta^5\text{-C}_4\text{H}_4\text{S})(\text{Cp})][\text{BF}_4]$ as well as its facile H/D exchange reactions,¹⁵ we thought that it was a practical starting point for studying ruthenium thiophene complexes as coal liquefaction catalysts. Unfortunately, we have encountered difficulties in preparing the pure ruthenium complex using the published method ($[\text{RuCl}(\text{PPh}_3)_2(\text{Cp})]$ and AgBF_4 in the presence of thiophene) and modifications (TiBF_4 , neat thiophene solvent, etc.). Attempts to prepare S-bonded thiophene complexes $[\text{RuCl}(\eta^1\text{-C}_4\text{H}_4\text{S})_n(\text{PPh}_3)_{2-n}(\text{Cp})]$ ($n = 1, 2$) by scavenging PPh_3 from $[\text{RuCl}(\text{PPh}_3)_2(\text{Cp})]$ using elemental sulfur in the presence of thiophene (as solvent), a method which works for replacement of PPh_3 by carbon monoxide, leads to a green material which we have been unable to fully characterize. Thiophene does seem to play a role in the reaction, since a different (brown) product is obtained from $[\text{RuCl}(\text{PPh}_3)_2(\text{Cp})]$ and sulfur in refluxing benzene, and the rate of reaction is much slower. An attempt to prepare $[\text{Ru}(\text{thiophene})(\text{PPh}_3)_2(\text{Cp})][\text{PF}_6]$ by stirring $[\text{Ru}(\text{MeCN})(\text{PPh}_3)_2(\text{Cp})][\text{PF}_6]$ in refluxing thiophene gave recovered starting material, confirming that S-bonded thiophene is a weaker ligand than acetonitrile.

I.2.5 Molybdenum Thiophene Complexes

Since the most effective hydrodesulfurization catalysts contain molybdenum, we sought to gain some insight into the action of these catalysts by studying molybdenum thiophene complexes. As a simple extension of the iron thiophene work described above, we generated solutions of labile $[\text{Mo}(\text{BF}_4)(\text{CO})_3(\text{Cp})]$ by the known reaction of $[\text{Mo}(\text{CH}_3)(\text{CO})_3(\text{Cp})]$ with HBF_4 in CH_2Cl_2 .¹⁶ Subsequent addition of dibenzothiophene at -78°C gave a pink solution, possibly containing $[\text{Mo}(\text{dbt})(\text{CO})_3(\text{Cp})][\text{BF}_4]$, which decomposed on warming to room temperature. Further exploration of this reaction using cleaner $[\text{ML}(\text{CO})_3(\text{Cp})]$ ($\text{M} = \text{Mo or W}$; $\text{L} = \text{BF}_4 \text{ or PF}_6$), generated from reactions of $[\text{MH}(\text{CO})_3(\text{Cp})]$ with the appropriate $[\text{CPh}_3]^+$ salt at -78°C ,¹⁷ are planned with a variety of thiophenes.

Attempts to prepare π -bonded thiophene, benzothiophene and dibenzothiophene complexes of the $[\text{Mo}(\text{CO})_3]$ group were generally unsuccessful. We prepared numerous labile fac- $[\text{MoL}_3(\text{CO})_3]$ precursors, including $\text{L} = \text{acetonitrile}$ or pyridine and $\text{L}_3 = \text{cycloheptatriene}$ or diglyme , which are known to react with arenes to give $[\text{Mo}(\eta^6\text{-arene})(\text{CO})_3]$ under mild conditions. Reactions of $[\text{Mo}(\text{MeCN})_3(\text{CO})_3]$ with thiophene, benzothiophene and dibenzothiophene were carried out under a variety of conditions. In refluxing pentane for up to 72 hours, the molybdenum acetonitrile complex does not react with any of the thiophenes. In refluxing acetonitrile, no reactions are observed. In refluxing tetrahydrofuran or isooctane, reactions occur but we have been unable to isolate pure products from the reaction mixtures. However, there is evidence that desulfurization of the thiophenes occurs in isooctane at ca. 100°C .¹⁸ A black solid which precipitates from the reaction mixtures during heating is presumably MoS_2 , based on its reaction with H_2SO_4 to give H_2S . In the case of the benzothiophene reaction, a white, gelatinous material also forms upon cooling. Its infrared spectrum (1600 cm^{-1} , br) suggests that this is polystyrene, formed by hydrodesulfurization of benzothiophene to styrene with subsequent polymerization. Attempts to identify the organic products of these desulfurization reactions (presumably butadiene, styrene and biphenyl or their polymers) by gas chromatography were inconclusive.

Reactions of thiophenes with $[\text{Mo}(\eta^3\text{-diglyme})(\text{CO})_3]$ appeared more promising. Reaction with benzothiophene in tetrahydrofuran solvent leads to a deep yellow product whose infrared and proton NMR spectra were consistent with the structure $[\text{Mo}(\eta^6\text{-bt})(\text{CO})_3]$. Unfortunately, the lability of the complex prevented its complete characterization.

Similar results were obtained using $[\text{Mo}(\text{pyridine})_3(\text{CO})_3]$ with thiophene, benzothiophene and dibenzothiophene. In the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ or AlCl_3 (which are added to coordinate to liberated pyridine) only green to black, intractable solids were obtained. Based on our observations and the known lability of molybdenum arene complexes relative to chromium and tungsten, these efforts have been largely abandoned.

I.2.6 Chromium Thiophene Complexes

Our work with chromium complexes has been more successful. As a test system, known $[\text{Cr}(\eta^6\text{-benzo}[b]\text{thiophene})(\text{CO})_3]$ ¹⁷ has been prepared by three different methods. The most efficacious method is the simple reaction of $[\text{Cr}(\text{CO})_6]$ with bt in a refluxing mixture of *n*-butyl ether and tetrahydrofuran (85%). Two other methods, $[\text{Cr}(\text{pyridine})_3(\text{CO})_3] + \text{BF}_3 \cdot \text{Et}_2\text{O} + \text{bt}$ (88%) and $[\text{Cr}(\eta^6\text{-naphthalene})(\text{CO})_3] + \text{bt}$ (80%), also work but the starting materials must be prepared in a separate step. We have utilized the same methods to prepare known $[\text{Cr}(\eta^6\text{-dibenzothiophene})(\text{CO})_3]$ ²⁰ and $[\text{Cr}(\eta^5\text{-thiophene})(\text{CO})_3]$ ²¹ in improved purity and yield. The complexes have been submitted for catalyst testing.

We also have begun investigating the group 6 metal chemistry of 3,4-benzothiophene (5, benzo[c]thiophene). The preparation of benzo[c]thiophene proceeds according to Scheme I.²² Since 5 itself is not thermally stable, we are hoping to prepare chromium tricarbonyl complexes of intermediates 6 and 7 (and byproduct 8) in order to generate $[\text{Cr}(\eta^6\text{-benzo[c]thiophene})(\text{CO})_3]$ in situ. Reaction of 3 with $[\text{Cr}(\eta^6\text{-naphthalene})(\text{CO})_3]$ leads surprisingly to $[\text{Cr}(\eta^1\text{-S-dihydro-benzo[c]thiophene})(\text{CO})_5]$ (9) in ca. 40% yield. Two carbonyls are scavenged from the reaction medium. Complex 9 is formed in 95% yield from $[\text{Cr}(\text{CO})_6]$ and dihydrobenzo[c]thiophene (10) under ultraviolet irradiation. Attempts to convert 9 to $[\text{Cr}(\eta^6\text{-dihydrobenzo[c]thiophene})(\text{CO})_3]$ by thermolysis in refluxing isooctane, by ultraviolet irradiation and by addition of trimethylamine-N-oxide were not successful. Another approach to $[\text{Cr}(\eta^6\text{-benzo[c]thiophene})(\text{CO})_3]$ is to make $[\text{Cr}(\eta^6\text{-1,2-bis(chloromethyl)benzene})(\text{CO})_3]$ and to carry it through the reaction sequence of Scheme I. The required 1,2-bis(chloromethyl)benzene complex has been prepared in 65% yield using $[\text{Cr}(\eta^6\text{-naphthalene})(\text{CO})_3]$, and its reaction with Na_2S is now under study.

Scheme I.

sulfur is pyramidal, as anticipated. The Cr-S bond length of 2.436(1) Å falls in the range 2.42 Å to 2.46 Å observed in similar chromium carbonyl sulfide complexes.²³ The methylene protons of 9 resonate as a singlet in its ¹H NMR spectrum at room temperature, but the signal broadens and splits into an AA'BB' pattern below -40°C due to the slowing of pyramidal inversion at sulfur.

Some of the most effective hydrodesulfurization catalysts are multimetallic, typically containing a group 6 metal (Mo or W) along with a later transition metal (often Fe or Co). We have sought to model these catalysts by using heteronuclear organometallic complexes. Known $[\text{FeMo}(\text{CO})_5(\text{Cp})_2]$ was prepared by ultraviolet irradiation of a mixture of $[\text{Fe}_2(\text{CO})_4(\text{Cp})_2]$ and $[\text{Mo}_2(\text{CO})_6(\text{Cp})_2]$.²⁴ and was submitted for catalyst testing. We hope to learn whether the preformed mixed-metal complex is more effective than the homonuclear components alone, or a simple mixture of the two components.

Reactions of $[W_2(OCMe_3)_6]$ with alkynes have been reported to give alkylidyne complexes $[W(\equiv CR)(OCMe_3)_3]$ (R = alkyl, etc.), a class of very active, homogeneous, alkyne metathesis catalysts.^{2b} The reaction of $[W(\equiv CEt)(OCMe_3)_3]$ with $[Fe(C\equiv CCH_3)(CO)_2(Cp)]$ proceeded via evolution of 2-pentyne to give a spectroscopically

identified carbide complex, $[(\text{Me}_3\text{CO})_3\text{W}\equiv\text{C}-\text{FeM}(\text{CO})_2(\text{Cp})]$. This iron complex is extremely labile, preventing its full characterization. The ruthenium alkynyl complex $[\text{Ru}(\text{C}\equiv\text{CCH}_3)(\text{CO})_2(\text{Cp})]$ was prepared by a new method, reaction of $[\text{RuCl}(\text{CO})_2(\text{Cp})]$ with $\text{Me}_3\text{SiC}\equiv\text{CMe}$ and KF in methanol. Its reaction with $[\text{W}(\equiv\text{CEt})(\text{OCMe}_3)_3]$ at room temperature gave $[(\text{Me}_3\text{CO})_3\text{W}\equiv\text{C}-\text{Ru}(\text{CO})_2(\text{Cp})]$ (11), a red solid which is much stabler than its iron congener, in up to 30% yield. Infrared and ^1H NMR spectra support this formulation, and its mass spectrum displays $[(\text{Me}_3\text{CO})_3\text{W}\equiv\text{C}]^+$ and $[\text{Ru}(\text{CO})_2(\text{Cp})]^+$ fragments. A single crystal X-ray diffraction study of 11 has been carried out and refined to $R = 6.8\%$, $R_w = 9.5\%$ with thermal disorder evident in the carbonyl and tertiary butoxide ligands. The central portion of the molecule is well-defined (Figure 4) with a $\text{W}\equiv\text{C}$ distance of $1.75(2)$ Å, a $\text{Ru}-\text{C}$ distance of $2.09(2)$ Å, and a $\text{W}\equiv\text{C}-\text{Ru}$ angle of $177(2)^\circ$. Reactivity studies to determine how well this complex models surface carbides are in progress.

Figure 4.

I.2.8 Coal Liquefaction in Tetralin

The coal samples used were KY #11 and two biologically treated samples of this coal. KY #11 coal (KCERL 91182) which has been crushed to pass 200 mesh was obtained from the KCERL. Two bio-treated coals were treated by culture from acid mine drainage and Sulfolobus brierleyi, respectively, as part of the project.

Analyses of these coals are given in Table 1. Fourteen different homogeneous catalysts were used. Eight catalysts were commercially available; the rest were synthesized as part of the project.

Procedure

All experiments were conducted in duplicate in stainless steel tubing bombs (0.424" ID x 4.5") sealed at each end with Swagelock caps. In a typical experiment, 2.0 g of coal and 4.0 mL of solvent (tetralin) were placed in the tubing bomb, and a certain amount of catalyst was added. Two tubing bombs were mounted in a reactor holder connected to a variable speed electric motor. The rotary

motion of the motor was converted to reciprocating motion by using a cam shaft. The fluidized sand bath was preheated to about 3 degrees above the desired reaction temperature, and the tubing bomb was quickly immersed into the bath. The tubing bomb was shaken vertically along its axis at 800 rpm. After the immersion of the tubing bomb, the temperature of the sand bath slightly decreased because of the heat loss to the shaft and the tubing bombs.

A typical temperature profile is illustrated in Figure 5. The reaction time was estimated from the time when the temperature of the reaction mixture reached 250°C below the desired temperature until the bomb was removed from the sand bath. It was then quickly plunged into an aluminum container of cold water until it was cooled to room temperature (about 2 to 3 minutes). After the tubing bomb was opened and the products were transferred into a beaker by using toluene and a steel spatula, the contents were filtered through a cellulose thimble which had been already dried at 105°C to a maximum weight change of 5 mg between successive dryings.

Soxhlet extraction of the tubing bomb residue in toluene proceeded for 24 hours under nitrogen. After extraction, the thimble and residue were dried in the vacuum oven at 105°C and 29" Hg and placed in a desiccator. This procedure was repeated until the weight change became within 10 mg between successive weighings. The conversion of coal was calculated by using the following equation, assuming that every catalyst remained as pure metal after the liquefaction reaction.

$$\text{Conversion (\%)} = \frac{C_d - R + W_{\text{cat}}}{C_{\text{daf}}} \times 100$$

C_d = weight of coal on dry basis
 C_{daf} = weight of coal on dry-ash-free basis
 R = weight of residue in the thimble
 W_{cat} = weight of catalyst metal

The results of 27 liquefaction runs using KY #11 coal are presented in Table 2. Fourteen different catalysts were used and the concentration ranged from 1 to 3%. Concentration is defined as metal weight % of coal. Two temperatures, 400°C and 425°C, were studied and reaction times varied from 10 to 60 minutes.

Effect of Catalyst Concentration (Runs 7, 8, and 9)

The effect of catalyst concentration was studied by using $\text{Fe}(\text{CO})_5$ at 425°C for the reaction time of 60 minutes. The coal conversion increased from 77.8 to 82.7% when the metal concentration of catalyst increased from 1 to 3%. The result is shown in Figure 6.

Effect of Reaction Time (Runs 1, 2, 3, 4, 5, 6, and 9)

The effect of reaction time on conversions for catalytic ($\text{Fe}(\text{CO})_5$) and non-catalytic cases was studied. Figure 7 shows the coal conversions against reaction time. The conversions increased from 66.3 to 81.9% and from 72.1 to 82.7% for the non-catalytic and catalytic reactions, respectively, when the reaction time increased from 20 to 60 minutes. The difference was about 6% at 20 minutes while no significant differences were found at 40 and 60 minutes.

Effect of Various Catalysts on Conversion (Runs 5, 14-27)

Catalytic activities of various catalysts were compared at 425°C for the reaction time of 20 min. Metal concentration of catalysts was fixed at 3 wt% of coal. Under these conditions a conversion of 66.3% was found without added catalyst. $\text{C}_7\text{H}_8\text{Mo}(\text{CO})_3$, $\text{Mn}_2(\text{CO})_{10}$ and an $\text{Fe}(\text{CO})_5$ - $\text{Mo}(\text{CO})_6$ binary catalyst exhibited high catalytic activities, in the liquefaction of KY #11 coal. The conversions of these catalysts were 76.0, 75.3, 74.2%, respectively. $\text{Fe}(\text{CO})_5$, $\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ also showed high catalytic activities, with conversions above 71.0%, while $\text{Cr}(\text{CO})_6$, $\text{Cp}(\text{CO})_2\text{FeMo}(\text{CO})_3\text{Cp}$, $\text{C}_{10}\text{H}_8\text{Cr}(\text{CO})_3$, $\text{CpFe}(\text{CO})_2\text{Cl}$ and $(\text{CpN})_3\text{Cr}(\text{CO})_3$ gave conversions below 65.0%.

Figure 8 summarizes all the results and indicates that five of the catalysts had a negative effect on conversion.

Effect with a Bio-Treated Coals (Runs 28-36)

The results of 9 liquefaction runs using two kinds of bio-treated coal are summarized in Table 3. In both cases the bio-treated coals

Fig. 8 EFFECT OF VARIOUS CATALYSTS ON CONVERSION

gave slightly higher conversions under similar conditions than the untreated KY #11 coals. The increase was 2.3% at 425°C and 20 minutes for the culture from acid mine drainage. The increase for the *Sulfolobus brierleyi*-treated coal (BT-2) was only 1.4%, but that comparison is at 40 min where differences tend to be less. Similar results were obtained for the $\text{Fe}(\text{CO})_5$ and $\text{Mo}(\text{CO})_6$ runs with BT-1. The bio-treated coals gave conversions 1.8 and 2.2% higher, respectively.

For the BT-2 sample the results were mixed when comparing similar runs with untreated coal. The $\text{Fe}(\text{CO})_5$ and $\text{W}(\text{CO})_6$ catalysts gave lower conversions with bio-treated coal, but the other three catalysts listed in the table all gave from 1.4 to 2.2% higher conversions with BT-2.

I.2.9 References and Notes

1. Watanabe, Y.; Yamada, O.; Fujita, K.; Takegami, Y.; Suzuki, T. *Fuel*, 1984, **63**, 752.
2. Suzuki, T.; Yamada, O.; Fujita, K.; Takegami, Y.; Watanabe, Y. *Fuel*, 1984, **63**, 1706.
3. Suzuki, T.; Yamada, O.; Fujita, K.; Takegami, Y.; Watanabe, Y. *Ind. Eng. Chem. Proc. Des. Dev.*, 1985, **24**, 832.
4. Suzuki, T.; Yamada, O.; Takahashi, Y.; Watanabe, Y. *Fuel*, 1985, **10**, 33.
5. Yamada, O.; Suzuki, T.; Tien, J. H.; Ando, T.; Watanabe, Y. *Fuel Process. Tech.*, 1985, **11**, 297.
6. Reger, D. L.; Coleman, C. J.; McElligot, P. J. *J. Organomet. Chem.*, 1979, **171**, 73.
7. a. Churchill, M. R.; Wormald, J. *Inorg. Chem.*, 1971, **10**, 572.
b. Churchill, M. R.; DeBoer, B. G.; Kalra, K. L. *Inorg. Chem.*, 1973, **12**, 1646. c. Churchill, M. R.; Kalra, K. L. *Inorg. Chem.*, 1973, **12**, 1650. d. Hartmann, G.; Frobose, R.; Mews, R.; Sheldrick, G. M. *Z. Naturforsch. B.*, 1982, **37**, 1234. e. Albano, V. G.; Braga, D.; Busetto, L.; Monari, M.; Zanotti, V. *J. Chem. Soc., Chem. Commun.*, 1984, 1257. f. English, R. B.; Nassimbeni, L. R.; Hanines, R. J. *J. Chem. Soc., Dalton Trans.*, 1978, 1379.
8. Bechtel, F.; Chasseau, D.; Gaultier, J.; Hauw, C. *Cryst. Struct. Commun.*, 1977, **6**, 699.
9. Rosenblum, M.; Giering, W.; Samuels, J. *Inorganic Syntheses*, 1986, **24**, 161.
10. Kuhn, N.; Schumann, H. *J. Organomet. Chem.*, 1984, **276**, 55.
11. Kuhn, N.; Schumann, H. *J. Organomet. Chem.*, 1986, **315**, 93.
12. Kuhn, N.; Schumann, H. *Inorg. Chem. Acta*, 1986, **116**, L11.
13. Gaertner, R.; Tonleyn, R. *J. Am. Chem. Soc.*, 1951, **73**, 5872.
14. Braitsh, D. M.; Kumarappan, R. *J. Organomet. Chem.*, 1975, **84**, C37.
15. a. Spies, G. H.; Angelici, R. J. *J. Am. Chem. Soc.*, 1985, **107**, 5569. b. Draganjac, M.; Ruffing, C. J.; Rauchfuss, T. B. *Organometallics*, 1985, **4**, 1909.
16. Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.*, 1980, **102**, 2698.
17. Sunkel, K.; Ernst, H.; Beck, W. *Z. Naturforsch. B.*, 1936, **33**, 474.
18. a. Alper, H.; Blair, C. *Fuel*, 1980, **59**, 670. b. Doyle, G. *Prepr., Div. Petrol. Chem. ACS*, 1976, **21**, 165. c. Luh, T. Y.; Wong, C. S. *J. Org. Chem.*, 1985, **50**, 5413. d. Alper, H.; Paik, H. N. *J. Org. Chem.*, 1977, **42**, 3522.
19. Lumbroso, H.; Segard, C.; Roques, B. *J. Organomet. Chem.*, 1973, **61**, 249.
20. Fischer, E. O.; Goodwin, H. A.; Kreiter, C. G.; Simmons, H. D., Jr.; Sonogashira, K.; Wild, S. B. *J. Organomet. Chem.*, 1968, **14**, 359.
21. Fischer, E. O.; Goodwin, H. A.; Kreiter, C. G.; Simmons, H. D., Jr.; Sonogashira, K.; Wild, S. B. *J. Organomet. Chem.*, 1968, **14**, 359.
21. Fischer, E. O.; Ofele, K. *Chem. Ber.*, 1958, **91**, 2395.
22. Cava, M. P.; Pollack, N. M.; Mamer, O. A.; Mitchell, M. J. *J. Org. Chem.*, 1971, **36**, 3932.

23. a. Raubenheimer, H. G.; Breyens, J. C. A.; Lotz, S. J. *Organomet. Chem.*, 1976, 112, 145. b. Baker, E. N.; Larson, N. G. *J. Chem. Soc., Dalton Trans.*, 1976, 179.
24. Abrahamson, H. B.; Wrighton, M. S. *Inorg. Chem.*, 1978, 17, 1003.
25. Biloen, P.; Helle, J. N.; van der Berg, F. G. A.; Sachtler, W. M. H. *J. Catal.*, 1983, 81, 450.
26. Listemann, M. L.; Schrock, R. R. *Organometallics*, 1985, 4, 74.

Table 1. Analysis of Coal Samples^(b)

	<u>KY #11</u>	<u>BT1^(b)</u>	<u>BT2^(c)</u>
<u>Proximate Analysis</u>			
Fixed Carbon	53.07	55.04	56.69
Volatile Matter	39.15	39.00	37.70
Ash	7.78	5.96	5.61
Moisture	3.27	1.28	1.18
<u>Ultimate Analysis</u>			
Carbon	70.69	72.93	70.80
Hydrogen	4.95	4.89	4.86
Nitrogen	1.50	1.61	1.62
Sulfur	3.09	2.44	2.39
Pyritic Sulfur	nd ^(d)	0.08	0.06
Oxygen (by diff.)	11.99	12.17	14.72
Ash	7.78	5.96	5.61

(a) All values on dry basis, wt%.

(b) BT1 = Bio-treated coal by culture from acid mine drainage.

(c) BT2 = Bio-treated coal by Sulfolobus brierleyi.

(d) nd = Not determined.

Table 2. Hydroliquefaction of KY #11 Coal

Run	Catalyst	Concentration of Catalysts(a)	Temp. (°C)	Time (min)	Mean Conversion(%)
1	None		425	20	66.3
2	None		425	40	73.6
3	None		425	60	81.9
4	$\text{Fe}(\text{CO})_5$	3%	425	10	69.9
5	$\text{Fe}(\text{CO})_5$	3%	425	20	72.1
6	$\text{Fe}(\text{CO})_5$	3%	425	40	78.5
7	$\text{Fe}(\text{CO})_5$	1%	425	60	77.8
8	$\text{Fe}(\text{CO})_5$	2%	425	60	79.7
9	$\text{Fe}(\text{CO})_5$	3%	425	60	82.7
10	None		400	10	52.1
11	None		400	60	74.8
12	$\text{Fe}(\text{CO})_5$	3%	400	10	40.8
13	$\text{Fe}(\text{CO})_5$	3%	400	60	63.5
14	$\text{Mo}(\text{CO})_6$	3%	425	20	71.6
15	$\text{Cr}(\text{CO})_6$	3%	425	20	59.3
16	$\text{W}(\text{CO})_6$	3%	425	20	73.2
17	$\text{Fe}(\text{Cp})_2$	3%	425	20	70.4
18	$[\text{Fe}(\text{CO})_2\text{Cp}]_2$	3%	425	20	70.1
19	$\text{Cp}(\text{CO})_2\text{FeMo}(\text{CO})_3\text{Cp}$	3%	425	20	64.3
20	$\text{Fe}_2(\text{CO})_9$	3%	425	20	69.6
21	$\text{CpFe}(\text{CO})_2\text{Cl}$	1.7%	425	20	71.7
22	$\text{CpFe}(\text{CO})_2\text{Cl}$	3%	425	20	63.5

23	$(\text{CpN})_3\text{Cr}(\text{CO})_3$	1.7%	425	20	62.6
24	$\text{Mn}_2(\text{CO})_{10}$	3%	425	20	75.3 ^(c)
25	$\text{Fe}(\text{CO})_5\text{-Mn}(\text{CO})_6$ ^(b)	3%	425	20	74.2 ^(c)
26	$\text{C}_7\text{H}_8\text{Mo}(\text{CO})_3$	3%	425	20	76.0 ^(c)
27	$\text{C}_{10}\text{H}_8\text{Cr}(\text{CO})_3$	3%	425	20	64.5 ^(c)

(a) Metal wt% of coal.

(b) Fe:Mo = 10:1 by mole.

(c) One sample.

Table 3. Hydroliquefaction of Bio-Treated Coals

Run	Coal ^a	Catalyst	Concentration of Catalysts ^b	Temp. (°C)	Time (min)	Mean Conversion(%)
28	BT1	None		425	20	68.6
29	BT1	Fe(CO) ₅	3%	425	20	73.9
30	BT1	Mo(CO) ₆	3%	425	20	73.8
31	BT2	None		425	40	80.0
32	BT2	Cr(CO) ₆	3%	425	20	61.5
33	BT2	[Fe(CO) ₂ Cp] ₂	3%	425	20	71.5 ^c
34	BT2	W(CO) ₆	3%	425	20	69.0
35	BT2	Cp(CO) ₂ FeMo(CO) ₃ Cp	3%	425	20	66.4 ^c
36	BT2	Fe(CO) ₅	3%	425	20	68.4 ^c

^aBT1: Bio-treated coal using culture from acid mine drainage.

BT2: Bio-treated coal using Sulfolobus brierleyi.

^bMetal wt% of coal.

^cOne sample.

CO-PROCESSING OF COAL WITH HEAVY OIL
AND PETROLEUM RESIDUALS

October 1, 1985 - December 31, 1986

University of Pittsburgh

Y. T. Shah
Irving Wender

Title: Task II. Co-processing of Coal with Heavy Oil and Petroleum Residuals

PI's: Y.T. Shah and I. Wender

Report Coordinator: I. Wender
Phone Number: (412) 624-5281

Period: October 1, 1985 - December 31, 1986

Objective

II.1 The principal objective of this work is to explore the mechanisms involved in the rather remarkable findings obtained for the co-processing of coal with residual oils, heavy virgin crudes and heavy oils. We will endeavor to use as large a proportion of coal to oil as possible, hopefully over 40% coal to 60% oil.

Scope

II.1 Co-processing may indeed be the bridge that leads to a new process for the direct liquefaction of coal. A remarkable synergism has been found when coal slurried in heavy oil is treated under coal liquefaction conditions. Coking is inhibited and heavy metals are relegated to the pitch fraction. The product is easy to upgrade to distillates. An understanding of the role of coal in inhibiting the thermal foundation of coke upon addition of coal to heavy oils would be of great benefit in evolutionary advances in present processes for the direct liquefaction of coal.

Final Report

1.0 INTRODUCTION

Modern direct liquefaction processes, such as H-coal, EDS, SRC-II, etc., recycle a portion of the product oil to slurry coal into the reactor. Typically, the reactor feed consists of two parts of recycle oil per part of coal. Thus, only one third of the reactor capacity is effectively utilized for liquefaction of the feed coal. Further, the recycle oil must have a good hydrogen donor capacity. The recycle stream adds to the complexity of such plants, and increases the cost of production. Co-processing, where coal is liquefied in a once-through mode using petroleum-derived or other heavy oil slurrying media, such as heavy crudes, residual oil, tar sands, etc., has the potential to provide a solution to some of the difficulties in direct liquefaction of coal, as well as in the processing of heavy oil streams which usually contain metals that act as catalyst poisons.

This work presents results of studies on the thermal, non-catalytic co-processing of 10 - 40 wt % of Illinois No. 6 hvC bituminous coal with Maya (650°F+) ATB residual oil and 10 - 25 wt % Illinois No. 6 coal with whole Boscan crude. The chief aim was to investigate the action of coal in the demetallization of heavy or residual oil during co-processing. Heteroatom removal during co-processing has also been investigated.

2.0 EXPERIMENTAL

Co-processing experiments were carried out using Illinois No. 6 coal with two different petroleum feedstocks -- Maya (650°F+) ATB and Whole Boscan crude. Tables 1 and 2 give the analyses of the coal and of the oils, respectively. Experiments were also carried out with char made from cellulose and activated carbon.

All experiments were carried out in a 20 ml horizontal microreactor in a batch mode under isothermal conditions. Products were characterized as oils, asphaltenes and coke, depending upon their solubility behavior, as follows:

Oils:	Products soluble in pentane
Asphaltenes:	Products soluble in tetrahydrofuran (THF) but insoluble in pentane
Coke:	Product insoluble in THF

The metal content of various fractions was determined by x-ray absorption spectroscopy.

The details of the experimental and analytical techniques are presented elsewhere.⁽¹⁾

TABLE 1

Proximate and Ultimate Analysis of
Illinois No.6 hvC Bituminous Coal

<u>Proximate Analysis (wt%)</u>		<u>Ultimate Analysis (wt%)</u>	
Moisture	4.24	Hydrogen	5.04
Volatile Matter	36.93	Carbon	67.18
Fixed Carbon	48.18	Nitrogen	0.89
Ash	10.56	Sulfur	2.98
		Oxygen	13.26
		Ash	10.56
 <u>Sulfur Forms (wt%)</u>			
Sulfate	0.03		
Pyritic	1.16		
Organic	1.79		

TABLE 2

Analysis of Petroleum Feedstocks

	Maya (650 °F+) ATB	Boscan Crude
Gravity, API	8.8	10.0
H/C atomic ratio	1.52	1.55
S (wt%)	4.60	5.30
N (wt%)	0.48	0.60
V (ppm)	400	1100
Ni (ppm)	78	100
Asphaltenes (wt%)*	19.0	11.9

*Components soluble in tetrahydrofuran but insoluble in pentane.

3.0 RESULTS AND DISCUSSION

3.1 Effect of Coal on Product Yields

Thermal processing of heavy oils in the presence of hydrogen yields significant amounts of coke at direct liquefaction temperatures. Large amounts of coke were obtained between 410 and 450°C during the thermal processing of Maya (650°F+) ATB in the absence of coal. The variation of coke from Maya ATB with reaction temperature is shown in Figure 1. Less than 2 wt % of coke was obtained at a one hour residence time at 410°C; as the temperature increased to 450°C, the coke yield rose to 20 wt %. Data points on figures represent either the actual data or the average of several data points. The comprehensive data is given in reference 1.

The Maya ATB contained 81 wt % of pentane-solubles. Thermal cracking of Maya ATB yielded significant amounts of coke which was accompanied by changes in the amount of pentane-solubles. The pentane-soluble yield increased slightly during the heat-up period but fell with increasing residence time. The decrease in the yield of pentane solubles was severe at high temperatures as shown in Figure 2.

Co-processing experiments using Illinois No. 6 hvC bituminous coal and Maya ATB were conducted between 410 and 450°C. The effect of coal concentration on coke yields at 425°C is shown in Figure 3.

The "coke" (THF-insolubles) yields comprise "unreacted" coal along with inorganic matter and the high molecular weight materials produced during the reaction. The coke yield is of importance in demetallization because most of the metals removed are found in this fraction. In all cases, at short residence times there was a decrease in coke yields. There are at least two feasible explanations for the drop in coke yields during the first 15 minutes of co-processing. Part of the coal may be liquefying under hydrogen pressure at 425°C. Perhaps a more logical explanation for this drop in coke yields is that the so-called trapped or mobile phase is being removed from the coal under these conditions. It is now believed⁽²⁾ that coal is a physical mixture of a crossed linked macromolecular network with a large number of relatively small molecules that have a wide variety of structures. These small molecules may represent as much as 10 - 50 wt % of the whole coal, except for coals of very high rank. The trapped molecules may consist of straight chain n-alkanes (about C12-C18) including pristane and other biological markers. It is quite possible that benzene rings with long carbon chains are entrapped. It is this mobile phase that is most likely to be dissolved out of the coal resulting in less THF-insolubles. As we shall see later, metals are removed even while the coke yield is decreased. At short residence times, the amount of coke formed from the Maya ATB is negligible. At longer residence times, significant amounts of coke are formed by the repolymerization of species derived from both coal and heavy oil.

As the concentration of coal is increased, the formation of coke is increased. This increase may be largely due to the inability of the heavy oil to donate hydrogen to the coal. The rate of coke

Figure 1. Effect of Reaction Temperature on THF-Insoluble Yields for 100 wt% Maya (650 °F+) ATB and 6.9 MPa Initial Hydrogen

Figure 2. Effect of Reaction Temperature on Pentane-Solubles for 100 wt% Maya (650 °F+) ATB and 6.9 MPa Initial Hydrogen

Figure 3. Effect of Coal Concentration on THF-Insoluble Yields with Maya (650 °F+) ATB at 425 °C and 6.9 MPa Initial Hydrogen

formation varied with coal concentration. A change in the rate of coke formation is seen if a change in the slope of the coking curve occurs. Coal concentrations below 25 wt% showed a negligible increase in the rate of coking over the thermal coking rate of Maya ATB alone. However, for a 40 wt % coal concentration, there was a significant increase in the slope of the coking curve (Figure 3).

Only 4.4 wt% of the Illinois No.6 hvC bituminous coal is extractable with THF while THF dissolves all of the Maya ATB. During co-processing, part of the coal is dissolved in the host oil. The amount of coal converted to THF solubles during co-processing was determined under the assumption that the heavy oil yields the same amount of THF-insolubles, independent of coal concentration (Equation 3-1).

$$\% \text{ Coal Conversion} = 1 - \frac{A - B \times C - D \times E}{E \times (1-D)} \times 100 \quad (3-1)$$

where: A = grams of coke from co-processing/gram of feed
 B = gram of coke from cracking of oil alone/gram of oil
 C = gram of oil/gram of feed
 D = gram of ash/gram of coal
 E = gram of coal/gram of feed

With this assumption, at low temperatures, coal conversions increased during short residence times and then leveled off, while at high temperatures, conversion decreased due to retrogressive reactions after a point of maximum dissolution (Figure 4).

Coal conversions decreased during processing at high temperatures while coke yields rose at temperatures between 410 and 450°C for 25:75 coal:Maya mixtures (Figure 5). Coal conversion for various coal/Maya mixtures dropped with increasing coal concentrations (Figure 6). Pentane solubles decreased with longer residence time for all coal concentrations under hydrogen pressure (Figure 7). These yields are summarized in Table 3.

TABLE 3

Yields of Pentane Solubles (Oils) During Coprocessing at 425 °C, 1 hr Residence Time and 6.9 MPa Initial Hydrogen

FEED COMPOSITION

MAYA (650 °F+) ATB	100	90	75	60
Illinois No.6 hvC	---	10	25	40
Bituminous Coal				
WT % Pentane Solubles	71.1	57.8	53.4	45.8

Figure 4. Effect of Reaction Temperature on Coal Conversion for a 25 wt% Illinois No.6 hvC Bituminous Coal:75 wt% Maya (650 °F+) ATB Mixture at 6.9 MPa Initial Hydrogen

Figure 5 . Effect of Reaction Temperature on THF-Insoluble Yields for a 25 wt% Illinois No.6 hvC Bituminous Coal/ 75 wt% Maya (650 °F+) ATB Mixture at 6.9 MPa Initial Hydrogen

Figure 6. Effect of Coal Concentration on Coal Conversion for Various Coal/Maya (650F+) Mixtures at 6.9 MPa Initial Hydrogen at 425 °C

Figure 7. Effect of Coal Concentration on Pentane Soluble Yields at 425 °C and 6.9 MPA Initial Hydrogen

Thermal processing of the Boscan crude alone resulted in a coke yield of 9.1 wt% at 425°C as compared to 7.9 wt% of coke from Maya at the same temperature. The coking rates obtained after about 15 minutes from the addition of coal to Boscan crude were similar to that of the thermal coking of the Boscan crude alone (Figure 8). In all cases larger amounts of coke were obtained using the heavier Boscan crude compared with Maya ATB at various coal concentrations (Figure 9). Slightly less net coal conversion results were obtained using Boscan crude over Maya ATB (Table 4).

TABLE 4
Comparison of Host Oil Effects
on Coal Conversion at 425 °C and 6.9 MPa

<u>FEED COMPOSITION</u>				
Maya ATB	90	---	75	---
Boscan Crude	---	90	---	75
Illinois No.6 hvc	10	10	25	25
Bituminous Coal				
<u>RESIDENCE TIME 30 (min)</u>				
Coal Conversion	64	40	57	48
<u>RESIDENCE TIME 60 (min)</u>				
Coal Conversion	53	40	50	46

Material balances generally exceeded 90% with both coal/Maya and coal/Boscan mixtures. Reaction temperature showed that as the temperature rose, the material balance fell. The average material balance for a 25/75 coal/Maya mixture fell from 100.2 ± 0.8 at 410°C to 82.4 ± 10.4 at 450°C. This decrease is from the formation of product gases and lighter components and experimental error.

3.2 Role of Coal in the Removal of Vanadium

The ability of coal to remove vanadium from host oils during co-processing was examined with Maya (650°F+) ATB and whole Boscan crude. Illinois No.6 coal was used as the coal additive in the presence of hydrogen and in the absence of any added catalyst. Experiments were also conducted to determine the role of other carbonaceous materials as metal "sinks" in co-processing.

3.2.1 Thermal Demetallization of Maya (ATB) with Coal

The Maya (650°F+) ATB contained 400 ppm of vanadium. Various coal-to-heavy oil ratios were investigated to study the demetallization effect of coal on Maya ATB. The distribution of vanadium in the Maya (650°F+) ATB, without treatment, showed that 66.5% of vanadium was in the asphaltenes and 33.5% of vanadium was in the pentane-solubles. During co-processing there was a continuous increase in the vanadium content of THF-insolubles with increasing

Figure 8. Effect of Coal Concentration on THF-Insoluble Yields with Whole Boscan Crude at 425 °C and 6.9 MPa Initial Hydrogen

Figure 9. Comparison of THF-Insoluble Yields from Coal/Maya and Coal/Boscan Mixtures at 425 °C and 6.9 MPa Initial Hydrogen

residence time for all coal concentrations (Figure 10). The percentage of vanadium removed to the THF-insolubles during co-processing at one hour residence time and 425°C is summarized in Table 5. For the 10:90 coal-to-Maya ratio 69.4 wt% of the vanadium was removed from the mixture to the THF-insolubles; with the 25 coal:75 Maya mixture, 87.7 wt% of the vanadium was removed. The highest coal/Maya ratio investigated was 40:60; here 89.1 wt% of vanadium was removed to the THF-insolubles. In lower coal concentrations the rest of the vanadium was found in the asphaltene fractions. The distribution of vanadium between the asphaltenes and oils at higher coal concentrations is shown in Table 5.

TABLE 5

Percent Vanadium in Product Fractions After
Coproprocessing at 425 °C with 1 hr Residence Time

FEED COMPOSITION

Maya ATB (wt%)	100	90	75	---	---	---
Boscan Crude (wt%)	---	---	---	100	90	75
Illinois No.6 (wt%)	---	10	25	---	10	25
% Vanadium in THF-insolubles	65.4	69.4	87.7	72.5	80.7	84.1
% Vanadium in Asphaltenes	32.5	25.4	7.6	25.7	18.4	15.2
% Vanadium in Pentane solubles	2.1	5.2	4.7	1.8	0.9	0.7

Co-processing resulted in removal (to the THF-insolubles) of more vanadium than was achieved by thermal processing of the oil alone. As more coal was added to the host oil, there was an increase in both coke yields and vanadium removal. The coke yields versus wt% of vanadium removed to the THF-insolubles for the 10:90 and the 25:75 coal/Maya mixtures are shown in Figure 11. For the 10:90 mixture, as the coke yields rose, the rate of vanadium removal appears to have remained constant, but similar results were not noted for the 25:75 mixture. In this case, the rate of vanadium removal to the THF-insolubles was higher at lower residence times (less than 30 minutes), but at longer residence times a (slight) decrease in the rate of vanadium removal to the THF-insolubles was obtained. In any case, as coal concentrations increased, more vanadium was removed to the THF-insolubles.

The vanadium content of the pentane-solubles in Maya ATB fell during co-processing. As the coal-to-heavy oil ratio increased, the amount of vanadium removed from the pentane solubles rose and the yields of pentane-solubles decreased. The 40/60 coal-to-heavy oil mixture showed pentane-soluble yields of 40.4 wt% and a 95% vanadium removal during co-processing while 72 wt% of the vanadium was removed with the 10/90 mixture.

Figure 10. Removal of Vanadium to THF-Insolubles for Coal/Maya Mixtures at 425 °C and 6.9 MPa Initial Hydrogen

Figure 11. THF-Insolubles Yields versus Removal of Vanadium for 10:90 and 25:75 Coal/Maya Mixtures at 425 °C and 6.9 MPa Initial Hydrogen

3.2.2. Role of Coal in the Thermal Demetallization of Whole Boscan Crude During Co-processing

Whole Boscan crude contains 1100 ppm of vanadium; the higher metal content (as compared to the Maya ATB) highlights demetallization during co-processing. A solvent extraction with THF and pentane on the crude at ambient conditions showed 63.2% of the vanadium was in the asphaltenes and 36.8% was in the pentane-solubles. On processing whole Boscan crude (no coal added), a 72.5 wt% of the vanadium was removed to the THF-insolubles (essentially coke formed solely from the Boscan crude). The removal of vanadium from Boscan crude by addition of various amounts of coal is shown in Figure 12. These results are summarized in Table 5. The coal was equally effective in the removal of metals from a high metallic oil. These results are similar to the work of Shinn et al.⁽³⁾

The extent of coking of the coal/Boscan crude mixtures is shown in Figure 8. As expected, coke yields increased as the coal concentration rose. Vanadium removal increased as coke yields rose. Pentane-solubles decreased with increasing coke formation. These drops are shown in Table 6. The metal content in the pentane-solubles fell to 5% of the original vanadium content with the 10/90 mixture and 4% with the 25/75 mixture.

TABLE 6

Decrease in Pentane-Soluble Yields for Coal/Maya Mixtures at 425 °C and 6.9 MPa Initial Hydrogen

Feed Composition

Maya (650 °F+) ATB	100	90	75	60
Illinois No.6 hvC	---	10	25	40
Bituminous Coal				

Pentane-Solubles Yields

Residence Time (min)

0	86.4	79.3	65.5	56.1
60	71.1	58.9	53.4	40.4

It appears that operating with small amounts of coal, 10 wt% coal to 90 wt% heavy oil, significant vanadium removal would be obtained with low coke yields. This would allow one to operate with a mixture that yields both good demetallization and low coke yields. Attempts to increase the coal concentration with concomitant increased demetallization and lower coke formation is a desirable goal.

Figure 12. Removal of Vanadium to THF-Insolubles for Coal/Boscan Mixtures at 425 °C and 6.9 MPa Initial Hydrogen

3.3 Organic Solids "Resembling" Coal for Demetallization of Heavy Oils

Many researchers have noted that cellulose, heated to high temperatures (330 - 475°C), usually in an inert atmosphere, yields chars whose elemental analysis and infrared spectra resemble those of coal. Cellulose, under these conditions, is easily converted to phenolic and polynuclear structures. The "rank" of the char as compared to that of a particular coal depends chiefly on the temperature at which the cellulose is heated. It is important to note, however, that these "artificial" coal-like chars contain only trace amounts of inorganic compounds. The resemblance of the products from the hydrogenation of sucrose and cellulose provides evidence of the coal-like characteristics of these pyrolysis products of carbohydrate-like material. It was thus of interest to add these chars made from cellulose to heavy oils and treat them in a co-processing mode. The questions raised were (a) will the cellulose char function as well as coal in demetallization or is coal peculiarly suited for this purpose, (b) what part does the inorganic material in coal play in demetallization during co-processing.

The infrared spectra of Illinois No.6 hvC bituminous coal and a cellulose char are shown in Figure 13. It is observed that the char spectra resemble, to an extent, the coal spectra. There is a difference between the cellulose, starting material for the char, and the char in the FTIR spectra.

Among the various solid carbonaceous materials (coal, artificial char, active carbon) added to Maya (650°F+) ATB, artificial char made from cellulose at 415-425°C and under 5.2 MPa nitrogen was found to be the most effective in the removal of vanadium to the THF-insolubles. This char was used in a 10:90 char to Maya mixture and showed that at a one hour residence time, 80.4% of the vanadium was removed to the THF-insolubles. Illinois No.6 coal at the same ratios gave a 69.4% removal of vanadium. A 20:80 char:Maya mixture gave a 72.1% removal of vanadium to THF-insolubles. Coal gave an 87.7% removal of vanadium to the THF-insolubles for a 25:75 mixture.

There is a noticeable difference in the ability of char to remove metals from the Maya (650°F+) ATB between the 10:90 and 20:80 mixtures. This could possibly be explained by the fact that the chars were of different "maturity" corresponding to coal rank. The char used in the 20:80 mixture was made at 4.8 MPa nitrogen and 400°C, while the char used in the 10:90 was made at 5.2 MPa nitrogen and between 415 - 425°C. The char in the 10:90 mixture was more coal-like as shown in Figure 13. These results show that the preparation of the coal-like char is an important factor in determining the ability of the char to remove metals. Both chars contain only traces of inorganics, so the inorganics seem to play no special role in the removal of vanadium from heavy oils.

The other carbonaceous solid added to the Maya ATB in the absence of coal was activated carbon (NUCHAR). This was used to determine whether liquefaction of part of the coal in the heavy oil

Illinois No.6 hvC Bituminous Coal

Artificial Coal-Like Char

Figure 13. FTIR Spectra of Illinois No.6 hvC Bituminous Coal and Artificial Coal-Like Char

was necessary for the removal of metals. Activated carbon was found to be as effective as Illinois No.6 coal as a demetallizing agent for the removal of vanadium from heavy oil while yielding considerable amounts of THF-insolubles. The activated carbon and the coal at a 10:90 ratio removed 69% of the vanadium to the THF-insolubles. The activated carbon at a 25:75 ratio gave an 87.9 wt% removal of vanadium while the coal gave an 87.7 wt% removal. The coke yields obtained with activated carbon were extremely high (Figure 14), with yields exceeding 40 wt%. It is quite likely that the flat porphyrin structures which are aromatic in nature are removed mostly by adsorption in all cases; coal, cellulose char, and activated carbon. It is also probable that it would be difficult to remove the metals from the coke since it is known that adsorbed materials in the ppm range are very difficult to remove from activated carbon⁽⁴⁰⁾.

3.4 Desulfurization and Denitrification During Co-processing

Illinois No.6 hvC bituminous coal contains 2.98 wt% sulfur and 0.67 wt% nitrogen, while the Maya (650°F+) ATB contains 4.6 wt% and 0.48 wt%, respectively. In most cases studied the net amount of heteroatoms in the THF-solubles decreased. Treating 10:90 and 25:75 coal/oil mixtures for one hour removed 40 - 50% of the sulfur to the product gas and THF-insolubles. A 35 wt% sulfur removal was noted when processing the Maya ATB alone.

Nitrogen removal to the THF-insolubles increased with higher coal concentrations. As the coal concentration rose to 25 wt%, the removal of nitrogen rose from 8 wt% (processing the oil alone) to 55 wt% in the THF-insolubles and products gas. These results seem to show that in addition to demetallization of the heavy oil noticeable sulfur and nitrogen removal can be obtained. These results have been found to be consistent with other investigations.⁽³⁾

4.0 CONCLUSIONS

This study has shown that co-processing with coal and heavy oils or bottom of the barrel fractions enhances the removal of vanadium to the THF-insolubles. The artificial char experiments furnished evidence that the inorganic matter in coal may not be necessary for demetallization. They also showed that the aromaticity of the char (H/C ratio) is an important factor in its ability to remove metals from heavy oils. The addition of activated carbon instead of coal to the heavy oils showed that high surface area solid carbonaceous materials can extract metals probably by adsorption. It is probable that many high molecular weight aromatic or hydroaromatic organic materials could be effective as demetallization agents. The fate of vanadium is not completely known, but most likely it is adsorbed on the surface of the solid in co-processing.

Co-processing of coal and heavy oil has shown that the sulfur and nitrogen contents decrease significantly in the final products. Co-processing of coal and heavy oil exhibits a type of synergism in

Figure 14. THF-Insoluble Yields Obtaining for Various Activated Carbon/Maya Mixtures at 425 °C at 6.9 MPa Initial Hydrogen

which significant amounts of heteroatoms are removed with this treatment. The mechanism for this is unclear and further investigations should be performed to develop an understanding of the role of coal in the removal of heteroatoms during co-processing. This study has shown that mixtures low in coal concentrations appear to be efficient in thermal, non-catalytic co-processing. For demetallization, low coke yields and reasonable metal removals have a higher appeal than the higher coal concentrations, which result in extremely high amounts of coke and good metals removal.

5.0 REFERENCES

1. Miller, T.J., "The Role of coal in the Removal of Metals from Heavy Oils," M.S. Thesis in Chemical Engineering, University of Pittsburgh, Pittsburgh, PA, 1987.
2. Gorbaty, M.L, Larsen, J.W., and Wender, I., "Coal Science," Vol. 3, p. 202, Academic Pres, NY, 1984.
3. Shinn, J.H., Dahlberg, A.J., Kuehler, C.W., and Rosenthal, J.H., "The Chevron Co-Refining Process," Proceedings of the 9th Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, -CA, 1984.
4. Manes, M., Personal Communications, 1986.

LIQUEFACTION RESEARCH IN PYROLYSIS, CATALYSIS
AND COAL DISSOLUTION

October 1, 1985 - December 31, 1986

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Title: Task III. Liquefaction Research in Pyrolysis, Catalysis and Coal Dissolution

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Period: October 1, 1985 - December 31, 1986

Objectives

- III.1 To design a new type of catalyst for coal depolymerization based on the use of π - acceptor compounds. The techniques of EPR and optical spectroscopy will be used to examine the pathways by which these catalysts initiate the coal depolymerization reactions.
- III.2 Development of a new spectroscopic methodology for characterizing chemical intermediates in direct liquefaction and identifying active sites of liquefaction catalysts.
- III.3 To investigate the effect of catalysts viz. pyrite (FeS_2), pyrrhotite (Fe_7S_8) and Co-Mo/ Al_2O_3 on pyrolysis and hydrocarbonization of coals using in-situ electron spin resonance (ESR) spectroscopy.
- III.4 The use of novel systems of solvents and antisolvents in coal dissolution with the efficient recovery of these solvents and the hydrogenation of coal liquids at low temperature and pressure.

Scopes

- III.1 A parallel investigation using model compounds will be undertaken to observe coal depolymerization via charge-transfer complexation. Magnetization and electron spin resonance will be used to study different coals with variable hydrogen and carbon content.
- III.2 In the low temperature pyrolysis studies, ESR/ENDOR spectroscopies will be used to study free radicals present in coal and coal liquefaction products.
- III.3 The coals will be observed under different environments and in the presence of common catalysts used in direct coal liquefaction.

III.4 In the area of coal dissolution, a novel technique will be studied for the dissolution and separation of liquid fuels from bituminous coals. This work features the enhanced utilization of a relatively unexplored class of solvents, the so-called "supersolvents." Emphasis is placed on the use of inverting or "antisolvents" to achieve efficient recovery of the solvent from the liquid and solid products. New methods will be explored to develop a low temperature liquefaction process by using supersolvents and employing CO and H₂O with transition metal catalysts and reductants. This phase of the study is directed toward developing a technology for coal liquefaction under mild conditions.

Final Report

III.1 EPR and Optical Studies of Coal Depolymerization via Charge-Transfer Complexation

During the past year, we have measured the equilibrium constants for charge-transfer complex formation for a number of different electron donors and electron acceptors. These constants were evaluated by the Foster-Hammick-Wardley modification[1] of the Scott equation.[2] In this method, the equilibrium constant (K) is determined as the negative slope of the plot of $A/D[D] [A]$ against $A/[A]$; where A is the optical absorbance of the solution at a particular wavelength of light, and $[D]$ and $[A]$ are the initial donor and acceptor concentrations. We have gathered together the results of this year's work in Table I where benzyl phenyl ether (BPE) and benzyl phenyl sulfide (BPS) represent typical C-O and C-S bonds which might be found in coal. Also included in this table are relative rate data, since all of these compounds undergo bond cleavage reactions when heated to a sufficiently warm temperature in acetonitrile. Notice that in all cases, the relative magnitude of the equilibrium constants is in reasonable agreement with the relative reaction rates of bond cleavage reactions. This is highly surprising, since the enthalpy of complex formation is only slightly exothermic. Even benzyl ether (BE) which is a non-conjugated ether undergoes reactions in correspondence to the magnitude of the equilibrium constant.

An additional accomplishment during the past year has been the construction of a uv spectrophotometer with which to monitor the reactions carried out at high temperatures. Although a long delivery time for crucial components impeded construction, we now have a fully installed system and expect to begin our study of high temperature reactions shortly. Thus, we are capable of variable temperature uv-vis spectroscopy from -40 degrees centigrade to 150 degrees centigrade.

The significance of these results to coal liquefaction is that these compounds provide models for the types of reactivity expected in coal. Since these bond cleavage reactions occur at temperatures far below those normally used for liquefaction, the use of these catalysts or catalysts of similar structure may be envisioned to lead to lower temperature and lower pressure liquefaction conditions.

III.2 ESR, ENDOR and Electron Spin Echo Characterization of Free Radicals and Catalytically-Active Sites in Metal-Oxide Catalysts

Our goals for this period were:

1. To develop an ESR/ENDOR as a new methodology for characterizing the free radicals in a typical West Virginia coal and/or its volatile/liquefied fraction in terms of average carbon-hydrogen bonding parameters.

Table 1. Equilibrium Constants Determined in this Study

Electron	BPS			BPE			BE		
	.mu.	K[a]	k[rel][e]	.mu.	K[a]	k[rel][e]	.mu.	K[a]	k[rel]
TCNE	565	0.68	-[c]	502	0.74	-[c]	397	1.2	-
TCNQ	557	0.50	6.2	-[b]	-[b]	8.1	-[b]	-[b]	
TCNQF ₄	705	0.89	11	-[d]	-[d]	22	-[b]	-[b]	
DDQ	625	2.1	5.8	554	1.2	2.5	-[b]	-[b]	

- a) Solvent used was methylene chloride unless otherwise specified
- b) Could not be measured due to overlap with the acceptor UV spectrum
- c) Does not initiate reaction
- d) Complex favors complete electron transfer
- e) This work supported by the West Virginia University Energy Research Center.

2. To investigate the possibility of using the temperature dependence of electron spin-lattice behavior as a new methodology for elucidating the chemical structures of the paramagnetic oxyanions of pentavalent chromium, molybdenum, and tungsten. Such paramagnetic species have been implicated as the active sites in coal catalysis, but no easily available spectroscopic technique is available for their identification.

3. To develop electron spin-echo methodology as a complementary method for ESR and ENDOR for paramagnetic metal-oxide species (of interest in coal catalysis) which might not be amenable to detection by ESR or ENDOR at catalysis temperatures. This could well be the cause for the species exhibiting very short (10^{-10} s) electronic spin-lattice relaxation times.

4. To embark on the synthesis, possibly as single crystals of new compounds of pentavalent chromium, molybdenum, and tungsten with a view of developing them as model compounds and spin-concentration-standards for characterizing the catalytically-active sites (involving the respective pentavalent metal) in coal catalysis by metal-oxide catalysis.

We believe that we have accomplished a significant portion of the proposed research. The only task not completed is (3) - the development of electron spin-echo methodology - due to the unavailability of the instrumentation. The technique involving this equipment has shown to possess high selectivity and is selective in identifying paramagnetic species which are thought to be playing some key roles in low temperature coal conversion processes.] Our

accomplishments related to the remaining three tasks will be summarized under two main headings: (i) new analytical applications of ESR and (ii) new uses of electron double resonance (ENDOR) in coal catalysis and liquefaction.

New Applications of ESR Spectroscopy

***Paramagnetic Relaxation as a New Method for Identifying Paramagnetic Oxyanions of Interest in Coal Catalysis**

While the oxyanions of pentavalent Cr, Mo, and W have been implicated as the possible catalytically-active sites in heterogeneous catalysis, there are no easily available methods to find the actual chemical structure of such species[3]. For example, in the reactions involving Cr(V), there were no easily available techniques to determine if a chromium oxyanion contained three or four oxygens. Such structural information is a key parameter for understanding the mechanism of the underlying catalytic reaction, and hence for an improvement in the reaction selectivity and product yield. One of the major obstacles is that the dominant oxygen isotope has $I = 0$, hence NMR-inactive. Also, the use of oxygen-17 is both quite expensive and experimentally tedious. We thus proposed that one could possibly utilize the temperature dependence of the electronic spin-lattice relaxation times (T) as a possible parameter for assessing the number of oxygen atoms in the paramagnetic oxyanion. As found earlier for stable paramagnetic complexes[3], the tetraoxyanions should exhibit a broader ESR signal than trioxy anions and the difference should increase (approximately) exponentially with increase in temperature, since T is expected to decrease exponentially with temperature. Thus a comparative study of the temperature dependence of ESR linewidths, rather than line positions (as normally done in standard ESR) should provide a sensitive probe of the tetrahedral versus trigonal structure of an oxyanion. This hypothesis was first verified by examining the temperature dependence of the ESR linewidth of the perchromate (3-) ion which has been positively identified in potassium dihydrogen phosphate-type of crystals[4]. The results indeed verified the above hypothesis. The technique was then applied to differentiate between the perchromate (3-) ion and the chromium trioxide anion in potassium dichromate samples where these two ions were simultaneously present[3]. Measurement of temperature dependence of the ESR linewidths of these ions and their analysis in terms of relaxation times clearly showed that the earlier identification of these ions, based on only their line positions, was in error. A preliminary account of this work has been published [3] and we believe that it opens up a new avenue for identifying paramagnetic oxyanions which are of high significance in coal catalysis and are hard to detect otherwise.

***New ESR Spin Probes and Standards for Catalytically-active Sites Involving Cr(V)**

The above discussed ESR studies of the chromium oxyanions showed that new compounds were needed for a quantitative estimate of the catalytically-active sites involving Cr(V) in catalysis based on

chromia, since no suitable compound of Cr(V) was easily available. We thus embarked on synthesizing peroxychromate (3-) salts of Li, Na, K, Rb, and Cs. The identity of the samples was confirmed through chemical analysis. ESR and magnetic susceptibility measurements showed that all these compounds indeed contain Cr(V) and temperature dependence of magnetic susceptibility and specific heat measurements showed that these compounds constitute a new class of low-dimensional magnetic materials [5]. X-ray diffraction studies are underway to discern the bonding in these novel compounds which should provide new Cr spin concentration standards for identifying and quantifying the role of pentavalent chromium in catalytic reactions of chromia-based catalysts. It is intended to extend these studies to pentavalent molybdenum and tungsten with a view of identifying catalytically-active sites in the reactions of catalysts based on molybdenum and tungsten oxides.

New Applications of ENDOR

*ENDOR Spectra of a West Virginia Coal and Its Volatile Component

The feasibility of obtaining ENDOR spectra of some typical West Virginia coals at room temperature and above was explored with a view of developing a new methodology for characterizing the free radicals ubiquitously present in these coals and their volatile residues. This task was important to our understanding of role of free radicals in the low temperature pyrolysis since free radicals are known to play key roles in this process. At the same time these free radicals are hard to characterize by standard ESR and other spectroscopic methods.

After a systematic, variable temperature measurement of the electronic spin-lattice relaxation and spin-spin relaxation times, and using computer averaging techniques, it was possible to obtain ENDOR spectra of an Arkwright West Virginia coal and its volatile residue at temperatures up to +50 degrees centigrade. A Bruker ER 200D EPR/ENDOR spectrometer was used for obtaining the ENDOR spectra. The spectrum shows a derivative peak of peak-to-peak width about 450 kHz flanked symmetrically by two satellites about 550 kHz apart. The width of the main line and the separation between the satellites was found to be temperature dependent between 320 K and 120 K. While the cause of the temperature dependence of the ENDOR lines is under further investigation, the fact that at least three distinct lines are observed implies that the Arkwright coal contains at least two distinct types of C-H average distances. This is the first time that it has been demonstrated that there are at least two slightly different (average) C-H distances in West Virginia coals. Experiments are being continued to understand the implications of these new spectra and to extend the ENDOR measurements to other coals being used by other workers in this program. Furthermore it is not clear why the average C-H of apprx. 5.5 angstroms estimated by us for the Arkwright coal is so very different from the value of apprx. 2.8 angstroms reported for a solvent-refined Pittsburgh coal. The role of the different ENDOR instrumentation utilized in the various ENDOR studies is being investigated. Nevertheless the

current research opens up a powerful new way of elucidating the structure of the coal-based radicals.

*ENDOR as a New Methodology for Discriminating Between Reactions of Pentavalent Chromium with Organic Ligands

It is anticipated that the catalytic cracking reactions of chromia would involve pentavalent chromium complexes as the reaction intermediate[1]. However, due to the high reactivity of Cr(V), very few Cr(V) compounds are available for help as guides in the structural characterization. One exception was the reaction involving the oxidation of alcohols by potassium dichromate, known as the Westheimer reaction, in which a transient Cr(V) complex has been postulated. While this reaction was thought to be the model for many organometallic oxidation-reduction reactions of interest in the catalytic reactions of chromia, it has been controversial lately because the earlier postulated structure of the Cr(V)-alcoholato complex has been questioned by several workers[6]. Since the Cr(V) species is paramagnetic, ESR had been used as a direct method in the earlier studies[6]. However, a preliminary examination of a model reaction involving the Cr(V)-ethyleneglycolato complex showed that perhaps the origin of the controversy resulted from the low resolution of the ESR technique and the smearing out of the extreme lines in the ESR spectra due to the rotational-diffusional motion of the complex in the liquid phase. We thus explored the feasibility of utilizing the higher resolution possible with the ENDOR technique. Using the hyperfine splitting measured with ENDOR, we simulated ESR spectra of the Cr(V) complex based on seven and eight equivalent protons. Our simulations clearly showed that the complex contained eight equivalent protons as postulated in the original Westheimer mechanism, rather than seven as postulated recently[6].

III.3 Magnetic Studies of Pyrolysis and Hydrocarbonization of Coals with and without Catalysts

The objectives of the first year was to develop a microwave cavity-heater system for the high temperature in-situ ESR spectroscopy of coals and then to carry out pyrolysis studies of several bituminous coals using in-situ ESR spectroscopy. After some initial difficulties in obtaining temperatures above 400 degrees centigrade, in-situ sample temperatures of up to 650 degrees centigrade can now be routinely obtained in the ESR cavity. Using this system, ESR studies on the pyrolysis of eight bituminous coals have now been completed. The results of these studies, summarized below, have appeared in two recent papers.[7,8]

Based on the temperature variation of the spin concentration N_s of the thermally generated free radicals, we have identified four distinct temperature stages in the pyrolysis of bituminous coals. In stages 1 (25-300 degrees centigrade) and 3 (450-600 degrees centigrade), N_s increases with increasing temperatures signifying generation of free radicals and in stages 2 (300-450 degrees centigrade) and 4 (>600 degrees centigrade), N_s decreases with increasing temperatures indicating quenching of free

radicals. Using Arrhenius relation, the activation energies for thermal dissociation of the free radicals in stages 1 and 3 are respectively 4 to 6 kcal/mole and 20 to 30 kcal/mole, the variation being due to coal type. Based on these values, we associate stage 1 with dissociation of weaker bonds in the coal structures, stage 2 with coal swelling, stage 3 with coal depolymerization, and stage 4 with repolymerization. In recent studies, we have shown that these stages can be shifted to lower temperatures by approx. 100 degrees centigrade by the action of certain catalysts.

III.4 Solvents and Coal Dissolution

Detailed experiments involving solvent extraction of three West Virginia bituminous coals were carried out using the solvent N-methyl-2-pyrrolidone (NMP), followed by recovery of the extracted material. These experiments produced two coal fractions: the first, a solid residue made up of unextracted organic matter and greater than 99% of the ash in the original coal sample; the second, an almost ash-free organic fraction. The latter fraction demonstrates the preparation of an organic coal-derived product which could be used as an ultra-clean fuel or feedstock for subsequent processing to liquid fuels or chemicals.

It was found that this procedure produces a solid coal fraction characterized by very low ash contents (as low as 0.1%), high energy densities (as high as 15,000 BTU/lb) and complete removal of all pyritic and inorganic sulfur-containing species. The percent recovery of the soluble fraction on a moisture and ash-free basis (MAF) ranged from 36% to 74% and was dependent on the coal seam from which the parent coal was mined. Solvent recovery of up to 97% was achieved in laboratory-scale experiments.

Experimental Methodology

Extraction studies for Pittsburgh, Sewell, and Bakerstown coals were conducted as follows: The coal samples were obtained directly from the mine face and immediately stored under nitrogen to prevent oxidation. They were subsequently ground and sieved to produce two different particle size fractions, one of approximately 70 microns and another of approximately 240 microns. Again the samples were stored under nitrogen. Predetermined amounts of hot solvent (NMP) and coal were mixed and extractions were carried out in conventional glassware, under nitrogen, by refluxing the raw coal in the solvent at its normal boiling point (202 degrees centigrade). After a set period of time, the undissolved material was separated from the solution by vacuum filtration. The extract was then recovered by precipitation upon the addition of an antisolvent (water), followed by filtration. Both the solid fractions were washed with methanol and dried under vacuum to constant weight (ca. 24 hours). The extent of extraction or yield was then calculated and overall material balances were performed. Samples of raw coal and the two solid fractions were subjected to a range of standard ASTM tests including: ultimate and proximate analyses, heating value, sulfur forms, and free swelling-index (See Tables below).

Results

*Extraction Studies

Representative values obtained for the extraction of three West Virginia bituminous coals along with the percent extraction on a weight basis as well as a moisture and ash-free (MAF) basis are shown in Table 1. Also included is an indication of the mass closure calculated from these data (100% being perfect mass closure).

Table 2. Percent Extracted and Mass Closure for Solvent Extraction of Pittsburgh, Sewell and Bakerstown Coal with NMP.

Coal Seam	Sample Weight (grams)	Residue Weight (grams)	Extract Weight	% Extracted (by weight)	% Extracted (MAF)	% Mass Closure
Pittsburgh	20.005	13.650	6.658	33.28	37.73	101.50
Sewell	10.041	5.796	4.240	42.23	45.62	99.95
Bakerstown	10.040	4.664	5.348	53.27	74.16	99.72

Representative extraction results for a 10:1 solvent-to-coal ratio, refluxed at the normal boiling point of NMP (202 C) for 1 hour.

Two points should be noted:

1. EXCELLENT MASS CLOSURES (less than 1.5% deviation in all cases) WERE FOUND, indicating not only the ease with which the products are recovered, but also very little if any solvent retention in the recovered fractions.
2. THE AMOUNT OF COAL EXTRACTED VARIES WIDELY ACCORDING TO THE COAL SEAM from which the coal was mined, from a minimum of 33% by weight for the Pittsburgh seam to a maximum of 53% for the Bakerstown. No attempt has been made to further enhance or optimize the yields although a comprehensive parametric study has been completed (see below). The amount extracted as calculated on an MAF basis is particularly meaningful since this quantity represents the amount extracted based only on the TOTAL amount of organic material available for extraction. The ash was found to be unaffected by the solvent.

The ultimate and proximate analyses and heating values for the raw coal and the recovered fractions for all three coals used in this study are shown in Tables 3, 4, and 5. The most dramatic result reported in these tables is the drastic differences in ash content of the two fractions obtained from each coal. IN ALL CASES THE RECOVERED SOLUBLE FRACTION WAS FOUND TO HAVE AN ASH CONTENT OF LESS THAN 1% suggesting that this product may be an excellent source of low-ash, high energy fuel for many specialized applications or a FEEDSTOCK for further coal conversion processes. The heating value of the extract was found to be equal to or higher than that of the

raw coal, and IN ONE COAL (BAKERSTOWN) THE HEATING VALUE WAS INCREASED BY 40%. This increase in heating value is particularly pronounced for raw coals with a relatively high ash content such as the Bakerstown. THUS THIS PROCEDURE CAN UTILIZE A RELATIVELY LOW GRADE COAL AND SUBSTANTIALLY UPGRADE IT TO A HIGH-QUALITY SOLID FUEL OR FEEDSTOCK. Finally, it should be noted that in all cases the percentage of sulfur in the recovered soluble fraction is lower than that of the parent coal indicating some desulfurization has occurred as a result of ash removal.

Table 3. Proximate and Ultimate Analyses and Heating Values of Raw PITTSBURGH Coal and Solid Fractions

	% Moisture	% Ash	% S	% Volatile Matter	% Fixed Ca
Raw Coal	1.0	10.9	2.61	37.1	50.9
Unextracted Solid	0.2	17.8	3.35	34.5	47.1
Recovered Extract	0.9	0.78	1.25	42.5	55.1
		% C	% H	% N	BTU/lb
Raw Coal		82.6	5.16	1.26	13,387
Unextracted Solid		66.4	4.76	1.62	11,963
Recovered Extract		81.6	5.80	2.31	14,725

Table 4. Proximate and Ultimate Analyses and Heating Values of Raw SEWELL Coal and Solid Fractions

	% Moisture	% Ash	% S	% Volatile Matter	% Fixed Ca
Raw Coal	0.8	6.2	0.61	29.2	63.8
Unextracted Solid	0.6	10.0	0.57	27.9	61.5
Recovered Extract	1.2	0.1	0.57	40.8	57.9
		% C	% H	% N	BTU/lb
Raw Coal		81.95	4.95	1.24	14,423
Unextracted Solid		77.75	4.65	1.63	13,422
Recovered Extract		86.76	5.64	2.05	14,019

Table 5. Proximate and Ultimate Analyses and Heating Values of Raw BAKERSTOWN Coal and Solid Fractions

	% Moisture	% Ash	% S	% Volatile Matter	% Fixed Carbon
Raw Coal	1.5	26.4	3.94	24.7	47.4
Unextracted Solid	0.2	48.7	6.24	16.8	34.2
Recovered Extract	0.2	0.31	1.32	33.4	66.7
	% C	% H	% N	BTU/lb	
Raw Coal	61.3	3.94	1.00	10,797	
Unextracted solid	38.9	2.48	1.02	6,667	
Recovered Extract	84.9	5.71	2.28	15,049	

To further quantify the nature of the sulfur reduction, the raw coals and their recovered fractions were analyzed for sulfur forms. The results of these analyses are shown in Table 6. IT WAS FOUND THAT VIRTUALLY ALL PYRITIC SULFUR WAS REMOVED FROM THE SOLUBLE FRACTION and was concentrated in the unextracted insoluble fraction. The ash was distributed in this way because the solvent extracts only the organic species and not the inorganic pyritic sulfur. Thus the process not only de-ashes the coal but also accomplishes some desulfurization as well, the degree of which depends on the distribution of sulfur forms in the original coal.

Table 6. Sulfur Forms Analyses for Raw Coals and Solid Fractions Showing Distribution of Sulfur-Containing Species

PITTSBURGH COAL

	% Total Sulfur	% Sulfate	% Pyrite	% Organic Sulfur
Raw Coal	2.61	---	1.51	1.10
Unextracted Solid	3.35	---	2.42	0.93
Recovered Extract	1.25	0.01	---	1.24

SEWELL COAL

	% Total Sulfur	% Sulfate	% Pyrite	% Organic Sulfur
Raw Coal	0.62	---	---	0.62
Unextracted Solid	0.59	---	0.15	0.44
Recovered Extract	0.61	---	0.10	0.51

BAKERSTOWN COAL

	% Total Sulfur	% Sulfate	% Pyrite	% Organic Sulfur
Raw Coal	3.94	0.27	3.05	0.62
Unextracted Solid	6.24	0.45	5.42	0.37
Recovered Extract	1.32	---	---	1.32

Parametric Study on the Extent of Extraction

Extensive studies were undertaken to determine the effect on the extent of extraction by the dominant physical independent variables of this procedure viz. the solvent-to-coal ratio, the coal particle size, and the time of extraction. This portion of the study was confined to the Bakerstown and Sewell-seam coals and was carried out by varying one independent variable at a time.

The effect of solvent-to-coal ratio (expressed on a gram solvent/gram coal basis) on extent of extraction is shown in Table 7.

Table 7. Effect of Solvent-to-Coal Ratio on the Extent of Extraction for the BAKERSTOWN Coal Treated for 1 hour at 202 degrees centigrade in NMP. Particle Size is 70 micron.

Solvent-to-coal ratio (by weight)	% Extracted (by weight)	% Extracted (MAF Basis)
5:1	51.15	70.94
10:1	50.72	70.35
15:1	52.10	72.26
20:1	48.48	67.24

It was determined that THE SOLVENT-TO-COAL RATIO HAS LITTLE EFFECT ON THE EXTRACTION in the range studied, thus the lowest possible solvent-to-coal ratio may be favored economically. However, it was found that there is a lower limit beyond which the viscosity of the solution becomes large, causing problems with subsequent steps. At this time, a solvent-to-coal ratio between 5:1 and 10:1 appears to be optimum.

Table 8 illustrates the effect of the particle size of the raw coal fed into the extraction step. Two particle sizes were chosen: a 60 mesh cut (246 micron) and a 200 mesh cut (70 micron). The former represents a size easily obtained by conventional crushing equipment while the latter size is generally produced by conventional grinding operations.

Table 8. Effect of Particle Size on the Extent of Extraction for BAKERSTOWN and SEWELL Coals Treated for 1 Hour at 202 degrees centigrade in NMP and a 10:1 Solvent-to-Coal Ratio.

Particle Size (micron)	% Extract (by weight)	% Extract (MAF Basis)
BAKERSTOWN COAL		
apprx. 240	49.63	68.83
apprx. 70	50.72	70.35

Table 8 (cont.)

SEWELL COAL

apprx. 240	41.73	44.86
apprx. 70	42.43	45.62

For both of these coals, VIRTUALLY THE SAME EXTRACTION YIELD WAS REALIZED WITH THE TWO PARTICLE SIZES. This result has significant importance to the economics of the procedure since the grinding operations needed to produce particles in the 70 micron range are considerably more expensive than the crushing operations which produce the larger particle sizes. Further studies are underway to examine the effect of using larger-sized particles.

The final independent variable to be studied to date is the time over which the extraction step is carried out. The extraction time was varied from 2 minutes to 90 minutes and the results of these experiments are shown in Table 9 for both Bakerstown and Sewell coal. The same data are plotted in Figure 1 for the Bakerstown coal.

Table 9. Effect of Treatment Time on the Extent of Extraction of BAKERSTOWN and SEWELL Coals, Treated at 202 degrees centigrade in NMP and a 10:1 Solvent-to-Coal Ratio. Particle Size is apprx. 70 micron.

Extraction Time (minutes)	% Extracted (by weight)	% Extracted (MAF Basis)
---------------------------	-------------------------	-------------------------

BAKERSTOWN COAL

2	11.06	15.34
15	47.00	65.19
30	50.16	69.57
60	50.72	70.35
90	51.53	71.47

SEWELL COAL

30	41.72	44.86
60	42.43	45.62

The amount extracted was found to increase very sharply with time in the 0 to 10 minute range and after approximately 20 minutes, no further material was observed to be extracted. This trend was also observed for the Sewell Coal. Thus THE OPTIMUM TREATMENT TIME WAS FOUND TO BE CA. 20 MINUTES implying that a residence time of 20 minutes is required for this step in a multi-step continuous process. With this data, the design of a reactor (i.e. its size for a given reactor type and throughput) can now be initiated.

Figure 1. The effect of extraction time on the extent of extraction for Bakerstown coal in NMP.

Solvent Recovery

Following the filtration step in which the soluble fraction is recovered from an NMP/water mixture, the separation and recovery of the solvent (NMP) from the water was carried out, and the solvent was recycled for further use. Solvent recovery was performed by utilizing conventional laboratory distillation apparatus and performing a two-stage distillation, first at atmospheric pressure, then followed by a vacuum distillation. Using this procedure, 97.2% SOLVENT RECOVERY WAS OBTAINED. Small losses of NMP to the atmosphere during transfer and filtration operations were unavoidable with the lab-scale experimental apparatus. However, if the processing steps were conducted in a closed system, it is expected that solvent recovery for recycle can be improved.

Summary

A novel extraction procedure has been developed which utilizes a specialized solvent/antisolvent system to extract organic material from bituminous coals. The procedure is carried out at atmospheric pressure and relatively low temperature (202 degrees centigrade). The extracted product is recovered as a solid in good yield and is found to contain essentially no ash and a reduced concentration of sulfur species. The process is particularly effective with high ash coals containing large amounts of pyritic sulfur. A parametric study involving some of the main independent variables has been completed and has yielded data which are useful for preliminary process design.

References

- [1] Foster, R.; Hammick, D. Ll.; and Wardley, A. A. J. Chem. Soc., 1953, 3817.
- [2] Scott, R. L. Proc. Int. Conf. on Co-ordination Compounds, Amsterdam, 1955, 265; Recl Trav. Chim. Pays-Bas Belg., 1956, 75, 787.
- [3] For a recent reference, see S. R. Maple and N. S. Dalal, J. Am. Chem. Soc. 107, 4082 (1985).
- [4] N. S. Dalal, Advan. Mag. Reson. 11, 119-217 (1982).
- [5] a. N. S. Dalal et al., in Proceedings of the XXIII Congress AMPERE, Rome, Italy 1986, pp. 466-467.
b. K. Singh et al., ibid., pp. 468-469.
- [6] See, for example, M. Mitewa et al., Inorg. Chim. Acta 1974, p. 17-23 and references therein.
- [7] M. S. Seehra, B. Ghosh and S. E. Mullins, Fuel 65, 1315-1316 (1986).
- [8] B. Ghosh and M. S. Seehra, Proc. Third Annual Pittsburgh Coal Conf. (University of Pittsburgh) pp. 704-716 (1986).

Publications and Presentations

- 1. S. R. Maple and N. S. Dalal, Electron Paramagnetic Relaxation as a New Technique for Characterizing Paramagnetic Oxyanions, J. Am. Chem. Soc. 107, 4082-4083 (1985).
- 2. N. S. Dalal, et al., Single Crystal Growth, EPR, Magnetic Susceptibility and Specific Heat Measurements of Potassium Peroxychromate: A New Low-Dimensional Cr(V) Antiferromagnet, Proceedings of the XXIII Congress, AMPERE, Rome, Italy, 1986, pp. 466-467.
- 3. K. Singh, N. S. Dalal and J. S. Moodera, EPR Characterization of Single Crystals of Cr(V) Peroxychromates of Li, Na, Rb and Cs, Proceedings of the XXIII Congress AMPERE, Rome, Italy, 1986, pp. 468-469.
- 4. A. H. Stiller, J. W. Zondlo, E. A. Mintz, P. Jagodzinski, and C. W. Leong, Interaction of Supersolvents with Coal. Conference Proceedings, Second Annual Pittsburgh Coal Conference, Pittsburgh, PA, September 16-20, 1985 p. 413.
- 5. K. Renganathan, J. W. Zondlo, E. A. Mintz and A. H. Stiller, Deashing of Coal Using Solvent Treatment at Mild Conditions. Accepted for Presentation at the 12th International Conference on Slurry Technology, New Orleans, LA, March 31 to April 3, 1987.
- 6. K. Renganathan, M.S. Thesis, Department of Chemical Engineering, West Virginia University, Morgantown, WV, 1987.
- 7. K. Renganathan, J. W. Zondlo, E. A. Mintz and A. H. Stiller, Parametric Study of Coal Deashing Using Solvent Treatment at Mild Conditions. Submitted to the 1987 International Conference on Coal Science, Maastricht, The Netherlands, October 26-30, 1987.

INTEGRATED COAL LIQUEFACTION/CHARACTERIZATION

October 1, 1985 - December 31, 1986

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Period: October 1, 1985 - December 31, 1986

Objectives

- IV.1 To generate urgently needed information on composition and concentration of hydrocarbon-rich components, e.g., resin-ites and sporinites, in carefully selected and prepared coals.
- IV.2 To develop novel, efficient extraction and liquefaction methods for these hydrocarbon components which will produce a high quality hydrocarbon product as well as a commercially valuable residue. The more efficient extraction and liquefaction methods will include investigation of new reaction regimes such as mild (below the softening temperature of coals) temperatures, and/or the use of selective site- or bond-specific catalysts.
- IV.3 To perform a detailed analysis of the composition of the hydrocarbon rich coal liquids obtained using advanced spectroscopic methods and an integrated data analysis approach.
- IV.4 To develop improved numerical techniques for data correlation and reduction as well as for computer modeling of extraction and liquefaction processes (infrastructure development).

Scopes

- IV.1 Three coals will be studied, Wyoming Wyodak, Kentucky Elkhorn and Utah Hiawatha. These coals will be processed and stored under standardized conditions and subjected to a battery of analytical tests.
- IV.2 Coals will be subjected to differential liquefaction experiments utilizing solvent and thermal extraction, as well as pyrolysis and mechanical separation techniques to produce hydrocarbon rich fractions. These experiments will be carried out as a collaborative project between researchers in three different colleges and several departments.

- IV.3 With the more precise analytical methods available today, definitive data can be obtained on the resins and other easily dissolvable fractions of coals to be studied. Identification of the presence and abundance of functional groups and moieties in these materials will be performed. This will be accomplished by integration of results from conventional composition analysis with FTIR, NMR, and Py-MS.
- IV.4 All coal and coal liquid analytical data will be integrated and correlated by means of sophisticated, computerized data analysis techniques using SIMGA, a new software package for multivariate statistical analysis under development at the University of Utah Biomaterials Profiling Center. The potential of the three coal types for generating hydrocarbon rich feedstocks, e.g., for use as high density jet fuel precursors, by means of differential liquefaction methods will be compared and evaluated.

Final Report

TASK IV.1 COLLECTION AND PREPARATION OF FEEDSTOCK COAL AND RESINITE SAMPLES AND METHODS DEVELOPMENT

Task IV.1.1 Coal and Resin Samples

This is a summary of the samples studied.

(1) Hiawatha coal (Utah)

(a) pyrolysis tar prepared by Black, Sivalls & Bryson from coal received from UP&L using a fixed bed Wellman Galusha gasifier. The hydrocarbon fraction of this tar was analyzed using IR, MS, PMR, CMR and data integration and correlation procedures were used to extract the common information. Reported in Task IV.4.

(b) samples catalytically hydrogenated in the absence of solvent at 350° and 400°. MS and gas analysis data (performed elsewhere) were correlated. IR by diffuse reflectance and photoacoustic techniques was done on the samples treated at 400°C. Reported in Task IV.3.1.

(c) fresh samples dried and ground under N₂ were Soxhlet extracted with THF and then cyclohexane and toluene. Weight data, proximate analysis, and IR data were obtained. Work is beginning on MS and CMR. Reported under Task IV.2.3.

(2) Wattis coal (Utah) obtained by R. Pugmire

(a) separation by density gradient centrifugation to study resinite. CMR using CP/MAS was done on selected samples. Reported under Task IV.2.1.

(3) Elkhorn coal (Kentucky) obtained by R. Pugmire

(a) petrographic analysis. Maceral separation is planned. Reported under Task IV.2.2.

(4) Adaville #6 coal (Wyoming) fresh sample, dried & ground under N₂ at UUBPC

(a) Soxhlet extractions in THF and then cyclohexane and toluene. Weight percent of extractibles was obtained. Reported in Task IV.2.4.

(5) Purified resinite (Hiawatha coal, Utah)

(a) commercially produced samples from American Resin Company from Hiawatha coal. Sink/float separation, solvent extractions, petrographic fluorescence, CMR by CP-MAS were begun. Solvent extractions, ultimate analysis of the fractions, and IR and MS. The data are currently being evaluated. Reported under Task IV.2.5 and IV.2.6.

Task IV.1.2. Methods Development

(1) Infrared Spectroscopy (E.M. Eyring)

(a) photoacoustic IR spectroscopy using polarizable gases such as xenon compared with diffuse reflectance

(b) matrix isolation spectra of Lewis acid base adducts. Both (a) and (b) reported under Task IV.3.3.

2) Computerized data integration and correlation (W. Windig)

(a) a method for canonical correlation analysis of up to 10 data sets simultaneously has been developed based on the algorithm by Carroll [Proc. 76th Annual Convention, A.P.A., 1968].

TASK IV.2 SEPARATION OF COAL AND RESINITE

Task IV.2.1 Wattis Coal - Density Gradient (R.J. Pugmire)

Work was initiated on density gradient centrifugation separation of Wattis coal in order to study the resinite present at high concentrations in this coal. Two separate sink float separations were made on the Wattis coal. The float fractions were subjected to Density Gradient Centrifugation (DGC) separation runs with samples collected over the density range 1.029-1.163g/cm³. The density distribution on the two float samples were similar. Selected DGC functions were analyzed by CP/MAS ¹³C NMR techniques. The aromaticity was determined to be 0.23 ± 0.01 based on the triplicate analysis of the float sample. Aromaticity measurements were performed on five DGC samples from a single DGC separation run. The average value of f_a was found to be 0.15 ± 0.02. The density range of these samples is 1.029-1.101g/cm³. The discrepancy between f_a values of the float and the individual DGC samples is not clear at this time. The NMR spectra of the sink and whole coal have not yet been obtained.

Task IV.2.2 Kentucky Elkhorn Coal - Density Gradient (R.J. Pugmire)

The sporinite-rich Kentucky coal has been examined and petrographic analysis is given in Table IV.1. The density profile of the coal is shown in Figure IV.1. Separation into sporinite, vitrinite, and inertinite fractions will begin shortly.

Figure IV.1 Density distribution of Kentucky Elkhorn Coal

Task IV.2.3 Hiawatha Coal Solvent Extraction (L.L. Anderson)

Hiawatha coal was Soxhlet extracted with tetrahydrofuran and then fractionated into cyclohexane soluble, cyclohexane insoluble--toluene soluble and toluene insoluble fractions. Yield data from these extractions are shown in Table IV.2, whereas ultimate analyses of the coal(dry ash content 6.55%) and the solvent fractions are given in Table IV.3.

Table IV.2
Solvent Extraction Yields for Fresh Hiawatha Coal

Tetrahydrofuran soluble	- 10.78% of maf coal
Cyclohexane soluble	- 5.84% of maf coal
Toluene soluble	- 2.84% of maf coal
Toluene insoluble	- 2.1% of maf coal

Table IV.3
Ultimate Analysis of Fresh Hiawatha Coal and Solvent Fractions

	Coal (maf)	THF Insoluble	THF Soluble	THF Soluble		
				Cyclohexane Soluble	Toluene Soluble	Toluene Insoluble
Carbon	80.1	80.0	87.7	87.2	82.8	80.5
Hydrogen	6.4	5.6	8.8	10.46	7.4	6.1
Nitrogen	1.65	1.45	.82	.28	1.11	1.5
Sulfur	.79					
O (difference)	11.1					
H/C (atomic)	.96	.84	1.21	1.4	1.1	.92

Residue fractions were also analyzed to obtain proximate analyses, including heating value (see Table IV.4). Residue fractions are very similar in composition to the coal since the fraction extracted is minor. The ultimate analyses show that the soluble fractions are relatively richer in hydrogen and that N and S contents are lower for these fractions.

Table IV.4
Proximate Analysis Data for Fresh Hiawatha Coal and Residue

	Coal (dry)	THF Residue	Cyclohexane Insoluble
Volatile matter-(wt%)	44.6	41.6	42.6
Ash	5.8	5.9	5.8
Fixed Carbon	49.5	52.5	51.6
Gross heating Value (MJ/KG)	33.70	29.47	29.88

IR Spectra show that the soluble fractions are relatively richer in aliphatic compounds than the coal or insolubles and lower in aromatic and OH bonded compounds. Cyclohexane solubles (oils) were especially high in aliphatics, as expected. The nuclear magnetic resonance spectroscopy results show Hiawatha coal to have 59% carbon aromaticity ($f_a = .59$) and the THF insoluble to have $f_a = .65$.

Hiawatha coal was Soxhlet extracted with normal hexane, cyclohexane, toluene, and tetralin separately. Data from these extractions are given in Table IV.5.

Table IV.5
Soxhlet Extract Yields of Fresh Hiawatha Coal

Solvent	n-Hexane	Cyclohexane	Toluene	Tetralin
Extracts				
(% of dry coal)	.34	.22	3.02	8.1
(% of maf coal)	.36	.23	3.20	8.6

From Table IV.2, cyclohexane soluble parts from tetrahydrofuran extracts of Hiawatha coal were 5.8% of maf coal. This clearly shows the effect of tetrahydrofuran on coal extraction. Obviously, cyclohexane cannot be used as the only solvent to extract Hiawatha coal despite the relatively good quality of the extracts produced (mostly resinite).

Mass spectrometry of Hiawatha coal extractions from THF with further fractionation using cyclohexane and toluene showed the presence of BHT, di-t-butyl hydroxytoluene, a stabilizer found in the THF solvent. The concentration of BHT in the samples is currently being estimated.

IV.2.4 Adaville Coal - Solvent Extractions (L.L. Anderson)

One predried subbituminous coal from Adaville, Wyoming, was used to determine yields of successive Soxhlet extractions with tetrahydrofuran, cyclohexane, and toluene. Samples were separated into two groups: one group was dried at 104°-110°C under vacuum for 24 hours before extraction; one group was not. The proximate analyses of Adaville coal and data from extractions are shown in Table IV.6 and IV.7.

Table IV.6
Proximate Analysis Data on Fresh Adaville Coal
(average of three determinations)

	(weight percent of as-received coal)
Moisture	18.80
Ash	5.99
Volatile matter	33.36
Fixed carbon	41.89
Calorific Value (Btu/lb)	9,868
% S	0.38

Table IV.7
Extraction Data from Fresh Adaville Coal

	Extraction Data (as % of maf coal)	
	<u>Dried Sample</u>	<u>"As Received" Sample</u>
THF soluble	5.7	9.5
Cyclohexane soluble	3.2	3.0
Toluene soluble	1.2	3.2
Toluene insoluble	1.3	3.3

Task IV.2.5 Resinite - Density and Solvent Extraction (R.J. Pugmire)

Work is progressing on solvent extraction of pure resinite obtained from commercial resinite. The commercial resinite is ground and then subjected to a sink/float procedure in order to completely separate the coal particles from the resinite. The float is then extracted with various solvents (DMSO, n-hexane, CHCl_3 , THF, CH_2Cl_2 , and toluene). Solubility of pure resinite in DMSO is limited (approximately 7%) while solubility in other solvents is quite high (see Figure IV.2). The petrographic analysis of the resinite using blue light reveals the apparent differential solvation of different resinite species (Table IV.8). While these data are preliminary, it appears that the three different fluorescent species (green, yellow, orange) may have different extraction characteristics. These extractions will be repeated and carefully analyzed to determine the validity of our initial observation.

Figure IV. 2

Table IV.8
Resinite Fluorescence Analysis

Rare Resinite:

green	76.6%
yellow	20.1%
orange	6.3%

Solvent Extraction of Pure Resinite with:

CHCl ₃	green	95.0%
THF	green	88.4%
	orange	11.6%
n-hexane	green	95.0%
n-hexane residual	green	8.9%
	yellow	75.9%
	orange	15.1%

Task IV.2.6 Resinite - Solvent Extracted (L. L. Anderson)

The samples investigated were concentrates obtained by physical separation from the Hiawatha coal waste stream from the washing plant. The resin concentrate is being commercially produced by American Resin and the sample of concentrate was obtained from the company.

Samples of a resin concentrate from Hiawatha coal were obtained and tested. This resin concentrate was extracted with chloroform (CHCl₃) and found to be approximately 87 per cent soluble. Analyses (weight %) for the resin concentrate, CHCl₃--solubles and residue from the CHCl₃ extraction (dry basis) are listed in Table IV. 9.

Table IV. 9
Ultimate Analysis and Ash Content of Hiawatha Resin
Concentrate, Extract and Residue

	Resin-Concentrate	CHCl ₃ soluble	CHCl ₃ Residue
C	84.7	87.0	75.9
H	11.0	11.6	5.8
N	.4	.3	1.4
O (by difference)	3.1	.7	14.4
S	.4	.4	.6
Ash	.4	.2	1.7
H/C (Atomic)	1.55	1.60	.92

Infrared analysis of the resin and fractions showed this material to be mostly aliphatic hydrocarbons. A comparison of the IR Spectra from CHCl₃--solubles from coal and CHCl₃--solubles from the resin-concentrate showed these materials to be very similar in all absorption bands.

TASK IV. 3 SPECTROSCOPIC EXAMINATION OF COALS AND SAMPLES

Task IV. 3.1 Pyrolysis MS Analysis of Hydrotreated Hiawatha Coal (T. Chakravarty)

Ten samples of Hiawatha coal, catalytically hydrogenated at 350°C and 400°C (five samples from each temperature) for reaction times, up to 60 minutes without any solvent, were received from Dr. Frank Derbyshire (Pennsylvania State University). Aliquots of these samples were made into fine suspensions in methanol (5mg/ml) under nitrogen. The suspensions were analyzed using Curie-point pyrolysis mass spectrometry under the following conditions: samples size approximately 20 micrograms; Curie-point temperature 610°C; temperature-rise time approx. 5 s; total heating time 10 s; electron energy (set value) 12 eV; mass range scanned 20 to 260 amu; scan speed 1000 amu/s; number of scans 100. Each sample was analyzed at least in triplicate. The resulting thirty mass spectra were normalized for multivariate data analysis.

The data were separated into two batches, based on the temperature of hydrotreating; one at 350°C, the other at 400°C. Preliminary data analyses showed the effect of hydrogenation is more pronounced at 400°C; the nature of chemical changes being the same in both cases. Additionally, more data is available at 400°C. Therefore, all further analyses refer to the data at 400°C.

Figure IV.3a and IV.3b show the average spectra of the hydrogenated coal sample after reaction times of 10 minutes and 60 minutes. Phenols are the most abundant homologous ion series in pyrolysis mass spectra; other major components dominating the spectra are the benzenes, naphthalenes, and the short chain alkenes. We also observed signals at m/z 34 (H_2S^+), 60 (CH_3COOH^+), 44 (CO_2^+) and 64 (SO_2^+).

Factor analysis resulted in three important factors accounting for 74% of the variance in the data. Figure IV.4a shows the plot of the scores of the first two factors; the variance diagram corresponding to this subspace is shown in Figure IV.4b. Three components are marked in Figure IV.4 accounting for major grouping of the variables in this subspace. Component A comprises variables that are responsible for the change between sample at 5 minutes and after. The corresponding spectra in Figure IV.5a showing signals at m/z 34 (H_2S^+), 44 (CO_2^+), 64/66 (SO_2^+ , $HSSH^+$), 80 (CH_3SSH^+), 88 ($C_3H_7COOH^+$) and 110 (dihydroxybenzene) suggests that this direction is associated with desulfurization and deoxygenation. Component B can be linked to the changes that occur between 10 and 15 minutes (not shown). The variables dominating the spectra are at m/z 52 (?), 60 (CH_3COOH^+) and 78 (benzene). The third and the most predominant component C is shown in Figure IV.5b and shows the signals of almost all the peak series found in fresh coals. This is an important piece of information showing that this dry catalytic hydrogenation technique, besides effecting initial desulfurization and deoxygenation, also increases the amount of hydrocarbons that constitute the major portion of coal.

Figure IV. 3 a) Average spectra of Hiawatha coal after hydrotreating for 10 minutes, b) average spectra of Hiawatha coal after hydrotreating for 60 minutes.

Figure IV.5b Numerically extracted spectra for pure component C showing the presence of aliphatic and polynuclear aromatic hydrocarbons.

To correlate the information from pyrolysis mass spectrometry with the information from gas chromatographic measurements on light gas yields and chloroform-soluble extracts, canonical correlation was performed. The results are shown in Figure IV.6. Figure IV.6a and IV.6b shows the score plot and the corresponding variance diagram in the subspace of canonical variates I and II for the Py-MS data; Figure IV.6c and IV.6d shows the same for the data on light gas yields and soluble extracts. The two sets of data appear to correlate very well. The initial desulfurization and deoxygenation axis in the Py-MS data lines up with the formation of CO_2 , CH_4 , H_2S and extracts, while the major component axis comprising polynuclear aromatic hydrocarbons matches up with the evolution of CO and C_3H_8 .

To find a concentration distribution of the three components that separate out in the factor analysis-variance diagram techniques, factor analysis with correlation around the origin was performed on the Py-MS data. Figure IV.7 shows the change in the concentration (based on total ion current as 100%) of the components A, B and C with reaction time. Component A, which consists of small sulfur and oxygen containing molecules, is reduced about 2 1/2 times throughout the total period. Component C, on the other hand, is increased by two times during this period. Note that the changes in A and C occur, to a major extent, towards the earlier and later period respectively. The component B, which is mainly small aliphatic acids and benzenes, goes through a maximum and may reflect the sum of two opposing contributions.

The infrared group obtained diffuse reflectance infrared spectra (IR) and IR spectra using a photoacoustic cell on the five samples hydrogenated at 400°C . Results will be integrated with Py-MS and conventional data.

IV.3.2 Low Voltage MS of Solvent Extracts (B. L. Hoesterey)

Low voltage Curie-point pyrolysis mass spectrometry was performed on resin and resin extracts obtained from L. L. Anderson (Task IV.2.6). The total resin contained ion series tentatively identified as coming from aliphatic compounds, such as C_nH_{2n} , $\text{C}_n\text{H}_{2n-2}$, aromatic compounds such as alkyl substituted benzenes, naphthalenes, indane/tetralins; and ion patterns found from sesquiterpenoid compounds. The sesquiterpenoid molecular ions, i.e. m/z 202, 204, 206 are associated with fragments m/z -43 such as 159, 161, 163, representing isopropyl substitution. We have seen this pattern in whole Hiawatha coal. An ion series m/z 94, 108, 122 . . . is either alkyl phenols or $\text{C}_n\text{H}_{2n-4}$. The elemental analysis result of 3.1% oxygen (by difference) of the whole resin (Table IV.9) suggests the alkyl phenol interpretation is correct. Comparison of the chloroform soluble and insoluble portions of the resin showed that most of the sesquiterpenoid compounds are in the CHCl_3 soluble extract portion. Other compounds in the extract include aliphatics (1, 2 and 3 units unsaturation) and aromatics (benzenes + naphthalenes). Hexane extraction of the resin into solubles and insolubles showed that sesquiterpenoids were found in both portions.

Figure IV. 4 a) Factor score plot in the subspace of F1/F2 showing the direction of chemical change with hydrotreating between the replicate samples marked 1, 2, 3, etc. b) variance diagram in the space described by the first two factors, F1 and F2 component axes A, B, and C describe the clustering of mass peaks

Figure IV. 6 a,b) Score plot and the VARDIA plot in the subspace of canonical variates 1 and 2 on Py-MS data for the coal samples c,d) score plot and the VARDIA plot in the subspace of the canonical variates 1 and 2 on conventional GC and soluble extract data for the same coal samples.

Task IV.3.3 Infrared Spectroscopy (E. M. Eyring, J. Liang, C. Story)

The infrared group has obtained transmission, reflectance and photoacoustic infrared spectra of various coal (Task IV.3.1) samples and coal liquid (Task IV.4) samples. These infrared spectra have been subsequently used in the factor analyses carried out by B. L. Hoesterey, W. Windig and H. L. C. Meuzelaar in their computerized integration of infrared, mass spectral, and NMR data.

The infrared group has also carried out two studies intended to refine the infrared methods available for examining solid coals and their liquefaction products. In the first of these studies a recent report by Urban and Koenig [Appl. Spectrosc. 39, 1051 (1985)] that polarizable gases such as xenon can enhance photoacoustic surface vibrational modes of absorbed species has been critically reexamined. The purported effect has not been detected in diffuse reflectance measurements on sample solids bathed by various polarizable gases including xenon. A tentative explanation for this discrepancy has been developed, and a manuscript has been written for possible publication.

In the second study mid-infrared matrix-isolation spectra of several Lewis acid-base adducts have been obtained. The intent of this work is the exploration of the utility of matrix isolation techniques in identifying species present in complex mixtures such as those encountered in coal liquefaction studies.

Task IV.3.4 Nuclear Magnetic Resonance (R. J. Pugmire)

Proton and Carbon 13 NMR of Hiawatha hydrocarbon subfraction samples obtained from the H. L. C. Meuzelaar group were taken using a Varian SC 300 instrument. Detailed description of the results is reported in Task IV.4.

NMR studies have been carried out on eleven samples submitted by Dr. Larry Anderson (Task IV.2.6). These samples were obtained from solvent extraction of resinite produced commercially by floatation of Hiawatha coal. The CP/MAS spectra of the resinite as received and on the n-hexane and chloroform extracts were identical. The f_a values were $0.16 \pm .01$. The CP/MAS spectrum of the n-hexane insoluble residue was similar to that of the raw Hiawatha coal. The insoluble residue occurs as small black particles contained within the resinite matrix which are liberated upon solvent extraction. The coal extracts appear to be much more heterogeneous and have higher aromaticity than the resinite. Hence, material other than resinite is being extracted from the Hiawatha coal along with the resinite.

Fundamental NMR parameters have been determined for resinite. These parameters are given in Table IV.10.

Table IV.10
Fundamental NMR Parameters for Resinite

H_{T1}	=	420	±	20	msec.
T_{CH}	=	100	±	7	micrograms msec.
H_{T1p}	=	27	±	2	msec.

The proton relaxation time, H_{T1} determines the rate at which a cross polarization (CP) pulse sequence can be repeated. T_{CH} is the time constant for transfer of proton spin magnetization to the carbon spins. H_{T1p} is the time constant for decay of the proton magnetization in the rotating frame. For a successful cross-polarization experiment, the relationship $T_{CH} \ll T_{1p}$ must exist and such is the case. Preliminary data on detailed dipolar dephasing studies have begun in order to provide information on the carbon skeletal backbone of resinite. Initial data is now being evaluated.

Samples were received from Larry Anderson's group (Task IV.2.3). Results are reported in IV. 2.3.

TASK IV. 4. COMPUTERIZED DATA INTEGRATION AND EVALUATION
(B. L. Hoesterey, H. L. C. Meuzelaar, W. Windig)

A pyrolysis tar from a high volatile B bituminous Hiawatha seam coal (Wasatch Plateau field, Utah) was obtained from the fixed bed Wellman Galusha gasifier operated by Black, Sivalls and Bryson in Minneapolis. Open column liquid chromatography (LC) on silica gel using four solvents and solvent mixtures of increasing polarity; i.e. hexane; hexane/benzene 8/1; benzene/ether 4/1; and benzene/methanol 1/1, was used to separate the whole tar into broad compound classes as described by McClennen et al. [McClennen, W. H., Meuzelaar, H. L. C., Metcalf, G. S., Hill, G. R., Fuel, 62 (1983)]. The hexane and hexane/benzene eluted fractions constituted of complex mixtures, principally composed of hydrocarbons. These fractions were combined and further separated by a second LC run. Fractions were eluted from the column with a nonlinear gradient beginning with 100% n-hexane and stabilizing at 10% benzene/90% hexane over a period of 30 min. Sixteen fractions were collected and weighed over a total of 40 minutes. Approximately 1 ml was taken from each sample for low voltage MS analysis. The remaining subfractions were then rotary evaporated and weights of residue were recorded. The calculated elution volumes are shown in Figure IV.8.

Low voltage mass spectra were run on an Extranuclear 5000-1 quadrupole mass spectrometer with Curie-point heating inlet. Low voltage mass spectra of subfractions 1-15 were obtained using 1/4

microliter glass capillary probe tips as described by McClennen et al. [Meuzelaar, H. L. C., McClennen, W. H., Haverkamp, J., Hileman, F. D., Tandem Mass Spectrometric Analysis (MS/MS) of Jet Fuels, Part I and II, Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force base, Ohio, AFWAL-TR-85-2047, Parts I and II, 1985]. Electron energy was set at 12 eV. Samples were scanned from m/z 20 to m/z 300. The inlet was heated to 200°C. Mass spectra from m/z 20 to m/z 300. The inlet was heated to 200°C. Mass spectra were stored on an IBM 9000 computer and printed out in the form of bar plots. Examples of low voltage mass spectra are shown in Figure IV.9.

FTIR spectra were obtained using neat samples on NaCl (salt) disks. The instrument was a Nicolet 7000 series spectrometer, resolution 4 cm⁻¹, 200 scans, operated in the absorbance mode. Samples were scanned from 4000-600 cm⁻¹. Absorbance intensities were recorded for 20-30 peaks in each spectrum. In this way 33 wavenumber variables were obtained. Examples of FTIR spectra are shown in Figure IV.10.

Proton NMR spectra of the hydrocarbon subfractions dissolved in CD₂Cl₂ (with TMS) were taken using a Varian 300 superconducting instrument over the 1-10 ppm region. Integrated peak intensities for eight regions of the spectrum were tabulated for each subfraction, in addition to a table containing an overall view of the number of aliphatic, aromatic and olefinic protons present.

Carbon 13 NMR spectra of subfractions were also run in CD₂Cl₂ on the Varian SC 300 from 0-180 ppm. Peak intensities were measured using integration curves. Twenty three variables were chosen. Table IV.11 shows overall proton and carbon aromatic, aliphatic and olefinic ratios.

Figure IV. 7 Changes in the relative concentrations of the components A, B, and C with time of hydrotreating.

Figure IV. 8 Reconstructed liquid "chromatogram".

Figure IV. 9 Low voltage mass spectra of (a) subfraction 1 and (b) subfraction 12.

Table IV.11
Integrated Intensities of Aliphatic Olefinic and Aromatic Regions of
the NMR Spectrum for Subfractions of the Hydrocarbon
Fraction of Hiawatha Tar

Subtract.	Aliphatic (.5-4 ppm)	Olefinic (4-6 ppm)	Aromatic (6-9 ppm)	Aliphatic H/- Aromatic H
(Proton NMR Data)				
1	1.0			
2	1.0			
3	0.959	0.041		
4	0.948	0.052		
5	0.962	0.038		
6	0.951	0.049		
7	0.905	0.043	0.052	17.40
8	0.909		0.091	9.99
9	0.827		0.173	4.78
10	0.822		0.178	4.62
11	0.789		0.211	3.74
12	0.786		0.214	3.67
13	0.849		0.151	5.62
(Carbon 13 NMR Data)				
1	1.0			
2	1.0			
3	0.98	.02		
4	0.922	.078		
5	0.922	.078		
6	0.885	.063	.052	
7	0.759	.121	.120*	
8	0.596		.404	1.48
9	0.513		.487	1.05
10	0.357		.643	0.56
11	0.333		.667	0.50
12	0.261		.739	0.35
13	0.211		.789	0.27

Subfractions 1-13 were chosen for multivariate analysis. Computerized multivariate analysis was carried out using the interactive SIGMA program package developed at the University of Utah Biomaterials Profiling Center which affords scaling, as well as factor, discriminant and canonical correlation analysis [Windig, W., Meuzelaar, H. L. C., SIGMA, System for Interactive Graphics-Oriented Multivariate Analysis, Proc. 34rd ASMS Conf. on Mass Spec. All. Topics, Cinn. (1986) 64-65]. Chemical components were numerically extracted using the Variance Diagram technique described by Windig et al. [Windig, W., Meuzelaar, H. L. C., Anal. Chem. **56** (1984) 2297-2303]. Figure IV.11 shows the variances calculated for the factors in each data set. For mass spectral and infrared data, only eigenvalues greater than 1.0 are shown, whereas all factors were used for the PMR and CMR data. The dashed line shows eigenvalues < 1.0, e.g. in the PMR, only Factor 1 had an eigenvalue > 1.0. Six factors

from each data set were used for the canonical correlation analyses. Figure IV.10 shows the percent variance from the original factors that was represented in the subspace spanned by the canonical variate functions. Between 40% (MS) and 80% (PMR) of the original variance is represented by Canonical Variate functions 1 + 2.

Our discussion of the factor analyses presented in Figure IV.12 will first identify components characteristic of early eluting samples and then move on to later eluting samples. Investigation of the correlated mass peaks loading on factors 1 and 2 (Figure IV.12) by means of the variance diagram method revealed 8 components. In Figure IV.12a component (a) (130°) represents the ion series $C_nH_{2n+1}^+$, whereas component (b) (160°) shows $C_nH_{2n}^+$ ions from monocyclics or alkenes. A large component (c) ($190-240^\circ$) contains $C_nH_{2n+1}^+$ ions (190°), $C_nH_{2n-2}^+$ ion (220°) as well as fragment ions at m/z 149, 163, 177, and 191 characteristic of terpenoid resins or other $C_nH_{2n-4}^+$ compounds (240°).

Aromatic compounds, such as short (C_n , $n = 1, 2, 3$) alkyl substituted benzenes occur at component (d) (280°), with longer chain (C_n , $n = 5, 6, 7$) benzenes + tetralins at 320° ; component (e). Component (f) at 0° is thought to represent $C_nH_{2n-10}^+$ series. Naphthalenes are found at component (g) (30°) and acenaphthene/biphenyl ions are present at component (h) (50° , Figure IV.12a). Note that the scores in this factor space roughly describe a circle, with the exception of fraction 13, which is found near sample 10. Factor 3 (not shown) distinguishes sample 13 from the others with a component axis containing anthracene/phenanthrene moieties as well as an ion series at m/z 180, 194, 208.

Factor analysis was performed on the IR spectra of subfractions 1 to 13 using 33 wavenumber variables. Figure IV.12b shows the factor score plot of the IR data in the F1 vs. F2 factor space. Samples 1-7 are very close together, implying that infrared spectroscopy does not detect much difference between these dominantly aliphatic mixtures. Analysis of the underlying correlation between variables by means of the variance diagram method showed a large component axis at 160° that contained peaks characteristic of aromatic CH stretches and C = C stretches and bends. The component axis at 350° represents methyl as well as methylene bends and stretches at 2870, 2850, 2920, 1460 and 720 cm^{-1} .

A third component axis at 240° which points to subfractions 12 and 13 represents peaks at 750, 1030, 1180 and 2950 cm^{-1} . Initially, we tentatively assigned C-O stretches to the peaks from the 1200-1000 region but further examination of infrared spectra of aromatic standards showed that these are probably C - H in-plane bends, e.g. 1030 cm^{-1} (benzene).

Figure IV. 10 FTIR spectra of (a) subfraction 1 and (b) subfraction 12.

Figure VI. 11 Percent total variance explained by (a) factors and (b) canonical variate functions.

Figure IV. 12 Factor score plots in FI/FII spaces of all four individual data set

An interesting feature of the IR data is the peak at 2868 cm^{-1} which correlates with the F1 aromatic axis, although it is believed to represent a combination of methyl and methylene stretches. Painter et al., [Kuehn, D. W.; Davis, A. and Painter, P. C., ACS Symp. Series, 252, Ch. 7 (1984), 100-114] also found this behavior in IR spectra of coal macerals. The data strongly suggest a reinterpretation of this peak assignment.

Several peaks in the F1+ direction of Figure IV.12b can be assigned as olefin CH out-of-plane bends. These turned out to be important in the combined (canonical variate) space and will be discussed later.

The factor score plot F1 vs. F2 (91% variance) of the PMR data in Figure IV.12c shows a general distribution of samples forming a circle. The variance diagram of F1 vs. F2 from the proton NMR data shows that the positive F1 axis contains methyl and methylene groups attached to aliphatic (sp^3 hybridized) carbon groups (a), and olefinic protons (b). The F1-axis contains aromatic protons, split into two groups. The component axis at 200° (c) represents methyl substituted benzenes (CH_3 + 1 ring aromatic), oriented toward fractions 9 and 10. The 170° rotation (d) contains 2-ring and 3-ring aromatics and longer chain aromatic substituents (CH_2) oriented toward fractions 11-13.

Factor analysis of the CMR data gave 6 factors with eigenvalues > 1.0 . The score plot of F1 vs. F2 (56% of the variance) (Figure IV.12d) shows that samples 1-7 appear to be similar in this dimension, oriented along the negative side of F1. Components in this direction include aliphatic peaks such as at 23, 30, 32 and 38 ppm and (with weaker loadings), at 97 and 114 ppm, probably olefinic carbons. Fraction 8 is somewhat removed from fractions 1-7 but still on F1-, and therefore predominantly aliphatic in character. Fractions 9-13 are widely spread on factor F1+. A component axis at 350° represents peaks at 20, 122, 126, 131 and 135 ppm. Fractions 10 and 11 have an associated component which includes the peaks at 40 and 134 ppm. Fractions 12 and 13 have an associated component axis with the peaks at 127, 129, 132 and 142 ppm. All peaks on F1+ (except at 20 and 40 ppm) are likely aromatic carbons. The 20 and 40 ppm peaks are sp^3 hybridized carbon substituents on aromatic rings.

Canonical correlation of the factor analysis results from the MS, IR, PMR and CMR data using 6 factors from each data set gave four canonical variate functions with correlation coefficient greater than 0.90. The variance associated with the four CV functions is shown in Figure IV.11. Figure IV.13 is a score plot of CV1 vs. CV2 for the four data sets. The scores from each fraction analyzed by the four methods are connected by lines. A small polyhedron implies that the methods "see" the sample in a similar way. The later eluting samples (9-13) appear to group into clusters that are widely separated from one another (e.g., 9 and 10, 11 and 12, 13) whereas early eluting samples (1-7) are close together in this space. Figure IV.14 shows a consensus picture of the component

Figure IV. 13 Combined score plots of integrated spectroscopic data in "common" CV1/CV2 space.

Figure IV. 14 Combined loading plot of integrated spectroscopic data in CV1/CV2 space showing common chemical components.

directions from each method found in this CV space. Correlated variables consistent with an interpretation of aliphatic compounds are clustered around CV1-, near fractions 1-4. Fraction 7 appears also in this direction. A component axis of alkyl benzenes (m/z 92, 106...) from the MS data loads weakly in this CV space. From the original factor analyses it can be seen that the mass spectral and PMR data clearly differentiated fraction 7 from the other fractions, but that other data sets grouped 7 with fractions 1-6. The PMR data did not have a unique component associated with sample 7. This says that the mass spectral picture of fraction 7 is in a sense unique, and does not appear in the CV space. A component axis corresponding to olefinic variables (IR, PMR, CMR) appears at 150°, in the direction of fractions 5 and 6. The mass spectral data show ion series with 2 and 3 units of unsaturation, one or more of these apparently being a double bond. The positive half of CVI reveals three components, each one consistent with an assignment of aromaticity. The PMR and IR (CH in-plane bend modes) show increasing fused ring aromaticity in the ccw direction (300° to 50°). The mass spectral data identified the component at 300° with indane/tetralins, the 0° component as > C₃ alkyl substituted naphthalenes and the 50° component as acenaphthene/biphenyls. A component axis at 80° (mass spectral data only) showed peaks characteristic of alkyl anthracene/phenanthrenes. The CMR data has not been interpreted in as great a detail, but groups of aromatic peaks found in these three directions are not inconsistent with interpretations from the other data sets. A point of interest is provided by the two CMR aliphatic peaks, 20 and 40 ppm (0°), which correlate with aromatic carbons and are from alkyl substituents.

Valuable information was gained by correlating the four analytical techniques. For example, mass spectral peaks of samples containing 2 and 3 units of unsaturation, were shown to contain double bonds by PMR and IR, whereas mass spectral peaks corresponding to molecules containing one unit of unsaturation were found to be cyclic. Since all the techniques showed the predominantly aromatic fractions to be very different from each other when moving to higher fused ring systems, a better understanding of spectral interpretation of aromatic hydrocarbons mixture data appears possible. The data correlation and integration results will be presented at the 1987 ACS meeting in Denver [Hoesterey, B. L., Meuzelaar, H. L. C., Eyring, E. M., Grant, D. M., Pugmire, R. J. "An Integrated Spectroscopic Approach to the Chemical Characterization of Pyrolysis Oils", Fuel Div. ACS, Denver, 1987].

A major limitation of the present study is that only that portion of the analytical data common to all four analytical techniques was interpreted. Future studies will have to address the highly important portions of the analytical data unique for each analytical method in order to reap the full benefits of the integrated spectroscopic approach.

BASIC PROCESS/RESOURCE EVALUATION TASK

October 1, 1985 - December 31, 1986

Kentucky Energy Cabinet

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Title: Task V. Basic Process/Resource Evaluation Task

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Period: October 1, 1985 - December 31, 1986

Objectives

- V.1 Collect and characterize coals from western Kentucky, and prepare maceral samples.
- V.2 Direct liquefaction conversions of collected coals.
- V.3 Detailed product characterization from the above coals.
- V.4 Establish relationship relating coal properties to direct liquefaction product yields.

Scopes

- V.1 Approximately 100 coal samples (channel, bench, washed) will be collected and analyzed (chemical and petro-graphic). Approximately 10 maceral enriched samples will be prepared (hand-picked, DGC).
- V.2 Direct liquefaction conversion data will be generated for the collected coals and maceral rich fractions using model compound, petroleum resid and/or coal derived process solvent.
- V.3 Based on preliminary conversion data, detailed characterization data will be obtained for product fractions (solubility and boiling range). This will initiate a data base for coal selection for further work in the larger scale reactors.
- V.4 Begin establishing relationships relating coal properties to direct liquefaction products and product quality.

Final Report

INTRODUCTION

A systematic evaluation of the relationship between basic characteristics of the feedstock resources and their subsequent behavior under various process conditions have been carried out at the Kentucky Energy Cabinet Laboratory (KECL). This program generated a substantial data base that is available to emerging liquefaction technologies. Ultimately, this effort will provide an industrial concern sufficient information to optimize feedstock selection for a number of processes.

The current year's activities include the following major tasks: a) characterization of the coals of the western Kentucky coal field, b) survey of coal conversions in small scale reactors and c) reactor product characterization.

EXPERIMENTAL

Coal Sampling

During the year, over 100 coal samples were collected for this project (Figures 1 and 2). Each dot on the Sample Location Map (Figure 3) represents a mine site where samples were collected. At each mine a 75 pound channel sample of the entire seam was collected. The seam was then benched, or divided into layers, based on visual differences in lithology. A 20 to 30 pound sample was collected from each of the separate benches of the seam. The visual changes in a seam are a result of changes in the components of the coal; therefore, each bench sample contains different proportions of coal macerals. It is also common for mineral matter, and pyrite especially, to be concentrated in layers of the coal seam. Taking bench samples provides a suite of samples at the same coal ranks which vary in maceral and mineral components.

All samples were taken as close as possible to the working face of a mine to avoid weathering of the coal. After taking the samples (ASTM D388), they were placed in plastic bags for transportation to the laboratory for preparation. The samples were expedited in the preparation process to avoid oxidation. After grinding, splits were taken for analyses and liquefaction (ASTM D2013). All splits were stored under argon until needed. The initial splits (1/4") used for liquefaction were ground further to minus 100 mesh just prior to the reactor runs.

Additional Coal Analyses

A Free Swelling Index (FSI) was determined for the coals using ASTM method D-720. Forms of sulfur was determined using ASTM D-2492. Heating values (BTU) were determined using a Leco AC-200 Automatic Calorimeter. The AC-200 is a Microprocessor Controlled Automatic Calorimeter based on the ASTM D3286 Isothermal Method.

Petrography and Reflectance

All petrography and reflectance measurements were made in accordance with the following standard ASTM procedures:

- a) Nomenclature - D2796
- b) Sample Preparation - D2797
- c) Maceral Counting - D2799
- d) Reflectance Measurements - D2799.

Because of the need to conserve sample, normal (1") petrographic pellets were not made with samples from the maceral separations. Instead, a one inch pellet of epoxy was made for each sample and then a 5/16" wide hole was drilled in the face. A split of the separation sample was placed into the hole and mixed with just enough epoxy to wet and bind all the particles. After hardening the pellet was ground and polished using normal procedures. The small size and close packing of the maceral separation particles gave sufficient material for a normal (1000 count) maceral analysis. As a check, regular one inch pellets were made of selected samples and the results were identical to the analyses of the smaller pellet samples.

Ultimate Analysis

Carbon, hydrogen and nitrogen were determined using a Leco CHN-600 Elemental Analyzer. The samples were combusted in oxygen at 950°C. The carbon, as CO₂, and hydrogen, as water, were measured by solid state infrared detectors. Nitrogen, as N₂, was measured by a thermal conductivity cell.

Total sulfur was determined using a Leco SC-132 Automatic Sulfur Analyzer. The samples were combusted in oxygen at 2500°F. The resulting SO₂ combustion products were selectively measured by a solid state infrared detector.

Oxygen was obtained by difference.

Proximate Analysis

Proximate analyses of coals and extracted coals were determined using a Leco MAC-400 Analyzer. The unit automatically programs furnace temperature and atmosphere to sequentially determine moisture (106°C in nitrogen atmosphere to constant weight), volatile matter (950°C in nitrogen atmosphere for 7 minutes), and ash (750°C in oxygen atmosphere to constant weight).

Proximate analyses of maceral concentrates were performed by TGA using a Perkin-Elmer TGS-2 controlled by a System 4 microprocessor; this technique minimizes the amount of sample needed for analysis. Typically less than 10 mg of samples was used for each analysis. The sample was heated to 110°C in a nitrogen atmosphere at a heating rate of 100°C/min. The temperature was held at 110°C for ten minutes. The weight loss at this stage is the sample moisture content. After the 10 minute hold, the sample

is heated to 950°C using the same heating rate. The sample weight loss from this stage is defined as the volatile matter. Upon reaching the 950°C temperature, oxygen is added to the system to combust the fixed carbon; the residue remaining is the ash content of the sample.

Microautoclave Reactor System

A description of operating procedures used are described in detail elsewhere (1). All liquefaction reactor runs were made using the following conditions:

- a) Solvent: 100% tetralin
- b) H₂ Pressure: 800 psig (cold; ca. 2200 psig at 445°C)
- c) Residence Time: 15 minutes
- d) Temperature: 385°C, 427°C, 445°C
- e) Coal/Solvent Ratio: 1:1.5
- f) Reactor Charge: 5g dry coal, 7.5g tetralin
- g) 400 oscillations per minute.

Reactor Product Analysis

Gas analyses were performed on a dedicated Carle 311H, Series S gas chromatograph. External calibration using a standard gas of similar qualitative and quantitative compositions was used for calculation of response factors. Calibrations were performed daily prior to analysis.

The method used for the determination of solubility class distributions of reactor products is described in detail elsewhere (2). The operational definitions of the solubility classes used here are as follows (all results are calculated on a moisture, ash free coal basis):

- a) oils - pentane soluble
- b) asphaltenes - benzene soluble, pentane insoluble
- c) preasphaltenes - pyridine soluble, benzene insoluble
- d) IOM - pyridine insoluble
- e) conversion - 100 - IOM.

Mobile Component Extractions

Extraction of the mobile component in coals were done in a conventional Soxhlet apparatus using a solution of benzene:ethanol (80:20 V:V). The extractions were considered complete when the extraction solution was a very pale yellow, typically 5 to 8 days. Solvent was removed by rotary evaporation. Final solvent removal was in a vacuum oven at 60°C and 22 inch vacuum; drying continued until a constant weight was obtained for both the extracts and extracted coals. Elemental balances were calculated and indicated very little, if any, extraction solvent was retained by the coal and extract.

¹H NMR

Approximately 0.50 grams of material and 1.0 ml of CDCl₃ were

placed into a 5 mm n.m.r. tube. The resulting mixture was placed in a sonicator for 0.5 hours to facilitate the dissolution process.

The spectra and integrals were recorded on the Varian XL-200 over a 2600 Hz sweep width. Each spectra consisted of 24 transients, with each transient consisting of a 3.0 microsecond pulse (350 flip) and an acquisition time of 5 seconds for a total run time of two minutes. The integrals were divided into the seven conventional regions (3).

Proton n.m.r. structure parameters were calculated by the method described by Canter (4).

Molecular Weight

Molecular weight determinations were obtained using a Wescan Vapor Pressure Osmometer Model 233. The reported results are the average of three determinations at different concentrations (1,3,5 mg/ml) using pyridine as the solvent. Benzil was used as the standard to obtain the thermodynamic constant for the VPO apparatus.

Curie Point MS

Sample Preparation. About 3 mg of each coal and extracted coal were separately weighed and suspended in 0.5 ml of MeOH, the level of solvent was noted and the coal was ground by hand to produce a fine, uniform suspension. The solvent level was adjusted to compensate for evaporation losses and then an additional 0.5 ml of solvent was added to make the concentration of the suspensions about 3 mg/ml. The benzene/ethanol extract samples were prepared by dissolving about 2 mg in 1 ml of a 1:1 benzene/methanol mixture. These solutions were stored at -10°C until analyzed.

PY-MS Analysis. From each sample a 5 μ l drop (corresponding to 15 μ g of coal or extracted coal, or 10 μ g of extract) was applied to the tip of a 610°C Curie-point filament which was slowly rotated in a filtered air stream. After the solvent had evaporated the filament was drawn back into a glass reaction tube. In the case of the extracts the filament was drawn back into the reaction tube before it was completely dry. The coated filament was inserted into the mass spectrometer and analyzed under the following conditions: pyrolysis temperature 610°C, rise time approximately 5.5 - 6.0 s, total heating time 10 s, electron energy 12 eV, mass range scanned 20 to 260 amu, scan speed 1000 amu/s, number of scans 100. The scans were stored and summed (signal averaging) on an IBM system 9000 microcomputer. Each sample was analyzed in triplicate. The resulting spectra were normalized using the SIGMA program to reduce variations due to sample size. Analysis of the data was done on whole data set as well as on coals and extracted coals.

Density Gradient Separations (DGC)

The raw coal were crushed to -100 mesh and processed as described by Taulbee et al. (5). Briefly, 40 + 1.0 g aliquots of coal were demineralized at room temperature with two successive 400

ml aliquots of 24% HF. Neoformed mineral fluorides were removed with a saturated boric acid solution followed by six water rinses. Pyrite reduction was accomplished by centrifugation instead of the more commonly used chemical dissolution techniques (HNO_3 or LiAlH_4). (Note: no bitumin extraction step was employed prior to DGC; this was conducted after the DGC step for the coals.)

The density gradient was formed by pumping aliquots of aqueous CsCl solutions of various densities, depending on the coal used, stepwise to the outer wall of the rotor which was spinning at 2000 rpm. This was followed by 8 g of demineralized coal sonically dispersed in 150 ml of aqueous surfactant solution (Brij-35/coal ratio of 1:4) to the middle of the spinning rotor. The rotor speed was increased to 16000 rpm for 1 hour resulting in a force of 7000-25000 G's across the rotor. The rotor speed was slowly reduced to 2000 rpm and the CsCl gradient was forced from the rotor by pumping an immiscible high density fluorocarbon (Fluorinert) to the outer wall of the rotor. The solution exiting the rotor was routed through a portable density meter to determine collection breakpoints. Macerals were recovered by filtration through 0.45 μm pore size teflon filters at which time they were thoroughly rinsed with water and sonicated to reduce the residual surfactant content.

Variable amounts of demineralized coal was processed in this manner with the appropriate density fractions from each run being combined to provide a sufficient quantity of material for subsequent studies. These combined fractions were soxhlet extracted overnight with benzene/methanol (4:1) to remove surfactant remaining in the maceral concentrates following the filtration step.

RESULTS AND DISCUSSION

I. Geology and Chemistry of Kentucky Coals Used During Report Period

A. Geology

The Illinois Basin covers approximately 53,000 squares miles ($85,346 \text{ km}^2$); about 4,500 ($7,246 \text{ km}^2$) of which are in Kentucky (Figure 1). The Illinois Basin contains reserves of over 91 trillion tons of coal, 21 percent of the total reserve base of the United States. Of this, about 12 trillion tons are in Kentucky (6). These estimates are for seams thicker than 28 inches and having less than 1,000 feet of overburden.

At least 80 different coals have been identified in the Illinois Basin; however, most of these are present in seams that are too thin for commercial development (7). Most production in Kentucky is from the Western Kentucky #9 (Springfield) and Western Kentucky #11 (Herrin) seams; these are commonly from four to six feet thick.

Stratigraphy of Western Kentucky Region

Pennsylvanian aged rocks of western Kentucky are divided into four formations; these are, in ascending order, the (a) Caseyville,

(b) Tradewater, (c) Carbondale, and (d) Sturgis Formations (Figure 2).

(a) Caseyville Formation. The continuity of this formation throughout the coal field is poor. In some areas the coal seams are interbedded with shales and siltstones while other areas are dominated by thick sandstones. Few coals in this formation have current economic value. The Breckinridge seam was sampled to provide a high liptinite coal for our study. This seam is a boghead coal, rich in bituminite.

(b) Tradewater. This formation is predominately composed of thick sandstones with thin layers of coal and limestone (8). It is best exposed in the southeastern part of the coal field in Butler County; this is where samples from the Amos and Foster seams were taken. Coals from these seams are low in both sulfur and ash. The Amos is extraordinary in having very low fusinite and semi-fusinite contents (9). These unusual coals add to the range of variations for the coals in this study.

(c) Carbondale Formation. Approximately 350 feet (106.7 m) of alternating sandstone and shale with thinner layers of coal and limestone make up this formation. The Springfield (Western Kentucky #9) and Herrin (Western Kentucky #11) seams of this formation are the most laterally continuous and commercially productive seams in western Kentucky. Both seams are high in sulfur and vitrinite. The Herrin (Western Kentucky #11) is almost always above 80% vitrinite while the Springfield (Western Kentucky #9) shows more vertical variation within the seam and the vitrinite content is usually lower (10). The majority of our samples were collected from this formation.

(d) Sturgis Formation. This formation is approximately 2,000 feet (610m) of interbedded sandstone, siltstones, shale, limestone and coal. The coal seams in this formation are neither uniformly thick nor wide-spread, but are often mined locally. The Paradise (Western Kentucky #12) seam has a high total vitrinite and low inertinite content (11); it is the third most economically valuable seam in western Kentucky (12). Several samples of the Paradise seam were taken for this project.

B. Chemistry and Petrology of the Coal Samples

Samples were taken from the operating mines of western Kentucky to represent the maximum possible variability of coal characteristics. Seams with numerous active mines were sampled throughout the area in an attempt to define regional variations, if any, in coal properties. Unusual seams, such as the Breckinridge, Amos and Foster, were sampled to extend the range of variables of the sample base.

Analytical data for all samples were entered into the Kentucky Energy Cabinet Laboratory's (KECL) coal data base. The data for the samples collected during the year closely match the data generated from earlier KECL studies of western Kentucky coals. The chemical and petrographic data of the coals are given in Appendix 1.

Coal Rank

Coal rank may be a significant factor in determining coal liquefaction characteristics. As rank increases, liquefaction yields decrease (13). It is believed that this is due to the increasing condensation of aromatic rings with increasing rank (14). Davis et al. (15) stated that coals of high-volatile bituminous rank were best for liquefaction. This was reaffirmed by Whitehurst et al. (16) who found that conversion and reactivity decreased markedly as coal rank increased beyond high-volatile bituminous. It was also found that, although yields were higher, coals below high-volatile B in rank were slower reacting. Because of this, the ideal rank range for liquefaction is that of high-volatile A & B coals (16, 17).

The sampled western Kentucky coals are high-volatile bituminous in rank (Figure 4). The samples taken for this study cover the rank variation available in the portion of the Illinois Basin that lies in Kentucky. The Western Kentucky #9 and #11 seams show the greatest rank variation based upon vitrinite reflectance (Figure 6*) [*Figure 5 is a key to Figures 6, 7, 8, 10, 11, 14 and 15. The seam name and number of samples are shown at the bottom of the box plot. The middle line in each box is the mean, while the ends of the box represent ± 1 standard deviation. The lines extend above and below the boxes to show maximum and minimum values, respectfully.] This is anticipated since these two seams represent the largest number of samples and because the sample sites are spread across the region (Figure 3) so that local rank variations should be encountered. Other rank parameters, volatile matter and carbon content, produce trends that compare to the one based upon reflectance (Figures 7 and 8).

A Van Krevelen diagram based on our suite of coal samples (Figure 9) exhibits hydrogen/carbon and oxygen/carbon values that are typical for high-volatile bituminous coals with high-vitrinite contents.

Ash

The effects of ash content and composition on liquefaction are poorly understood. It is difficult to determine the effects, or lack of effects, because the variation of the types and amounts of minerals in coal is so great (18). Some clays (19, 20) and iron bearing minerals (21, 22) have been shown to have a beneficial effect. Several researchers (16, 23) have reported a higher reactivity as ash, as a whole, increased.

The range of ash values for our samples is exhibited in Figure 10. The Western Kentucky #9, #10 and #12 coals show the normal spread of ash values for these seams. The Amos and Foster coals exhibit unusually low ash values, but this is characteristic of these two seams.

Our samples have the mineral assemblages typical of Illinois Basin coals. The most common minerals in these coals are illite,

kaolinite, mixed-layer clays, pyrite, marcasite, calcite, quartz, chlorite, sphalerite, and gypsum (24). The amounts and types of minerals in each sample varies due to different depositional and/or diagenetic conditions of the coal.

Sulfur

Many studies have reported on the catalytic effect of sulfur in coal (13, 25, 26), but the exact role of sulfur and of the different forms of sulfur is still not well understood (27). Because sulfur, or materials containing sulfur, may be an important liquefaction catalyst, it is one of the parameters we are investigating.

Illinois Basin coals are typically higher in sulfur than are Appalachian coals (28). Most of the samples collected have sulfur contents ranging from 2 to 5% (Figure 11). Some of our bench samples, however, have considerably more sulfur due to localized pyrite layers in the bench. The Amos and Foster coals, which normally have very low sulfur contents, help to extend the range of samples to include low sulfur coal.

Organic sulfur is considered to be part of the molecular framework of the coal, thus is almost impossible to clean out by mechanical means. There is always some present in any coal but it is unusual for a coal to contain more than 3 to slightly higher 4% organic sulfur. The organic sulfur contents of our samples (Figure 12) are, in this range, reflecting the typically high sulfur content of western Kentucky coals.

By far the most common forms of inorganic sulfur in coal are pyrite and marcasite; this is reflected in our samples as well. Other sulfur-bearing minerals such as sphalerite, chalcopryite, galena, and arsenopyrite are rarely seen in our suite of samples and are not commonly found in coals elsewhere.

Pyritic sulfur (which includes marcasite) occurs in a variety of forms and in sizes ranging from microscopic to large "boulders". This mineral may be concentrated in layers or zones within a coal seam or it may be distributed rather uniformly. The ease of removal of pyritic sulfur depends on the size and distribution of the particles within a coal. Large masses of pyrite are easily removed but small, disseminated crystals are nearly impossible to remove by methods available today. The pyritic sulfur values for our samples (Figure 12) range from a low of 0.03% (Amos seam) to a high of 8.87% (bench of the Western Kentucky #9 coal). Most of the samples contain 1 to 3% pyritic sulfur, which is normal for western Kentucky coals.

Petrology

Petrographic analyses were performed on each sample to determine the maceral (organic components of coal derived from plant material) composition. There are three major groups of macerals: vitrinites, liptinites, and inertinites. The vitrinites were derived from woody plant material. Western Kentucky coals are

unusually high in vitrinite, averaging greater than 85%. Liptinites are formed from resins, waxes, leaf cuticles, algal remains, and plant spores. The inertinite particles have varied origins, but many are believed to be remains of oxidation reactions such as fossil charcoal from peat fires.

The maceral composition is important because the maceral groups have very different chemical compositions and physical behavior. Because of this, they react differently under liquefaction conditions and the proportions of each type can influence liquefaction results (29-32). Liptinites and vitrinites are considered the reactive macerals; both groups react well and give good liquefaction yields (15, 33, 34). Inertinites are so-named since they are inert to most processes. Most forms of inertinite are fixed carbon, with little or no extractable components. A coal high in inertinite is not expected to liquefy to a significant extent (15).

All the western Kentucky coal samples are high in vitrinite, with two exceptions (Figure 13). The data point near the liptinite axis is the Breckinridge boghead coal, which is primarily composed of liptinite material. The coal plotted near the inertinite axis is a bench sample predominately composed of fusinite, a fossil charcoal. This high inertinite sample is very unusual for western Kentucky, as the proportion of reactive macerals (vitrinites and liptinites) in our other samples do not fall below 72% (Figure 14).

The proportion of reactive coal macerals affects plasticity because only vitrinite and liptinites exhibit plastic behavior (35). Plasticity relates to the mobile phase of coal and can thus be important to coal liquefaction (36). The Free Swelling Index was used as a measure of plasticity for the project samples. The results exhibit a spread of values typical for western Kentucky coals (Figure 15).

The project coals collected from the important seams in western Kentucky in the first year provide the necessary range of coal properties for the study of liquefaction.

II. Liquefaction Studies

A. Liquefaction of Project Coals

One hundred western Kentucky coals were liquefied, as described in the experimental section, at a reactor temperature of 427°C. In addition, selected samples of the #9 and #11 seams were liquefied using 385°C and 445°C reaction temperatures. The data obtained for these coals provided an extensive data base for the evaluation of the liquefaction reactivities of an important coal producing field as well as providing data for the initial evaluation of the effect of coal characteristics on conversion.

The analysis of the reactor products, presented by coal seam and reactor temperature, are shown in Figures 16, 17, 20, 21 and 24-28. The solubility class analyses were plotted on ternary

diagrams to provide a comparison of pertinent liquefaction data for each coal. Each coal was given a unique graph symbol; this is, for identification purposes for this report, associated with a KCERL number. The liquefaction data is tabulated in Appendix 2.

The products obtained from the conversion of #9 and #11 coals at a 385°C reaction temperature (Figures 16 and 17, respectively) show similar liquefaction responses. The largest variation in conversions (40-80 wt.% daf coal) were obtained at this temperature. Although the amount of conversion varied, the yield of oils plus gas remained fairly constant (10-16 wt.%). The primary products at a liquefaction temperature of 385°C are asphaltenes and preasphaltenes (SRC = asphaltenes plus preasphaltenes). Furthermore, the amount of SRC was linearly related to the total conversions for both the #9 and #11 coals (Figures 18 and 19, respectively). The curves for the #9 and #11 coals have similar slopes (0.99 and 1.04, respectively) and intercepts (-12.2 and -19.4, respectively). The 385°C data is consistent with the formation of a small, constant amount of gas plus oil from each coal within a seam. Thus, the coal properties determines only the total conversion and, hence, the amount of SRC.

The product compositions from the conversion of a "lower reactivity" coal liquefied using a 385°C reactor temperature are also shown in Figures 16 and 17 for a number of reaction times. The products from the "lower reactivity" coal (KCERL 71110) follow, with increasing reaction time, a product pathway that is similar to the one defined by a variety of coals from a particular seam except for, perhaps, a slight increase in the yield of gas plus oil with increasing reaction time.

The reactor product distribution obtained from the liquefaction of the #9 and #11 coals at 427°C are given in Figures 20 and 21, respectively. The primary difference in the liquefaction response obtained at this higher reaction temperature is an increase in the amount of coal that is converted. The range of conversions was similar for both seams; however, the conversion range was much smaller for this temperature compared to the results obtained at the lowest reaction temperature employed in this study. The primary products obtained at 427°C are again asphaltenes and preasphaltenes (SRC). The data in Figures 22 and 23 show that SRC production also increases with increasing conversion; however, the relationship was not as well defined at this temperature as it was at a reaction temperature of 385°C. The yields of oils and gases were larger than those obtained at 385°C and were fairly constant (ca. 20-30 wt.%) for samples of both coal seams. The data show that the coals from the #9 and #11 seams have very similar liquefaction responses at a reaction temperature of 427°C.

The product distributions for liquefaction of the #9 and #11 coals at 445°C are shown in figures 24 and 25, respectively. The conversions are very similar to those obtained at the 427°C; the primary difference in the product slate is a shift towards greater yields of oils and gases at the higher temperature. There was little difference between the #9 and #11 liquefaction results at this reactor temperature.

The product distributions from the conversion of the Western Kentucky #12, Amos and Foster seams at 427°C are very similar to those obtained at this temperature for the #9 and #11 seams (Figures 26-28).

B. Elemental Analysis of Reactor Products

Carbon and hydrogen analyses were completed for a set of asphaltenes and preasphaltenes, the major liquefaction products, to identify the changes, if any, in the composition of the products with conversion. The series of asphaltenes and preasphaltenes were selected to cover the range of conversions obtained at reaction temperatures of 385°C and 427°C. The atomic H/C ratios of the preasphaltenes do not vary significantly for the entire range of conversions for both temperatures (385°C, Figures 29 and 30; 427°C, Figures 31 and 32). In these four figures, the H/C ratios for the liquefaction products are connected by a broken line and the coals by a solid line. It is emphasized that these lines are used only to make the comparison of data for coals and for products easier. In general, the preasphaltenes appear to have a slightly lower H/C ratio than the parent coal while the asphaltenes have a slightly higher H/C ratio than the corresponding coal. However, for both products the ratio differs only slightly from the parent coal.

The heteroatom content of the asphaltenes and preasphaltenes obtained from the liquefaction of the #9 and #11 coals at a reactor temperature of 385°C remain fairly constant for the range of conversions obtained. The heteroatom content of the asphaltenes is smaller than that of the preasphaltenes. This is consistent with the higher carbon and hydrogen contents of the asphaltenes. The amount of heteroatom per gram of asphaltene or gram of preasphaltene was plotted against the amount of heteroatom per gram of coal. There was not a consistent relationship between the heteroatom content of these solubility classes and the heteroatom content of the parent coals; typical data are shown in Figure 33. The heteroatom content of the asphaltenes is approximately one-half that of the preasphaltenes.

C. Correlation Between Coal Properties and Liquefaction Product Yields

In order to evaluate the liquefaction response of potential coals, it is desirable to develop correlations between coal characteristics and the liquefaction yields. In the initial phase of this task, attempts were made to relate one of several coal properties to the yields of the solubility class distribution of the liquefaction products. The coal properties and liquefaction yields used for the correlations are given in Table 1. Each graph generated was examined for potential linear as well as non-linear relationships between a coal properties and liquefaction yields. No strong correlations were found for the liquefaction data generated at any of the three reaction temperatures. The absence of any strong correlation suggests that more than one coal characteristic may be influencing the liquefaction product yields and a multivariate regression analysis will be required. Multivariate

regression analysis of the data in addition to the examination of several models found in the literature is now in progress. Another factor is the absence of a reliable measure of the conversion that is more useful than the solubility class fractions.

D. The Role of the Mobile Component in Liquefaction

One model that has received much attention in the recent literature (37-39) regards coal as a three dimensional crosslinked macromolecular structure in which appreciable quantities of lower molecular weight compounds are trapped in the pores or voids. This molecular component has been designated "mobile component". Recent ¹H n.m.r. studies by Jurkiewicz et al. (40) and Marzec et al. (41) suggest that a substantial portion (ca. 40%) of bituminous coals are comprised of this component. The quantity of the mobile component found in bituminous coals has generated considerable debate on the subject (42). Irrespective of the amount of the mobile component found in bituminous coals or the amount of the mobile component which is extractable by solvents using conventional Soxhlet techniques, it has been suggested that this component may have a significant impact on the liquefaction response of coals. Brown and Waters (43, 44) have shown that the mobile component extracted with chloroform has an impact on the coking properties of coal; removal of this material severely reduces or destroys the coking properties of coal. Recently, Grint et al. (36) proposed that the mobile component can be modeled as highly condensed polynuclear aromatics in the coal carbonization process. The authors removed the mobile component by THF extraction, determined the extracted coal carbonization properties and compared the results to that of the parent coal. The loss of carbonization properties were apparent from the data. The polynuclear aromatic compounds, decacyclene and corenene, were blended with extracted coals and the determination of carbonization properties of the blends was carried out. The results of the carbonization of the blends were directly comparable to the parent coals. The authors suggested that the return of the carbonization properties were possibly due to the hydrogen shuttling ability of the model compounds and/or radical stabilization by the polynuclear aromatics. Neavel (45) suggested that the initial chemical reactions occurring in direct liquefaction are identical to those which occur in the coking process; therefore, the role of the mobile component in liquefaction may also be similar.

The objective of this task is to characterize and to determine the role of the extractable mobile component in the liquefaction of western Kentucky coals in the presence of a donor solvent. The experimental approach is similar to that used by Grint et al. (36). The mobile component was removed by Soxhlet extractions as described in the experimental section. The resulting extracted coal and a blend of the extracted coal plus extracted mobile component were liquefied in microautoclaves (385°C) and the conversions were compared to those obtained by the parent coal.

A series of bench and channel samples of the #9 and #11 seams were extracted in a conventional Soxhlet apparatus with a benzene:ethanol (80/20 V:V) solution. A minimum of six replicates

were performed for each of the 17 coal samples used in the study. Benzene:ethanol solvent was chosen because of the relative ease of its removal from the extract and extracted coal (46) and the fact that reactions involving covalent bond breaking do not take place when this solvent is used (47). Analyses of the extractable mobile component and extracted coals are given in Tables 2 and 3, respectively.

The yields of the mobile component extracted from the coals exhibit a rank dependence (Figure 34). The yields shows a maximum at about the 0.6 reflectance region of the curve. Although the region of the curves in which the maximum yield is defined is not the same, the shape of the curve is similar to those reported by Ouchi (48) and Raj (49).

Elemental analysis of the extracted mobile component indicates they are typically richer in hydrogen and poorer in oxygen than both the parent or extracted coals. As can be seen in a van Krevelen diagram of these samples (Figure 35), the extracts are not representative of the parent coals; however, the parent and extracted coals are similar. The fraction of organic sulfur of the parent coal that is present in the extractable mobile component varies from 2 to 8 wt.% (daf coal). The nitrogen content show little variation and is similar to that of the parent and extracted coals.

The average number molecular weight of the extracts were generally in the 500 to 600 daltons range, which are typical for molecular weights of extracts reported by other researchers (50, 51). Dormans et al. (52) reported that the molecular weight of the pyridine extractable mobile component has a rank dependence; however, as can be seen in Figure 36, the benzene:ethanol extractable mobile component molecular weight does not have a rank dependence. The factors responsible for this difference are being investigated.

Proton n.m.r. spectra were recorded and structure parameters calculated for a subset of the samples of the extractable mobile component. The proton aromaticity of the extracts, f_a , shows a rank dependence with the aromaticity increasing with increasing rank of the parent coals (Figure 37). The rank dependence of the aromaticity of the extract is similar to the results reported by Retcofsky (53) for pyridine extracts of bituminous coals.

As a measure of the hydroaromatic character of the extractable mobile components, the number of naphthene rings per average molecule was calculated from the n.m.r. data. As can be seen in Figure 38, the number of naphthene rings decreases with increasing rank of the parent coals.

Although the hydroaromatic nature of the extractable mobile component is small, hydrogen donation can be a viable role of the extract during the initial dissolution of coal. However, it seems likely that a more significant role of the mobile component would be as a hydrogen shuttling vehicle. The synergistic effect of light

and heavy recycle solvents during liquefaction has been reported by Derbyshire et al. (54) who suggest that the synergism observed was due to the hydrogen shuttling ability of the polycondensed aromatics in the heavy solvent. The aromatic nature combined with the high molecular weights of the extractable mobile component suggest that the extract is an effective hydrogen shuttling vehicle, especially since the extract is already located within the pore structure of the coals.

A subset of the parent and extracted coals and the extractable mobile component from the Western Kentucky #9 and #11 seams plus a Wyodak sub-bituminous coal were analyzed by Curie-point m.s. at the Biomaterials Profiling Center located at the University of Utah. The samples were specifically chosen to represent a large variation in rank for the evaluation of this technique.

Average py-ms spectra representing each of the three ranks are shown in Figure 39 (parent coals), Figure 40 (extracted coals), and Figure 41 (extracts). Note that the difference in rank is clearly reflected in differences in the mass spectra. Similar differences with rank have been observed in a large set of Rocky Mountain coals (55). Standard spectra for western U.S. coals of various ranks are shown in Figure 42. It is interesting that the spectra of the Kentucky coals are quite similar to those of western U.S. coals of corresponding rank in spite of differences in geohistory. (The Kentucky coals are Carboniferous, while the western U.S. coals are Cretaceous).

Representative spectra of the corresponding coal extracts are shown in Figure 41. In Figure 41a (hvAb) the mass peaks for naphthalenes are intense relative to those of phenols. In Figure 41b (hvCb) the naphthalene peak intensities have decreased relative to the phenols, but they are still the dominant mass series. In Figure 41c, (sub-bituminous) the phenols are the major mass series.

In order to more easily assess the differences which exist between the samples, the py-ms data were subjected to factor and discriminant analysis. Briefly, factor analysis creates independent linear combination factors of the variables (in this case mass peaks) that describe the variance in the data set as efficiently as possible. Generally, this results in a data reduction (fewer factors than variables) due to the correlated behavior of some of the variables. This correlated behavior can be interpreted by making a factor spectrum which is composed of the variables (mass peaks) that contribute to that factor. In discriminant analysis, discriminant functions are calculated that maximize the signal-to-noise ratio. As with the factors, the discriminant functions are composed of linear combinations of the mass variables and the discriminant functions can be utilized by examining their respective discriminant spectra.

The factor score plot (Figure 42) for the entire data set clearly shows a clustering of coals and extracted coals together and a less homogeneous extract cluster. The factor spectrum for factor 1 identifies the mass peaks that differentiate the extracts from the

parent coals/extracted coals. The ions at m/z 34 (attributable to H_2S^+), 64 (S_2^+ or SO_2^+), and 66 ($H_2S_2^+$) are higher in the coal spectra. Components at m/z 57, 71, 85, 99 (C_nH_{2n+1} , alkane fragments), at m/z 128, 142, 156, 170, 185 (naphthalene and alkyl naphthalenes), and at m/z 154, 168, 182, 196, 210, 224 (alkyl biphenyls, acenaphthenes) are higher for the extracts. Factor 2 distinguishes the extracts by the rank of the parent coals. Naphthalenes and biphenyls, for the higher rank samples, and dihydroxybenzenes, for the lower rank samples, are evident in the factor spectrum. The discriminant analysis did not reveal systematic differences between extract-coal pairs. The variance in the py-ms data for the coals and extracted coals is small compared with that of the extracts.

The remainder of the data treatment was performed on a data subset containing only the parent coals and extracted coals. The factor score plot is shown in Figure 43. Factor 1 accounts for 43% of the total variance and correlates with the rank of the coals, while factor 2 (20% of the variance) describes differences in depositional environment. Coal 71069 (sample 4) has the highest score on factor 2 and has a lower vitrinite maceral concentration. A similar pattern was observed by Meuzelaar et al. (55) in a study of coals from the Rocky Mountain province. The factor spectrum corresponding to the rank axis of Figure 43 shows benzenes (m/z 78, 92, 106) and sulfur compounds in the high rank direction and phenols (m/z 94, 108) and dihydroxybenzenes (m/z 110, 124, 139, 152) in the low rank direction. The factor 2 spectrum shows the py-ms products of coal 71069 to be higher in acids (m/z 46, 60, 74), alkenes (m/z 56, 70, 84, 98 . . .), dienes (m/z 54, 68, 82 . . .), and alkane fragments (m/z 57, 71, 85 . . .) relative to the other coals of the hvCb rank.

To determine the effect, if any, of the extractable mobile component in the conversion of western Kentucky coals, the extracted coals and the extracted coal plus extract blends were liquefied at 385°C to obtain data for the comparison to the liquefaction results with the parent coals. The set of samples were selected to cover the rank range of the #9 and #11 coal samples. The extract and extracted coal samples were blended to produce a composition that was the same as found in the parent coals.

The analysis (Table 4) of the liquefaction products obtained from the three sample types (parent coal, extracted coal, and blend) indicates the correlation between SRC production and conversions are very similar (Figure 44 to 46). As previously discussed, there is a linear correlation between SRC production and the conversion at a 385°C reaction temperature. The removal of the extractable mobile component, as well as the blending of the extracted coal and mobile component, has no significant effect on the correlation between SRC production and conversion. In fact, the three sets of samples have very similar slopes and intercepts and have a high degree of correlation (R^2 values $>.90$). This suggests that the coal dissolution mechanism was not effected by removal of this amount of extractable mobile component.

A comparison of the insoluble organic matter (IOM) contents (daf coal basis) for the parent and extracted coals (Figure 47) shows that generally, the yields of IOM are larger than those obtained by the parent coals, i.e., the extracted coals have lower conversions than the parent coals. The IOM yields were calculated on a dry, ash free basis for the parent coal and extracted coal charged in the reactor. These results are not unexpected, considering the method of calculating conversion. The removal of the soluble portion of a coal would produce a lower yield of total solubles (conversion) for the extracted coals, assuming that the mobile component did not undergo retrograde reactions during liquefaction. Initial liquefaction data indicate that the mobile component does not undergo retrograde reactions in a donor solvent at 385°C.

It is more appropriate to compare the parent coal conversions to the sum of the extracted coal conversions and the corresponding yields of extractable mobile component. Different results are obtained when this is done (Figure 48). These data indicate that six of the extracted coals still have lower conversions while two of the extracted coals have higher conversions than the parent coals. The conversion data of the two extracted coals showing higher conversions have been experimentally verified by additional microautoclave runs. This suggests that the extracts, or the extraction process, may have a detrimental or beneficial effect on liquefaction. The analytical data of the two coals, extracted coals as well as mobile components, provided no simple explanation for these results.

The general decrease in conversions obtained with the extracted coals is similar to the results reported by Larsen et al. (56). Although the reactor conditions were very different (non-donor solvent, 482°C or 460°C reaction temperatures) from the ones used in this study, Larsen found that removal of chloroform solubles caused a similar reduction in conversion for a bituminous and sub-bituminous coal. Addition of the extract yield to extracted coal conversion produced different results than reported here. The two extracted coals still had lower conversions than the parent coals when compared in this way.

Whitehurst et al. (57) reports still different results obtained with pyridine extracted coals. Again, the reaction conditions are different which makes direct comparisons difficult. Whitehurst obtained conversions using a synthetic liquefaction solvent (donor capability), a reactor temperature of 427°C and a residence time of approximately 5 minutes. The authors observed no difference in the conversions of the extracted and parent coals.

The similar results obtained for the chloroform and benzene: ethanol extracted coals may be due to the similar yields and the composition of the extractable mobile components (57). The pyridine extracted coals and the pyridine extracted mobile component have similar compositions (57) and this may be responsible for the different liquefaction response observed by Whitehurst. Clearly a more systematic study is necessary to define the role of the mobile component in liquefaction.

A comparison of the blend conversions and the parent coal conversions are shown in Figure 49. The amount of IOM in the reactor products of the blends was calculated on the basis of dry, ash free coal plus the amount of mobile component separated from the coal. The results show that, in general, the blends produced more IOM, i.e., lower conversions, than the parent coals. These results suggest that not only the physical presence of the mobile component has an effect on liquefaction, but the location of the extract in the pore structure is also an important factor. Otherwise, the extraction has introduced gross physical reordering of the coals or introduced significant chemical alterations to the coal.

E. Separation and Liquefaction of Western Kentucky Coal Macerals

The objective of this task is to examine the variation in the chemical properties within maceral groups and between maceral groups with respect to their liquefaction responses. The coals selected for the initial phase of this work were a Breckinridge coal, a Western Kentucky #11 and three Western Kentucky #9 coals. The Western Kentucky #9 and #11 coals have a reflectance range of .54 to .79 and were used for the isolation of the vitrinite group. The Breckinridge coal (R_0 ca. .54) was used to isolate a bituminite concentrate. Each maceral concentrate was the composite of several density gradient centrifugation (DGC) runs. This provided sufficient sample for chemical and petrographic analyses in addition to liquefaction runs in the microautoclaves. The four vitrinite concentrates were isolated from fractions with the same density range (1.280 - 1.290); the bituminite was isolated from a density fraction with a density range of 1.110 to 1.140. Chemical and petrographic analyses of the parent coals, demineralized coals and the maceral concentrates are given in Table 5.

The purity of the vitrinites were all greater than 96%, thus insuring that the observed property variations are due to changes in the structure of the vitrinites and not due to impurities. The bituminite maceral concentrate was enriched to 88%; the primary maceral contaminant in this concentrate was vitrinite.

Comparison of the data in Table 5 shows an interesting trend for the Western Kentucky #9 and #11 samples. The carbon content consistently increases for each set of samples in the series: vitrinite concentrate > demineralized parent > parent. This trend is also apparent in the atomic H/C ratios of the series of samples shown in Figure 50 as a function of the rank of the parent coal. It is apparent from this data that different H/C ratios are observed for the vitrinites obtained from the same density fraction. Although, H/C ratios do not give specific information, per se, on structural variations of the vitrinites, they do indicate there are differences within the maceral group and these differences are related to the rank of the parent coal. The results reported here are similar to those reported by Dyrkacz et al. (58). The trend of the carbon content previously discussed for the vitrinites is not observed for the bituminite concentrate. The H/C ratio of the demineralized coal is lower than either the parent or the

bituminite. The higher H/C ratio of the bituminite is likely due to the relatively high vitrinite concentration in the maceral concentrate. The atomic H/C ratios are significantly larger than those obtained for the vitrinites indicating the aliphatic nature of the bituminites (59).

King et al. (60) reported that the reactivity of coal macerals in short content time donor solvent liquefaction varies not only among the macerals but also within each maceral group. The conversions were related directly to the density fractions from which the macerals were isolated, i.e., increasing density of the maceral concentrates reduces the observed conversions. Dyrkacz et al. (58) also reported that the H/C ratio decreases with increasing density of each maceral group in bituminous coals which is related to the reactivity of the macerals; thus, increasing the H/C ratios within a maceral group produces lower conversion. In addition, King reported the conversions obtained for two vitrinites isolated from the same density fractions (1.290) from samples of different basins, which have much different ages, were the same even though the H/C ratios were different (.816 vs. .840). From the literature data, it can be suggested that vitrinites from the same density fractions should have the same conversions using similar reaction conditions.

From the discussion above, it would be predicted that the four vitrinites separated in this study should have similar conversions and the bituminite (lower density, higher H/C ratio) should have higher conversions than the vitrinites. Three of the vitrinites (all from the Western Kentucky #9 seam) do show very similar conversions at all three temperatures; this is expected. However, the vitrinite concentrate isolated from the Western Kentucky #11 coal (KCERL 71077) shows significantly lower conversions at all three reactor temperatures. In fact, the conversion of the #11 derived vitrinite is more comparable to the conversions of the bituminite at the lowest and intermediate reactor temperatures; this suggests possible structure similarities between these two. Comparison of the chemical and petrographic analysis of the vitrinites does not readily provide explanations for the anomalous conversions. The Kentucky #11 derived vitrinite was obtained from an intermediate rank coal (R_o max = .69), the atomic H/C ratio is intermediate compared to the other three vitrinites (Figure 50) and has been separated from the same density fractions as the Kentucky #9 derived vitrinites. These properties indicate that the conversions should be comparable. The fact that the parent coals from which all the vitrinites were separated have similar conversions at all three reactor temperatures suggests that the reason for the lower reactivity may be due to the separation procedure. It has been reported by Bishop and Ward (61) and Painter et al. (62) that little, if any, changes occur in the organic structure of bituminous coals during the demineralization procedures. Although the evidence is not strong, the data supports the supposition that no alteration occurs; therefore, alteration of the vitrinite during demineralization appears not to account for other lower conversions of #11 derived vitrinite.

The catalytic effect of coal minerals in coal liquefaction has

been the subject of much research (e.g., 63, 64, 65). The anomalous liquefaction behavior of the #11 derived vitrinite may be due to the sequential removal in the ash during sample preparation. Conversion does vary linearly with the ash content (dry basis) of the Kentucky #11 derived samples (parent, demineralized parent and vitrinite concentrate) at the intermediate and high reaction temperatures. The reason for the relationship existing for the Kentucky #11 vitrinite and not the Kentucky #9 derived vitrinites is not apparent. Further characterization of the sample series by Curie-point m.s. is in progress and may provide structural information.

The bituminite maceral concentrate shows very low conversions (Figure 51) at the lowest and intermediate reactor temperatures when compared to the vitrinite concentrates derived from the #9 coals. At the highest reactor temperature, the conversions are essentially the same. The low reactivity of the bituminite is likely due to the aliphatic character of the maceral. The generally excepted mechanism for the initial coal dissolution is the thermal cleavage of labile linkages forming free radicals which can be capped by hydrogen donation, rearrange to other free radicals or combine with other free radicals to form larger molecules (66). The conversion data suggests the low bituminite reactivity at the lower reactor temperature may be due to fewer labile linkages when compared to the Kentucky #9 vitrinites. The aliphatic nature of the bituminite suggests that many of the linkages may be saturated rings which are thermally more stable than the other linkages (e.g., ether) postulated to be important in initial coal dissolution. It follows from the discussion above that the products of liquefaction of the bituminite are expected to have a more condensed ring structure with higher molecular weights. The initial molecular weight data obtained for the asphaltenes indicate the molecular weights to be larger than those of a Kentucky #9 derived vitrinite of similar rank at all three reactor temperatures (Table 6).

The temperature response of the vitrinites are identical (Figure 51). Increasing the temperature from 385°C to 427°C dramatically increases the conversions of the vitrinite; however, increasing the reactor temperature to 445°C has little effect on the conversions. The bituminite shows a very different reactor temperature response. The conversions increased continuously with increasing temperature.

REFERENCES

1. Pina, B. P., "Hydroliquefaction Performance of Two Kentucky Coals in Solvents of Various Hydrogen-Donor Strengths", Masters Thesis, Dept. of Chemical Engineering, University of Louisville, Louisville, KY (1984).
2. Mimia, M. J., and Schultz, H., PETC/TR-80/3, 1980.
3. Burk, F. P., Wenschel, R. A., Pochapsky, T.C., "Development of a Correlation Between Slurry Oil Composition and Process Performance", U.S. DOE Contract DE-AC05-79Et-14503, Final Report, FE-14503-3, November 1983.
4. Canter, D. M., Anal. Chem., 50, 8, 1185 (1978).
5. Taulbee, D. N., Barron, L. S., Roble, T. L., and Hagan, M., 1985, Kentucky Oil Shale Kerogen Studies: Part I. Chemical and Pyrolytic Characterization of Maceral Concentrate Proceedings, 1985 Eastern Oil Shale Symposium, Kentucky Energy Cabinet, Lexington, KY, 291-300.
6. U.S. Bureau of Mines; "The Reserve Base of Bituminous Coal and Anthracite for Underground Mining in the Eastern United States", USBM Information Circular, 8655, 1974.
7. Palmer, J. E., Dutcher, R. R., "Depositional and Structural History of the Pennsylvanian System of the Illinois Basin: Part I. Road Log and Description of Stops", Illinois State Geological Survey Guidebook, S Series 15, 1979.
8. Whaley, P. W., Hester, N. C., Williamson, A. D., Beard, J. G., Pryor, W. A., Potter, P. E., "Depositional Environment of Pennsylvanian Rocks in Western Kentucky", Geological Society of Kentucky Guidebook, 1979.
9. Williams, D. A., Helfrick, C. T., Hower, J. C., Fiene, F. L., Bland, A. E., "Geology of the Amos and Foster Coals of Butler County", Kentucky Geological Society, Series XI, Information Circular, 1987, in press.
10. Hower, J. C., Trinkle, E. J., Bland, A. E., "Petrology, Geochemistry and Minerology of the Springfield (No. 9) and Herrin (No. 11) Coals in Western Kentucky", Kentucky Center for Energy Research Laboratory publication KCERL/85-138, 1985.
11. Trinkle, E. J., Hower, J. C., Wild, G. D., Geological Society of America Bulletin, V. 94, p. 1466, 1983.
12. Smith, G. E., Brant, R. A., "Western Kentucky Coal Resources", Institute for Mining and Minerals Research publication IMMR47-RRR8-80, September 1978.

13. Hoover, D. S., Joshi, S. V., Bland, A. E., Terrible, J. A., Lancet, M. S., "Effect of Feed Coal Variation on Demonstration Plant Performance", DOE/OR/03054-74, September 1983.
14. Sturm G. P., Jr., Pooley, J. E., Thomson, J. S., Woodward, P. W., Vogh, J. W., in Upgrading Coal Liquids, American Chemical Society Symposium Series, 1981, p 1.
15. Davis, A., Spachman, W., Given, P. H., in Energy Sources, Vol. 3, No. 1, Crane, Russach and Co., 1976, p. 55.
16. Whitehurst, D. D., Mitchell, T. D., Forcasiu, M., Dickert, J. J., Jr., "The Nature and Origin of Asphaltenes in Processed Coals", Vol. 2, EPRI AF 12198 Vol. 2, Final Report, 1979.
17. Given, P. H., Cronauer, D. C., Spackman, W., Lovell, H. L., Davis, A., Biswas, B., Fuel, Vol. 54, 34 (1975).
18. Mackowsky, M.-Th., in Stack's Textbook of Coal Petrology, (E. Stack, ed.), Gebrüder Borntraeger, p. 153, 1982.
19. Yokoyama S., Yoshida, R., Narita, H., Kodara, K., Mackawa, Y., Fuel, Vol. 65, p. 164, (1986).
20. Suzuki, T., Yamada, O., Takahashi, Y., Watanabe, Y., Fuel Processing Technology, Vol. 10, p. 33, (1985).
21. Given, P. H., Yamagiuchi, M., Erdemir, H. H., "Dependence of Liquefaction Behavior on Coal Characteristics, Part 7. Synergistic Effects in the Liquefaction of Coal Blends", DOE/PC/40784-T5, February 1985.
22. Mukherjee, D. K., Choudhury, P. B., Fuel, Vol. 55, p. 4 (1976).
23. Peel, R. B., Diaz, J. S., Luengo, C. A., Fuel, Vol. 58, p. 298 (1979).
24. Rao, C. P., Gluskoter, H. J., "Occurrence and Distribution of Minerals in Illinois Coals", Illinois State Survey Circular 476, 1973.
25. Klunder, E. B., Krastman, D. Mima, J. A., "Iron-Catalyzed Coal Liquefaction: Evidence for Isothermal Multiplicity", DOE/PETC/TR-86/4, March 1986.
26. Garg, D., Givens, E. N., Ind. Eng. Chem. Process Des. Dev., Vol. 21, No. 1, p. 113 (1982).
27. Neill, P. H., Given, P. H., "The Dependence of Liquefaction Behavior on Coal Characteristics, Part 6; Relationship of Liquefaction Behavior of a Set of High Sulfur Coals to Chemical Structural Characteristics", DOE/PC/40784-T4, Final Report, September 1984.

28. Hower, J. C., Wild, G. D., Trinkle, E. J., Pollock, J. D., Klapheke, J. G., Pryor, C. A., Graese, A. M., Bayard, D. N., "Petrographic Characterization of Western Kentucky Coals", Institute of Mining and Minerals Research Open File Report, IMMR841112.
29. Mudamburi, Z., Given, P. H., Organic Geochemistry, Vol. 8, No. 6, p. 441 (1985).
30. Shibaoka, M., Fuel, Vol. 60, p. 240 (1981).
31. Shibaoka, M., Fuel, Vol. 64, p. 606 (1985).
32. Yarza, R., Given, P. H., Spackman, W., Davis, A., Fuel, Vol. 59, p. 81 (1980).
33. Shibaoka, M., Stephens, J. F., Russell, N. J., Fuel, Vol. 58, p. 515 (1979).
34. Macphee, J. A., Ciavaglin, L. A., Nandi, B. N., "The International Conference on Coal Science", proceedings, p. 61, 1983.
35. Neavel, R. C., in Coal Science, Vol. 1, (M. L. Gorbaty, J. Larsen, I. Wender, eds.) Academic Press, p. 1, 1982.
36. Grint, A., Mehani, S., Trewhella, M., Crook, M. J., Fuel, Vol. 64, p. 1355, (1985).
37. Brenner, D., Fuel, 64, 167 (1984).
38. Green, T. K., Kovac, J., Brenner, D., and Larsen, J. W., in "Coal Structure", (R. A. Meyers, ed.), Academic Press, pp. 199-282 (1982).
39. Green, T. K. and Larsen, J. W., Fuel, 63, 1538 (1984).
40. Jurkiewicz, A., Marzec, A. and Pislewski, N., Fuel, 61, 647 (1982).
41. Marzec, A., Jurkiewicz, A., and Pislewski, N., Fuel, 62, 996 (1983).
42. Given, P. H., Marzec, A. Barton, W. A., Lynch, L. T., and Gerstein, B. C., Fuel, 65, 155 (1986).
43. Brown, H. R. and Waters, P. L., Fuel, 45, 17 (1966).
44. Brown, H. R. and Waters, P. L., Fuel, 45, 41 (1966).
45. Neavel, R. C., Fuel, 55, 237 (1976).
46. Given, P. H. and Derbyshire, F. J., "The Mobile Phase in Coals: Its Nature and Modes of Release", DOE/PC/60811-1-2, Tech. Prog. Report, February 1984.

47. Collins, C. J., Hagaman, E. W., Jones, R. M., and Raaen, V. F., Fuel, 60, 359 (1981).
48. Ouchi, K., Imata, K., Yamashita, Y., Fuel, 35, 9 (1976).
49. Raj, S., Ph.D. Thesis, Pennsylvania State University, University Park, PA, 1977.
50. Lazarov, L., Zgurovska, E., Angelova, G., Fuel, 50, 338 (1971).
51. Durce, R. A., Shewchyk, Y., Steinhell, S., Fuel, 45, 99 (1966).
52. Dormans, H. N. M., van Krevelen, D. W., Fuel, 39, 276 (1960).
53. Retcofsky, H. L., Applied Spectroscopy, 31, 116 (1977).
54. Derbyshire, F. J., Varghesse, P., Whitehurst, D. D. Fuel, 59, 686 (1980).
55. Meuzelaar, H. L. C., Harper, A. M., Hill, G. R., and Given, P. H., Fuel, 63, 640 (1984).
56. Larsen, J. W., Sams, T. L. and Rogers, B. R., Fuel, 59, 686 (1980).
57. Whitehurst, D. D., Farcasiu, M., Mitchell, T. O., and Dickert, Jr., J. J., "The Nature and Origin of Asphaltenes in Processed Coals, EPRI AF-480, Annual Report, July 1977.
58. Dyrkacz, G. R., Gloomquist, C. A. A. and Ruscic, L. Fuel, 63, 1166 (1984).
59. Shadle, L. J., Jones, D. A., Deno, D. C. and Given, P. H., Fuel, 65, 611 (1986).
60. King, H. H., Dyrkacz, G. R., Winans, R. E., Fuel, 63, 341 (1984).
61. Bishop, M., Ward, D. L., Fuel, 37, 191 (1958).
62. Painter, P. C., Coleman, M. M., Jenkins, R. G., and Walker, P. L., Fuel, 57, 125 (1978).
63. Tarrer, A. R., Guin, J. A., Pitts, W. A., Henley, J. P., Prather, J. W. and Styles, G. A., in "Liquid Fuels from Coal", (Ellington, ed.) Academic Press Inc., New York, NY, 1977.
64. Wright, C. H., and Siverson, D. E., ACS Div. Fuel Chem. Preprints, 16 (2), 568 (1972).
65. Curran, G. P., Struck, R. T., and Morin, E., Ind. Eng. Chem. Process Des. Dev., 6, 166 (1967).
66. Wiser, W. H., Fuel, 47, 475 (1968).

Figure 1. Map of Illinois Basin.

Figure 2. Generalized Stratigraphic Column for Western Kentucky Coals.

#12 - W. Ky #12 Coal
 #11 - W. Ky #11 Coal
 #9 - W. Ky #9 Coal

B - Breckinridge
 A - Amos
 F - Foster

Figure 3. Sample Location Map

Figure 4. Reflectance of Bituminous Coals, Showing Reflectances of Study Lot

Figure 5. Key to Figures 6,7,8,10,11,14,15.

Figure 6. Reflectance Maximum.

Figure 7. Volatile Matter (DAF).

Figure 8. Carbon (DAF).

Figure 9. Van Krevelen Diagram of Samples.

Figure 10. Ash (Dry).

Figure 11. Total Sulfur (DAF).

Figure 12. Sulfur Distribution of the Project Western Kentucky Coals

Figure 13. Petrology of Western Kentucky Coal Samples.

Figure 14. Total Reactive Macerals.

Figure 15. Free Swelling Index.

0 KCERL # 4 GRAPH SYMBOLS

ASPHALTENE + PREASPHALTENE

1	71068	a
2	71069	b
3	71071	c
4	71072	d
5	71092	i
6	71094	j
7	71095	k
8	71097	m
9	71098	n
10	71100	o
11	71144	r
12	71146	s
13	71149	t
14	71154	u
15	71155	v
16	71159	w
17	71170	x
18	71173	y
19	71110	SOLID TRIANGLE

Figure 16. Product Distributions @385°C of W. Ky. #9 Coals.

0 KCERL # 4 GRAPH SYMBOL

ASPHALTENE + PREASPHALTENE

1	71106	+
2	71107	#
3	71074	5
4	71083	9
5	71065	3
6	71109	*
7	71081	7
8	71110	DIAMOND
9	71064	2
10	71066	4
11	71077	6
12	71063	1
13	71082	8
14	71110	SOLID TRIANGLE

Figure 17. Product Distributions @385°C of W. Ky. #11 Coals.

Figure 18. Asphaltene + Preasphaltene Yields vs Conversion @385°C for #9 Coals.

Figure 19. Asphaltene + Preasphaltene Yields vs Conversion @385°C for #11 Coals.

Figure 20. Product Distributions @427°C of W. Ky. #9 Coals.

Figure 21. Product Distributions @427°C of W. Ky. #11 Coals.

Figure 22. Asphaltene + Preasphaltene Yields vs Conversion @ 427°C for #9 Coals.

Figure 23. Asphaltene + Preasphaltene Yields vs Conversion @ 427°C for #11 Coals.

0 KCERL 4 GRAPH SYMBOLS

ASPHALTENE + PREASPHALTENE

1	71068	a
2	71069	b
3	71071	c
4	71072	d
5	71092	i
6	71094	j
7	71095	k
8	71097	m
9	71098	n
10	71100	o
11	71144	r
12	71146	s
13	71149	t
14	71154	u
15	71155	v
16	71159	w
17	71170	x
18	71173	y

OILS + GAS

10M

Figure 24. Product Distributions @445°C of W. Ky. #9 Coals.

0 KCERL 4 GRAPH SYMBOL

ASPHALTENE + PREASPHALTENE

1	71106	+
2	71107	8
3	71074	5
4	71083	9
5	71065	3
6	71109	.
7	71081	7
8	71110	DIAMOND
9	71064	2
10	71066	4
11	71077	6
12	71063	1
13	71082	8

OILS + GAS

10M

Figure 25. Product Distributions @445°C of W. Ky. #11 Coals.

ASPHALTENE + PREASPHALTENE

0 KCERL 0 88 GRAPH
SYMBOL

1	71138	a
2	71139	b
3	71140	c
4	71141	d
5	71181	e
6	71182	f
7	71183	g

OILS + GAS

100

Figure 26. Product Distributions @427°C of Ames Coals.

ASPHALTENE + PREASPHALTENE

0 KCERL 0 88 GRAPH
SYMBOL

1	71177	1
2	71178	2
3	71179	3
4	71180	4

OILS + GAS

100

Figure 27. Product Distributions @427°C of Foster Coals.

Figure 28. Product Distributions @427°C of W. Ky. #12 Coals.

Figure 29. H/C Ratios of Preasphaltenes (385°C) vs Conversion for #9 and # 11 Coals.

Figure 30. H/C Ratios of Asphaltenes (385°C) vs Conversion for #11 and #9 Coals.

Figure 31. H/C Ratios of Preasphaltenes (427°C) vs Conversion for #9 and #11 Coals.

Figure 32. H/C Ratios of Asphaltenes (427°C) vs Conversion for #9 and #11 Coals.

Figure 33. Grams (N+S+O) Per Gram of Preasphaltene (427°C) vs Grams (N+S+O) Per Gram Daf Coal.

Figure 34. Rank Dependence of the Yields of the Extractable Mobile Component.

Figure 35. H/C vs O/C Diagram.

Figure 36. Molecular Weight of the Mobile Component vs the Rank of the Parent Coal.

Figure 37. fa of the Mobile Component by nmr vs Rank of the Parent Coal.

Figure 38. Number of Naphthene Rings Per Average Molecule of the Mobile Component vs the Rank of the Parent Coal.

Figure 39. Pyrolysis mass spectra of three coals of different rank (a) 71095 A (hvAb) (b) 71063 A (hvCb) and (c) 91648 A (subbituminous A).

Figure 40. Pyrolysis mass spectra of three extracted coals of different rank (a) 71095 B (hvAb), (b) 71063 B (hvCb) and (c) 91648 B (subbituminous A).

Figure 41. Description/pyrolysis mass spectra of the extracts of three co different rank (a) 71095 C (hvAb), (b) 71063 C (hvCb) and (c) (subbituminous A).

Figure 42. Factor scores 1 vs Factor scores 2 on whole data set.

Figure 43. Factor scores plot of subset, coals and extracted coals.

Figure 44. Asphaltene + Preasphaltene Conversion @385°C of the Parent Coals.

Figure 45. Asphaltene + Preasphaltene Yields vs Conversion @385°C of Extracted

Figure 46. Asphaltene + Preasphaltene Yields vs Conversion @385°C for Blends.

Figure 47. Parity Plot of the IOM of the Extraction Coal vs the IOM of the Parent Coal.

Figure 48. Comparison of the Sum of the Extracted Coal Conversions and the Extract Yields and the Parent Coal Conversions.

Figure 49. Parity Plot of the IOM of the Blends vs the IOM of the Parent Coals.

Figure 50. H/C Ratios vs Rank of the Parent Coal.

Figure 51. Conversion of the Maceral Concentrates vs Reactor Temperature.

Table 1

Variables Examined in the Regression Analysis of the Feed
Coal Properties and Liquefaction Data

<u>Feed Coal Properties</u>	<u>Liquefaction Data at 385°C, 427°C, 445°C</u>
R _o max	Conversion
V.M. (daf)	Oils
Pyritic S (daf)	Asphaltenes
Organic S (daf)	Preasphaltenes
Total S (daf)	Distillates (oils + gases)
C (daf)	SRC (asphaltenes + preasphaltenes)
FSI	
H/C atomic ratio	
O/C atomic ratio	
Total reactive macerals (vitrinites plus liptinites)	

TABLE 2. ANALYSIS OF THE EXTRACTABLE MOBILE COMPONENT

0 PARENT COAL KCERL #	1 PARENT COAL SEAM	2 C	3 H	4 N	5 S	6 O(DIF)	7 CONDENSED AROMATICS	8 NONCONDENSED AROMATICS	9 CYCLIC ALPHA	10 ALKYL ALPHA	11 CYCLIC BETA	
1	71071	89	83.46	6.68	1.56	1.66	6.64	0.1430	0.0701	0.1324	0.1467	0.1315
2	71072	89	82.30	7.11	1.47	1.51	7.61	0.1844	0.0392	0.1422	0.1699	0.1192
3	71092	89	83.53	6.81	1.71	1.74	6.21	0.1822	0.0646	0.1446	0.1220	0.1246
4	71094	89	82.90	6.66	1.62	1.62	7.20	0.2535	0.0289	0.1807	0.1118	0.1228
5	71095	89	82.98	6.97	1.45	2.35	6.25	0.1750	0.0398	0.1701	0.1360	0.1218
6	71155	89	83.86	6.85	1.23	1.73	6.33	0.2084	0.0587	0.1417	0.1213	0.1245
7	71159	89	84.57	6.63	1.31	1.51	5.98	0.2119	0.0587	0.1468	0.1180	0.1287
8	71146	89	83.51	6.82	1.51	1.92	6.24					
9	71149	89	82.51	6.80	1.54	1.41	7.71					
10	71144	89	83.99	6.75	1.48	1.79	5.99					
11	71063	811	82.18	6.65	1.24	1.94	7.99	0.1675	0.0465	0.1714	0.1485	0.1297
12	71064	811	81.59	6.87	1.14	2.33	8.07	0.1402	0.0608	0.1353	0.1358	0.1375
13	71077	811	83.32	6.67	1.47	1.37	7.17	0.1709	0.0723	0.1251	0.1469	0.1319
14	71081	811	81.98	6.37	1.52	1.76	8.37	0.1617	0.0421	0.1427	0.1356	0.1344
15	71110	811	82.41	6.59	1.60	1.59	7.81	0.1919	0.0640	0.1553	0.1436	0.1334
16	71109	811	84.05	6.49	1.15	2.14	6.17	0.1977	0.0591	0.1565	0.1269	0.1326
17	71106	811	83.10	6.43	1.30	1.42	7.75					

0 PARENT COAL KCERL #	12 ALKYL BETA	13 GAMMA	14 MW VPO	19 % EXTRACT	20 Pa nmr	21 QUINAPHTHENE RINGS nmr	
1	71071	0.2018	0.1745	523	8.82	0.66	0.63
2	71072	0.1699	0.1752	570	10.69	0.65	0.74
3	71092	0.2226	0.1394	499	4.00	0.68	0.47
4	71094	0.1854	0.1169	580	3.80	0.70	0.44
5	71095	0.1913	0.1660	504	4.18	0.65	0.60
6	71155	0.1998	0.1456	501	5.69	0.70	0.56
7	71159	0.1943	0.1416	589	7.47	0.68	0.51
8	71146			569	8.29		
9	71149			609	6.46		
10	71144			583	8.66		
11	71063	0.1698	0.1686	591	9.27	0.67	0.67
12	71064	0.2083	0.1821	570	10.80	0.64	0.75
13	71077	0.1785	0.1744	495	8.31	0.68	0.61
14	71081	0.2182	0.1653	556	9.76	0.67	0.60
15	71110	0.1644	0.1474	569	8.05	0.68	0.61
16	71109	0.1749	0.1523	534	9.53	0.70	0.54
17	71106			574	9.30		

TABLE 1. ANALYSIS OF EXTRACTED COALS

0 PARENT COAL KCERL #	1 VM(DAF)	2 FC(DAF)	3 C DAF	4 H(DAF)	5 N(DAF)	6 TS(DAF)	7 O(DAF) BY DIFFERENCE
1 71063	39.51	60.49	77.30	5.03	1.67	5.17	9.27
2 71064	42.25	57.75	78.42	5.17	1.60	3.95	10.80
3 71071	42.26	57.74	77.23	5.03	2.02	6.34	8.82
4 71072	42.25	57.75	79.27	5.11	2.02	2.84	10.76
5 71077	39.92	60.08	75.30	4.76	1.88	9.19	8.79
6 71081	42.32	57.68	77.57	5.11	1.93	3.06	12.33
7 71092	40.86	59.14	80.19	5.38	2.05	3.44	8.94
8 71094	40.40	59.60	78.85	5.17	1.85	5.98	7.16
9 71095	42.44	57.56	78.70	5.28	1.86	8.69	5.47
10 71110	41.15	58.85	74.63	4.82	1.88	9.16	9.51
11 71149	39.97	60.03	77.92	4.66	1.65	2.91	12.85

TABLE 4. LIQUEFACTION DATA @ 385 C FOR THE PARENT COALS, EXTRACTED COALS AND THE BLENDS

0 SOURCE COAL KCERL #	1 PARENT COAL IOM	2 EXTRACTED COAL IOM	3 BLEND IOM	4 PARENT COAL CONVERSION	5 EXTRACTED COAL CONVERSION	6 BLEND CONVERSION	7 PARENT COAL GAS
1	71064	35.25	27.15	17.32	64.75	72.85	82.58
2	71063	20.87	47.72	47.54	79.13	52.28	52.46
3	71077	33.03	52.50	54.83	66.97	47.50	45.17
4	71081	44.39	54.77	42.49	55.61	45.23	57.51
5	71110	18.53	51.60	42.62	81.47	48.40	57.38
6	71071	39.16	46.64	46.67	60.84	53.36	53.33
7	71072	42.24	52.39	50.81	57.76	47.61	49.19
8	71092	21.43	60.45	38.30	78.57	39.55	61.70
9	71094	45.62	56.91	51.75	54.38	43.09	48.25
10	71095	17.52	34.03	17.22	82.48	65.97	82.78
11	71149	49.47	49.71	38.80	50.53	50.29	61.20
11	71149	49.47	49.71	38.80	50.53	50.29	61.20

0 SOURCE COAL KCERL #	8 EXTRACTED COAL GAS	9 BLEND GAS	10 PARENT COAL OIL	11 EXTRACTED COAL OIL	12 BLEND OIL	13 PARENT COAL ASPHALTENE	14 EXTRACTED COAL ASPHALTENE
1	71064	1.48	1.41	10.55	14.07	12.88	33.52
2	71063	2.07	1.46	7.53	10.65	15.50	23.91
3	71077	1.47	1.57	11.12	12.76	16.92	23.85
4	71081	1.14	1.44	9.16	10.16	12.43	29.17
5	71110	1.74	1.60	11.57	19.33	17.10	26.88
6	71071	1.53	1.29	16.11	11.65	15.71	20.36
7	71072	1.42	1.26	12.38	13.63	11.60	25.04
8	71092	0.97	0.90	10.61	10.61	9.62	25.63
9	71094	0.76	0.79	10.01	9.51	10.48	26.64
10	71095	0.59	0.51	12.10	7.16	16.63	34.26
11	71149	2.46	2.16	10.02	11.11	11.00	16.53
11	71149	2.46	2.16	10.02	11.11	11.00	16.53

0 SOURCE COAL KCERL #	15 BLEND ASPHALTENE	16 PARENT COAL PREASPHALTENE	17 EXTRACTED COAL PREASPHALTENE	18 BLEND PREASPHALTENE
1	71064	24.17	19.78	33.81
2	71063	23.29	46.75	8.45
3	71077	20.27	31.35	13.17
4	71081	24.79	16.53	17.48
5	71110	20.58	42.42	11.53
6	71071	22.57	23.51	19.25
7	71072	16.29	19.47	17.04
8	71092	23.14	41.88	6.55
9	71094	23.52	17.12	8.27
10	71095	19.32	35.56	28.97
11	71149	18.33	23.22	18.57
11	71149	18.33	23.22	18.57

TABLE 5. CHEMICAL AND PETROGRAPHIC ANALYSIS

0	1 BRECKINRIDGE PARENT	2 BRECKINRIDGE DEMINEALIZED	3 BRECKINRIDGE BITUMINITE	4 71077 PARENT	5 71077 DEMINEALIZED	6 71077 VITRINITE	7 71071 PARENT	8 71071 DEMINEALIZED
1 SEAM	BRECKINRIDGE			111			89	
2								
3 DRY BASIS:								
4								
5 ASH	6.41	2.81	2.03	9.65	5.64	0.53	11.71	3.61
6 VM	69.50	67.35	70.83	37.71	10.00	39.37	38.50	19.18
7 FC	24.07	29.85	27.13	52.64	54.36	60.11	50.14	57.22
8								
9								
10 DAF BASIS:								
11								
12 VM	74.28	69.29	72.30	41.74	42.39	39.50	43.21	40.61
13 FC	25.72	30.70	27.70	58.26	57.61	60.42	56.79	59.16
14 C	80.68	80.88	81.59	76.96	79.52	84.55	76.80	77.71
15 H	0.51	7.99	0.44	5.37	5.27	5.23	5.41	5.10
16 N	2.13	2.07	1.79	1.63	1.51	1.59	1.90	1.68
17 S	1.81	2.10	1.03	6.19	6.54	2.01	6.76	5.52
18 O (DIFF)	6.89	6.96	7.15	9.85	7.16	6.62	9.14	9.77
19 ORG S	0.55			3.35			3.81	
20								
21								
22 PETROGRAPHY:								
23								
24 VITRINITES	14.10	7.50	11.00	92.50	96.10	98.50	90.90	90.20
25 INERTINITES	2.10	0.70	0.20	3.50	2.20	0.40	7.10	9.00
26 LIPTINITES	0.20	0.00	0.00	4.00	1.00	1.10	2.00	0.80
27								
28 BITUMINITE	83.20	91.80	88.80					
29								
30 Ro max.	0.55	-	-	0.69			0.54	

TABLE 5. CHEMICAL AND PETROGRAPHIC ANALYSIS

1 SEAM	89			89				
2								
3 DRY BASIS:								
4								
5 ASH	0.53	8.09	3.06	0.52	15.24	5.61	1.04	
6 VM	39.60	38.36	37.76	38.34	37.06	38.27	38.34	
7 FC	59.87	53.55	59.18	61.14	47.70	56.12	60.62	
8								
9								
10 DAF BASIS:								
11								
12 VM	39.81	11.74	38.95	38.54	43.73	40.54	38.74	
13 FC	60.19	38.26	61.05	61.46	56.27	59.46	61.26	
14 C	82.39	80.03	82.28	84.82	76.63	81.54	86.21	
15 H	5.30	5.23	5.14	5.15	5.10	5.29	5.31	
16 N	1.74	1.74	2.08	1.99	1.70	1.82	1.96	
17 S	2.20	5.11	4.79	2.11	8.43	6.67	2.31	
18 O (DIFF)	8.37	7.89	5.70	5.92	8.14	4.69	4.21	
19 ORG S		2.38			3.27			
20								
21								
22 PETROGRAPHY:								
23								
24 VITRINITES	96.40	87.30	90.20	98.00	89.50	92.40	98.00	
25 INERTINITES	2.60	10.00	8.40	1.80	7.40	5.40	1.80	
26 LIPTINITES	1.00	2.70	1.40	0.20	3.10	2.20	0.20	
27								
28 BITUMINITE								
29								
30 No max.		0.79			0.77			

Table 6

Molecular Weights of Asphaltenes Obtained from
the Liquefaction of a Bituminite and a Vitrinite Concentrate

	<u>Breckinridge Bituminite</u>	<u>KCERL 71071 Vitrinite</u>
at 385°C	827	582
at 427°C	1538	530
at 445°C	943	575

APPENDIX I. ANALYSIS OF WESTERN KENTUCKY COALS

1	2	3	4	5	6	7	8	9	10	11	12	13	14
KCERL	SEAM	SAMPLE TYPE	ASH AS RECEIVED	VM DAF	FC DAF	SULFATE S DAF	PYRITIC S DAF	ORGANIC S DAF	TOTAL S DAF	CARBON DAF			
1	71106	011	BENCH	7.59	43.09	56.91	0.70	0.59	3.04	4.33	77.94		
2	71107	011	BENCH	4.62	45.23	54.77	0.27	1.09	1.49	3.96	78.60		
3	71074	011	BENCH	15.75	42.59	57.41	0.72	2.35	1.00	6.07	76.04		
4	71083	011	BENCH	9.19	44.60	55.40	0.82	2.13	2.00	4.95	76.17		
5	71065	011	BENCH	9.97	43.36	56.64	0.42	2.55	3.65	6.62	77.78		
6	71109	011	BENCH	9.52	43.44	56.56	0.57	3.57	3.40	7.54	76.29		
7	71081	011	BENCH	4.43	43.23	56.77	0.17	0.64	2.21	3.01	78.28		
8	71110	011	BENCH	16.11	43.48	56.52	0.98	2.25	3.74	6.97	76.05		
9	71064	011	BENCH	9.56	47.47	52.53	0.06	1.06	3.11	4.23	78.80		
10	71066	011	BENCH	9.39	44.00	56.00	0.32	2.46	3.06	5.84	77.68		
11	71077	011	BENCH	9.06	41.74	58.26	0.75	2.09	3.35	6.19	76.96		
12	71063	011	CHANNEL	10.65	45.48	54.52	0.15	2.50	2.54	5.19	78.33		
13	71082	011	BENCH	10.13	42.58	57.42	0.50	1.47	2.16	4.12	77.09		
14	71057	011	BENCH	6.00	43.27	56.73	0.30	1.15	2.83	4.28	77.08		
15	71058	011	BENCH	14.69	44.06	55.94	1.19	2.88	3.93	8.00	73.49		
16	71059	011	BENCH	12.76	44.83	55.17	0.79	2.45	3.69	6.93	74.91		
17	71075	011	BENCH	7.26	41.01	58.99	0.68	1.36	2.10	4.14	78.62		
18	71076	011	BENCH	10.12	41.38	58.62	0.51	0.95	2.07	3.53	79.42		
19	71078	011	BENCH	9.17	41.86	58.14	0.51	1.44	2.44	4.39	77.96		
20	71079	011	BENCH	12.38	41.29	58.71	0.33	2.09	2.47	4.89	78.67		
21	71105	011	BENCH	10.89	44.00	56.00	0.67	2.14	3.59	6.41	76.95		
22	71185	011	BENCH	3.78	45.89	54.11	0.03	0.35	2.25	2.63	80.37		
23	71187	011	BENCH	8.07	44.76	55.24	0.45	2.78	2.47	5.70	78.18		
24	71060	011	CHANNEL	11.32	44.47	55.53	0.82	1.64	2.85	5.32	75.53		
25	71061	011	CHANNEL	11.87	44.97	55.03	0.61	1.39	2.63	4.63	76.45		
26	71055	011	CHANNEL	11.52	44.72	55.28	0.82	2.35	2.62	5.80	75.04		
27	71056	011	BENCH	11.02	47.23	52.77	0.48	1.04	2.82	4.33	76.91		
28	71080	011	BENCH	9.06	44.74	55.26	0.28	1.46	2.30	4.05	78.71		
29	71108	011	BENCH	7.33	43.65	56.35	0.37	1.03	2.48	3.88	78.84		
30	71184	011	CHANNEL	9.42	45.01	54.99	0.34	2.03	2.94	5.30	78.66		
31	71186	011	BENCH	7.33	42.65	57.35	0.07	0.53	2.17	2.77	80.84		
32	71188	011	BENCH	11.19	42.88	57.12	0.43	1.11	3.35	4.88	78.82		
33	71189	011	BENCH	22.76	43.97	56.03	0.19	2.54	2.80	5.54	79.00		
34	71068	09	CHANNEL	9.36	44.81	55.19	0.07	1.92	2.05	4.04	78.97		
35	71069	09	BENCH	11.23	43.82	56.18	0.27	1.38	1.94	3.59	78.69		
36	71071	09	BENCH	10.62	43.21	56.79	0.35	2.60	3.81	6.76	76.80		
37	71072	09	BENCH	9.04	42.90	57.10	0.14	0.53	1.91	2.57	79.19		
38	71073	09	BENCH	10.74	42.60	57.40	0.11	1.01	2.09	3.20	78.66		
39	71089	09	CHANNEL	10.14	43.33	56.67	0.26	1.78	2.67	4.71	79.78		
40	71090	09	CHANNEL	10.80	43.15	56.85	0.36	2.74	2.80	5.90	78.08		
41	71091	09	BENCH	14.98	44.17	55.83	0.12	1.11	2.64	3.87	81.53		
42	71092	09	BENCH	6.60	43.40	56.60	0.15	0.77	2.31	3.24	81.21		
43	71094	09	BENCH	7.80	41.74	58.26	0.32	2.41	2.38	5.11	80.03		
44	71095	09	BENCH	14.80	43.73	56.27	0.68	4.48	3.27	8.43	76.63		
45	71096	09	BENCH	16.06	43.43	56.57	0.62	4.03	3.32	7.97	77.78		
46	71097	09	CHANNEL	11.90	43.88	56.12	0.30	2.09	2.96	5.36	80.13		
47	71098	09	CHANNEL	10.86	44.20	55.80	0.44	1.55	2.78	4.78	77.43		
48	71100	09	BENCH	10.58	45.69	54.31	0.78	1.26	3.53	5.56	76.88		
49	71102	09	BENCH	6.93	43.75	56.25	0.46	0.87	2.79	4.12	77.61		
50	71104	09	BENCH	12.57	43.62	56.38	0.49	0.85	2.10	3.44	78.04		
51	71144	09	BENCH	5.26	42.99	57.01	0.09	0.45	2.31	2.85	79.30		
52	71146	09	BENCH	13.71	43.95	56.05	0.31	1.68	2.60	4.59	78.28		
53	71149	09	BENCH	5.48	43.96	56.04	0.09	0.75	1.79	2.63	80.41		

UPDATE 12/1/86

APPENDIX 1. ANALYSIS OF WESTERN KENTUCKY COALS

0	KCERL 0	15 HYDROGEN DAF	16 NITROGEN DAF	17 OXYGEN DAF	18 BTU DAF	20 FST	21 VIT	22 PVT	23 FUS	24 S+	5 MIC	26 MAC	27 EX	28 RES
1	71106	5.28	1.55	10.89	14115	2.5	87.1	0.3	4.5	3.1	0.7	0.0	3.4	0.9
2	71107	5.54	1.70	10.20	14621	3.0	89.8	0.8	3.4	2.8	0.5	0.2	2.1	0.4
3	71074	5.27	1.71	10.93	14168	3.0	86.5	1.1	4.7	2.3	0.9	0.0	3.8	0.7
4	71083	5.46	1.69	11.73	14156	2.5	91.7	0.2	2.5	1.9	1.1	0.0	2.4	0.2
5	71065	5.49	1.65	8.45	13691	2.0	86.3	1.0	5.2	3.1	1.5	0.0	2.4	0.5
6	71109	5.26	1.71	9.19	14483	2.5	89.2	2.2	2.2	4.7	1.7	0.6	2.1	0.3
7	71081	5.52	1.70	11.49	14357	3.5	91.9	0.1	2.5	1.5	1.4	0.1	2.0	0.5
8	71110	5.29	1.78	9.91	13972	2.0	81.6	2.5	8.3	3.1	1.0	0.1	3.1	0.3
9	71064	5.85	1.70	9.42	14229	4.5	88.9	1.3	1.8	1.5	1.5	0.0	4.0	1.0
10	71066	5.42	1.74	9.32	14104	3.5	92.1	0.0	2.1	3.1	0.8	0.0	1.6	0.3
11	71077	5.37	1.63	9.85	14149	4.0	90.3	2.2	1.7	1.3	0.4	0.1	2.4	1.6
12	71063	5.46	1.71	9.31	15913	5.0	89.4	0.4	2.8	2.6	1.2	0.1	3.1	0.4
13	71082	5.42	1.59	11.78	14059	2.5	89.1	0.1	5.1	2.3	0.3	0.1	2.3	0.7
14	71057	5.26	1.57	11.81	14102	3.5	92.3	0.1	2.6	2.3	1.3	0.0	1.2	0.2
15	71058	5.07	1.48	11.97	13513	1.5	93.3	0.0	1.7	2.4	0.5	0.1	1.5	0.5
16	71059	5.24	1.54	11.38	13787	1.5	89.7	0.0	3.3	3.8	1.1	0.1	1.9	0.1
17	71075	5.23	1.73	10.29	14286	3.0	88.4	0.5	5.7	2.5	1.0	0.1	1.3	0.5
18	71076	5.39	1.71	9.94	14475	3.5	89.8	0.1	4.4	2.2	0.4	0.0	2.1	1.0
19	71078	5.41	1.70	10.54	14345	3.5	89.7	1.1	4.2	1.6	0.5	0.0	2.5	0.4
20	71079	5.46	1.76	9.22	14524	3.0	88.9	1.8	3.4	3.3	0.4	0.1	1.5	0.6
21	71105	5.27	1.67	9.69	14366	2.0	86.8	1.2	3.9	3.4	1.0	0.1	3.2	0.4
22	71165	5.67	1.53	9.81	14536	2.0	89.4	0.0	1.8	4.9	1.6	0.0	2.2	0.1
23	71167	5.39	1.58	9.15	14169	2.5	91.2	0.0	2.0	3.4	1.0	0.1	2.2	0.1
24	71060	5.21	1.51	12.44	13661	2.0	89.8	0.3	3.2	3.1	0.4	0.2	2.9	0.1
25	71061	5.27	1.55	12.09	13913	2.5	85.0	4.3	3.4	1.2	1.1	0.1	4.5	0.4
26	71055	5.21	1.49	12.46	13783	2.0	92.5	0.4	2.1	2.3	0.6	0.2	1.7	0.2
27	71056	5.43	1.49	11.84	14059	3.0	94.1	0.3	0.8	0.6	0.6	0.2	2.8	0.6
28	71080	5.55	1.65	10.05	14538	3.0	93.6	0.0	2.1	0.9	1.0	0.1	2.2	0.1
29	71108	5.42	1.71	10.14	14532	3.5	88.3	0.1	2.8	4.2	1.3	0.2	2.1	1.0
30	71104	5.41	1.59	9.04	14220	2.5	91.8	0.6	2.8	2.3	0.6	0.0	1.7	0.2
31	71106	5.41	1.52	9.46	14470	3.0	87.3	0.0	5.1	4.5	0.1	0.0	2.6	0.4
32	71108	5.35	1.57	9.38	14185	2.5	87.1	1.0	4.8	5.0	0.7	0.0	1.1	0.3
33	71109	5.40	1.59	8.47	14160	2.5	86.4	0.6	3.7	5.3	0.9	0.3	2.2	0.6
34	71068	5.45	1.93	9.59	14745	3.8	81.0	0.7	6.0	5.1	2.7	0.4	3.6	0.5
35	71069	5.52	1.84	10.33	14060	2.0	73.5	0.0	9.7	8.8	2.6	0.1	4.2	1.1
36	71071	5.41	1.90	9.14	13875	2.5	90.9	0.0	2.9	2.4	1.4	0.2	1.8	0.2
37	71072	5.44	2.00	10.80	14112	3.5	89.2	0.0	6.1	2.1	0.5	0.0	2.0	0.1
38	71073	5.37	1.94	10.82	14044	3.5	87.0	1.6	4.6	1.8	0.9	0.1	4.0	0.0
39	71089	5.36	1.72	8.43	14638	7.0	83.2	3.8	4.8	2.9	0.7	0.1	3.3	1.2
40	71090	5.24	1.77	9.01	14762	7.0	84.0	4.3	4.9	3.6	1.2	0.1	1.3	0.6
41	71091	5.57	1.77	7.26	14920	5.5	83.0	3.9	5.0	6.0	0.7	0.3	2.4	0.7
42	71092	5.42	1.76	8.38	15036	5.0	76.0	1.9	8.0	6.4	2.1	0.0	4.1	1.5
43	71094	5.23	1.74	7.89	14845	8.0	79.8	7.5	7.8	1.4	0.6	0.2	1.7	1.0
44	71095	5.10	1.70	8.14	14405	6.5	86.7	2.8	3.9	2.4	1.0	0.1	2.5	0.6
45	71096	5.15	1.68	7.42	14559	7.0	82.6	5.8	5.1	2.3	0.9	0.5	1.9	0.9
46	71097	5.34	1.72	7.45	14836	7.0	77.6	6.7	6.3	2.7	2.4	0.0	3.4	0.9
47	71098	5.29	1.70	10.81	13814	3.0	86.4	0.1	8.1	8.0	1.7	0.1	3.7	0.9
48	71100	5.45	1.79	10.32	14210	1.5	69.8	0.9	5.1	8.8	10.0	1.3	4.5	0.4
49	71102	5.49	1.80	10.98	14183	3.0	92.1	0.0	2.8	1.8	0.6	0.0	2.3	0.4
50	71104	5.50	1.80	11.23	14331	2.0	89.6	0.0	3.6	4.1	0.8	0.1	1.8	0.0
51	71144	5.61	1.94	10.26	14561	3.5	74.4	1.0	6.4	12.4	3.2	0.0	2.6	0.0
52	71146	5.50	1.95	9.69	14282	3.0	88.2	1.0	3.6	4.8	0.7	0.0	1.6	0.1
53	71149	5.35	1.88	9.74	14277	1.5	67.0	0.1	8.8	15.8	3.3	0.9	4.6	0.2

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APPENDIX I. ANALYSIS OF WESTERN KENTUCKY COALS

0 KCERL 8 19 REFL

1	71106	0.597
2	71107	0.560
3	71074	0.737
4	71083	0.594
5	71065	0.540
6	71109	0.620
7	71081	0.561
8	71110	0.660
9	71064	0.550
10	71066	0.570
11	71077	0.689
12	71063	0.560
13	71082	0.590
14	71057	0.550
15	71058	0.532
16	71059	0.547
17	71075	0.673
18	71076	0.657
19	71078	0.673
20	71079	0.677
21	71105	0.570
22	71185	0.510
23	71187	0.550
24	71060	0.546
25	71061	0.531
26	71055	0.552
27	71056	0.537
28	71080	0.559
29	71108	0.580
30	71184	0.540
31	71186	0.540
32	71188	0.540
33	71189	0.570
34	71068	0.540
35	71069	0.590
36	71071	0.540
37	71072	0.580
38	71073	0.557
39	71089	0.750
40	71090	0.770
41	71091	0.740
42	71092	0.750
43	71094	0.790
44	71095	0.770
45	71096	0.770
46	71097	0.760
47	71098	0.570
48	71100	0.656
49	71102	0.590
50	71104	0.548
51	71144	0.491
52	71146	0.469
53	71149	0.430

UPDATE 12/1/86

APPENDIX I. ANALYSIS OF WESTERN KENTUCKY COALS

0	KCERL #	2	SEAM	3	SAMPLE TYPE	4	ASH AS RECEIVED	6	VM DAF	7	FC DAF	8	SULFATE S DAF	9	PYRITIC S DAF	10	ORGANIC S DAF	11	TOTAL S DAF	14	CARBON DAF
54	71154	09		BENCH		30.03		47.83		52.17		0.00		1.47		2.27		3.74		84.99	
55	71155	09		BENCH		6.80		42.68		57.32		0.00		0.10		2.08		2.18		81.15	
56	71159	09		BENCH		26.53		45.79		54.21		0.20		0.87		4.72		13.78		78.33	
57	71170	09		CHANNEL		8.96		44.15		55.85		0.27		1.15		2.73		4.15		78.69	
58	71173	09		BENCH		5.19		44.85		55.15		0.08		0.55		2.60		3.23		79.50	
59	71070	09		BENCH		6.13		43.80		56.20		0.21		1.00		2.05		3.26		78.40	
60	71150	09		BENCH		5.93		44.48		55.52		0.13		0.78		2.44		3.35		79.91	
61	71152	09		CHANNEL		11.17		45.36		54.64		0.18		1.59		1.82		3.60		81.02	
62	71153	09		CHANNEL		10.83		44.13		55.87		0.03		1.36		2.51		3.90		82.45	
63	71161	09		CHANNEL		10.45		44.24		55.76		0.28		1.86		2.31		4.45		79.30	
64	71165	09		BENCH		9.06		45.14		54.86		0.34		2.35		3.48		6.16		77.82	
65	71169	09		BELT		28.61		45.68		54.32		0.71		1.92		3.45		6.09		76.37	
66	71172	09		BENCH		6.63		44.16		55.84		0.15		0.60		2.78		3.53		79.76	
67	71156	09		BENCH		8.10		45.92		54.08		0.06		1.72		3.85		5.62		82.16	
68	71157	09		BENCH		8.84		43.78		56.22		0.03		1.21		2.31		3.55		83.21	
69	71158	09		BENCH		11.24		44.61		55.39		0.05		1.76		3.18		4.98		81.93	
70	71101	09		BENCH		5.43		44.59		55.41		0.74		0.97		2.81		4.52		77.22	
71	71103	09		BENCH		10.30		43.93		56.10		0.18		2.20		2.80		5.18		78.96	
72	71147	09		CHANNEL		9.17		44.22		55.78		0.10		0.87		1.85		2.82		80.18	
73	71171	09		BENCH		11.67		44.62		55.38		0.25		1.11		2.94		4.30		78.83	
74	71099	09		BENCH		24.57		46.01		53.99		0.73		1.76		3.05		5.55		76.61	
75	71175	09		BENCH		11.60		43.91		56.09		0.41		2.23		2.57		5.21		78.10	
76	71162	09		BENCH		26.43		46.29		53.71		0.20		1.95		2.41		4.59		77.49	
77	71163	09		BENCH		12.88		44.85		55.15		0.27		2.18		2.11		4.56		78.27	
78	71164	09		BENCH		6.05		43.73		56.27		0.14		0.63		1.85		2.63		80.21	
79	71166	09		BENCH		13.50		44.08		55.92		0.47		3.75		2.45		6.67		77.80	
80	71167	09		BENCH		12.15		44.17		55.83		0.16		1.23		1.92		3.30		80.08	
81	71168	09		BENCH		10.73		43.95		56.05		0.17		1.49		1.97		3.63		79.88	
82	71093	09		BENCH		6.02		43.28		56.72		0.24		1.35		2.51		4.10		80.97	
83	71176	09		BENCH		15.04		44.46		55.54		0.42		3.71		4.40		8.53		76.89	
84	71148	09		BENCH		14.87		46.10		53.90		0.17		1.35		1.70		3.22		79.59	
85	71151	09		BENCH		10.55		45.14		54.76		0.09		0.79		2.35		3.23		80.80	
86	71174	09		BENCH		6.16		43.39		56.61		0.08		0.28		2.85		2.51		80.42	
87	71142	09		CHANNEL		10.42		43.85		56.05		0.33		1.34		2.84		4.51		78.35	
88	71143	09		BENCH		10.25		43.75		56.25		0.10		0.55		2.46		3.10		79.18	
89	71067	012		CHANNEL		18.65		45.47		54.53		0.37		1.63		2.38		4.39		77.09	
90	71084	012		BENCH		18.60		46.06		53.94		1.03		2.17		3.81		6.21		76.93	
91	71085	012		BENCH		13.60		43.42		56.58		0.43		0.69		2.84		3.17		78.78	
92	71086	012		BENCH		10.94		43.02		56.98		0.18		0.60		1.49		2.67		78.61	
93	71087	012		BENCH		12.74		43.54		56.46		0.17		0.55		1.94		2.65		79.43	
94	71088	012		BENCH		17.97		44.33		55.67		0.42		1.07		2.11		3.60		77.41	
95	71190	012		CHANNEL		13.83		46.47		53.53		0.27		2.39		3.43		6.09		78.10	
96	71191	012		BENCH		10.34		48.02		51.98		0.36		2.77		2.53		5.46		77.76	
97	71192	012		BENCH		9.33		44.45		55.55		0.12		0.98		2.36		3.46		79.77	
98	71193	012		BENCH		12.50		44.31		55.69		0.13		1.21		2.52		3.85		79.85	
99	71194	012		BENCH		20.73		45.40		54.60		0.46		3.42		4.81		8.69		77.83	
100	71195	012		BENCH		17.50		45.42		54.58		0.30		1.25		2.78		4.32		80.18	
101	71138	AKOS		CHANNEL		1.98		40.30		59.70		0.01		0.13		0.76		0.91		82.05	
102	71139	AKOS		BENCH		1.80		41.50		58.50		0.02		0.22		0.81		1.04		81.87	
103	71141	AKOS		BENCH		1.34		40.44		59.56		0.01		0.09		0.66		0.70		81.68	
104	71181	AKOS		CHANNEL		1.67		39.45		60.55		0.06		0.35		0.91		1.32		80.73	
105	71182	AKOS U		BENCH		6.47		42.35		57.65		0.11		0.48		1.03		1.58		80.06	
106	71183	AKOS L		BENCH		1.53		39.57		60.43		0.02		0.16		0.82		0.99		80.76	

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APPENDIX I. ANALYSIS OF WESTERN KENTUCKY COALS

0	KCERL	8	15 HYDROGEN DAF	16 NITROGEN DAF	17 OXYGEN DAF	18 BTU DAF	20 FSI	21 VIT	22 PVT	23 FUS	24 SF	25 MIC	26 MAC	27 EX	28 RES
54	71154		6.16	1.90	3.13	15250	4.0	88.3	1.1	0.8	1.8	0.1	0.0	5.1	2.6
55	71155		5.67	1.85	6.16	15149	7.5	71.0	4.4	5.4	10.4	4.0	1.3	1.4	0.1
56	71159		5.51	1.95	0.43	14533	5.0	91.3	1.7	1.3	3.6	0.3	0.0	1.8	0.0
57	71170		5.42	1.92	9.82	14600	5.5	87.9	2.0	2.8	4.0	1.3	0.1	1.7	0.2
58	71173		5.54	1.93	9.79	14817	4.5	83.5	3.2	3.2	5.1	1.5	0.0	2.1	0.4
59	71070		5.42	1.90	11.03	14175	3.5	84.5	0.1	6.4	3.8	1.4	0.1	3.5	0.2
60	71150		5.42	1.95	9.36	14329	3.5	82.9	1.4	4.9	6.5	1.2	0.1	2.5	0.5
61	71152		5.35	1.94	8.09	14313	2.0	85.5	1.1	4.4	6.3	0.5	0.0	2.1	0.1
62	71153		5.54	1.92	6.19	14859	7.0	82.9	7.7	3.9	3.9	0.5	0.0	0.8	0.3
63	71161		5.51	1.92	8.82	14559	3.5	82.7	2.2	3.7	6.2	2.6	0.1	2.2	0.3
64	71165		5.37	1.87	8.77	14498	4.0	85.1	0.5	3.0	5.3	2.1	0.1	3.2	0.7
65	71169		5.50	1.95	10.01	13897	3.5	86.0	1.2	4.2	5.1	1.3	0.0	2.0	0.2
66	71172		5.51	1.93	9.28	14814	3.5	74.6	3.1	5.3	9.0	5.0	0.3	2.0	0.7
67	71156		5.55	1.92	4.76	15047	8.0	76.8	9.0	2.6	6.6	2.1	0.5	1.9	0.5
68	71157		5.50	1.88	5.77	15063	8.0	85.2	4.6	4.1	4.6	0.3	0.0	1.2	0.0
69	71158		5.55	1.90	5.64	14921	7.5	88.6	4.4	1.9	3.1	0.3	0.0	1.7	0.0
70	71101		5.52	1.86	10.88	14028	2.5	86.2	0.4	3.6	3.7	1.4	0.1	4.0	0.6
71	71103		5.51	1.85	8.50	14367	3.0	89.5	2.5	2.2	2.6	1.5	0.3	1.3	0.1
72	71167		5.44	1.92	9.64	14202	1.5	81.2	2.3	4.4	7.6	2.0	0.2	2.2	0.1
73	71171		5.65	1.86	9.37	14747	4.0	82.8	5.0	1.9	6.6	1.6	0.1	2.0	0.0
74	71099		5.57	1.82	10.45	14048	1.0	86.6	0.0	3.2	6.6	0.8	0.0	2.4	0.4
75	71175		5.32	1.90	9.47	14485	4.0	83.3	6.7	3.7	3.7	0.3	0.2	2.0	0.1
76	71162		5.72	1.94	10.26	14523	2.0	90.7	5.4	0.9	1.5	0.3	0.1	0.8	0.3
77	71163		5.55	1.88	9.74	14544	3.5	78.7	3.8	3.3	8.3	2.8	0.6	2.2	0.3
78	71164		5.53	1.86	9.77	14716	3.5	66.4	3.2	5.6	16.2	4.1	0.4	4.0	0.1
79	71166		5.21	1.82	8.50	14384	3.5	90.0	1.0	4.0	3.0	0.7	0.1	1.2	0.0
80	71167		5.47	1.93	9.22	14679	4.0	89.6	0.8	2.7	2.4	1.8	0.0	2.3	0.4
81	71168		5.51	1.90	9.08	14711	2.5	92.5	1.5	2.2	2.3	0.5	0.0	1.0	0.0
82	71093		5.41	1.74	7.78	14816	7.0	79.8	5.1	6.7	1.4	1.5	0.3	4.0	1.2
83	71176		5.34	1.92	7.32	14346	4.0	91.7	2.4	1.6	2.1	0.1	0.0	1.8	0.3
84	71140		5.62	1.90	9.47	14219	1.5	84.3	2.0	2.7	6.9	1.6	0.1	2.2	0.2
85	71151		5.23	1.90	8.76	14232	3.0	84.5	3.7	3.1	5.9	1.0	0.0	1.8	0.0
86	71170		5.37	1.89	9.81	14818	5.5	82.0	5.7	5.0	3.9	0.5	0.2	2.2	0.3
87	71142		5.54	1.89	9.72	14265	3.0	86.9	2.0	2.6	4.9	1.6	0.0	1.8	0.2
88	71163		5.67	1.91	10.13	14457	3.5	82.9	2.3	2.4	8.4	2.3	0.0	1.4	0.3
89	71067		5.52	1.71	11.29	14138	4.0	92.4	0.3	1.4	3.0	0.2	0.0	2.1	0.6
90	71084		5.62	1.88	9.43	13983	1.5	93.4	0.0	2.6	1.9	0.4	0.0	1.2	0.5
91	71085		5.68	1.86	10.52	14176	2.0	92.5	0.9	2.4	1.4	0.3	0.0	2.2	0.3
92	71086		5.66	1.86	11.19	14479	3.5	92.9	0.1	1.8	2.6	0.2	0.2	1.7	0.5
93	71087		5.47	1.87	10.57	14376	3.5	91.3	0.6	3.4	1.8	0.4	0.0	2.4	0.1
94	71088		5.56	1.95	11.47	14183	2.5	94.2	0.4	2.4	0.8	0.1	0.0	2.0	0.1
95	71190		5.49	1.57	8.75	14231	3.5	88.1	1.7	2.8	4.4	1.8	0.1	1.7	0.2
96	71191		5.59	1.60	9.39	14298	3.0	88.8	2.0	2.7	3.3	0.9	0.1	2.1	0.1
97	71192		5.54	1.67	9.55	14486	3.0	89.0	3.7	2.3	2.3	0.4	0.3	1.9	0.1
98	71193		5.51	1.66	9.13	14489	4.0	91.4	0.7	2.5	2.8	0.6	0.0	1.5	0.5
99	71194		5.35	1.58	6.55	14166	2.5	88.1	0.6	4.2	3.6	0.2	0.1	2.1	1.1
100	71195		5.41	1.64	8.44	14398	3.5	84.3	0.4	6.8	6.2	0.9	0.0	1.3	0.9
101	71196		5.43	1.93	9.67	14994	2.5	81.2	1.1	2.8	2.2	2.8	0.0	9.3	0.6
102	71198		5.53	1.95	9.68	14979	2.5	77.9	0.5	0.9	0.6	5.6	0.2	12.3	2.0
103	71141		5.47	2.00	10.14	14975	3.0	83.1	1.0	1.7	1.3	5.0	0.1	7.2	0.6
104	71101		5.40	2.06	10.49	14732	2.5	86.2	3.9	0.7	0.9	3.3	0.1	3.6	1.3
105	71102		5.61	2.02	10.72	14739	2.5	89.3	4.1	0.2	0.3	0.5	0.0	5.0	0.6
106	71103		5.37	2.03	10.84	14755	2.0	84.8	6.7	0.5	0.9	1.6	0.1	5.6	0.6

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APPENDIX I. ANALYSIS OF WESTERN KENTUCKY COALS

0 KCERL 0 29 REFL

54	71154	0.710
55	71155	0.730
56	71159	0.700
57	71170	0.614
58	71173	0.640
59	71070	0.540
60	71150	0.475
61	71152	0.439
62	71153	0.724
63	71161	0.560
64	71165	0.575
65	71169	0.616
66	71172	0.629
67	71156	0.733
68	71157	0.739
69	71158	0.721
70	71101	0.550
71	71103	0.557
72	71147	0.443
73	71171	0.618
74	71099	0.560
75	71175	0.633
76	71162	0.556
77	71163	0.592
78	71164	0.570
79	71166	0.574
80	71167	0.574
81	71168	0.585
82	71093	0.760
83	71176	0.634
84	71148	0.469
85	71151	0.469
86	71174	0.662
87	71142	0.489
88	71143	0.501
89	71067	0.570
90	71084	0.541
91	71085	0.595
92	71086	0.571
93	71087	0.627
94	71088	0.623
95	71190	0.470
96	71191	0.470
97	71192	0.510
98	71193	0.530
99	71194	0.520
100	71195	0.490
101	71138	0.549
102	71139	0.597
103	71141	0.569
104	71181	0.639
105	71182	0.619
106	71183	0.679

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APPENDIX 2. LIQUEFACTION DATA OF WESTERN KENTUCKY COALS

0 KCERL #	2 SEAM	3 SAMPLE TYPE	5 ASH AS RECEIVED	6 VM DAF	7 FC DAF	8 SULFATE S DAF	9 PYRITIC S DAF	11 ORGANIC S DAF	13 TOTAL S DAF	14 CARBON DAF
107	71177	FOSTER CHANNEL	7.11	41.01	58.99	0.12	0.88	0.83	1.83	80.33
108	71178	FOSTER U BENCH	4.94	42.51	57.49	0.49	2.49	1.39	4.38	78.49
109	71179	FOSTER M BENCH	5.83	41.53	58.47	0.12	1.04	1.15	2.31	80.63
110	71180	FOSTER L BENCH	6.79	40.00	60.00	0.05	0.13	0.83	1.00	81.22

0	KCERL #	15 HYDROGEN DAF	16 NITROGEN DAF	17 OXYGEN DAF	18 BTU DAF	20 PSI	21 VIT	22 PVT	23 FUS	24 SP	25 MIC	26 MAC	27 EX	28 RES
107	71177	5.40	1.90	10.54	14660	3.5	79.1	0.9	5.5	4.3	4.0	0.2	5.9	0.1
108	71178	5.35	1.89	9.90	14428	1.5	88.8	0.6	3.2	2.4	1.0	0.0	3.9	0.1
109	71179	5.38	1.93	9.74	14691	2.5	74.6	2.4	6.1	7.0	3.8	0.0	6.0	0.1
110	71180	5.35	1.96	10.47	14733	4.0	79.6	1.3	6.1	6.4	2.7	0.1	3.5	0.1

0 KCERL # 29 REFL

107	71177	0.354
108	71178	0.577
109	71179	0.596
110	71180	0.590

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APPENDIX 2. LIQUEFACTION DATA OF WESTERN KENTUCKY COALS

0	KCERL	1	SEAM	2	SAMPLE TYPE	3	GAS 305 C	4	OIL 305 C	5	ASPHALTENES 305 C	6	PREASPHALTENES 305 C	7	CONVERSION 305 C	8	GAS 427 C	9	OIL 427 C	10	ASPHALTENE 427 C
1	71106	011	BENCH	1.40	12.84	29.05	7.61	50.50	1.68	24.66	39.22										
2	71107	011	BENCH	0.78	11.19	31.02	8.38	51.37	1.58	23.26	45.96										
3	71074	011	BENCH	0.10	12.08	28.11	11.02	52.01	1.46	22.77	45.81										
4	71083	011	BENCH	0.93	12.77	28.86	9.86	52.42	1.92	25.56	44.13										
5	71065	011	BENCH	0.58	15.24	28.24	8.74	52.90	1.28	29.21	45.53										
6	71109	011	BENCH	0.74	11.58	27.20	11.22	53.74	2.00	24.30	42.99										
7	71081	011	BENCH	0.75	9.16	29.17	16.53	55.61	2.03	22.94	40.03										
8	71110	011	BENCH	0.79	11.94	32.57	13.46	58.76	1.56	24.03	41.30										
9	71064	011	BENCH	0.80	10.55	33.52	19.78	64.75	1.96	21.92	46.25										
10	71066	011	BENCH	0.16	14.99	24.75	26.37	66.57	1.37	28.02	46.71										
11	71077	011	BENCH	0.15	11.12	23.85	31.35	66.97	1.90	18.05	40.68										
12	71063	011	CHANNEL	0.93	7.53	23.91	46.75	79.12	1.13	21.12	41.48										
13	71082	011	BENCH	0.75	14.18	28.04	38.60	81.57	1.72	24.82	44.64										
14	71057	011	BENCH						2.57	27.45	32.69										
15	71058	011	BENCH						2.50	32.00	34.42										
16	71059	011	BENCH						2.01	34.30	31.56										
17	71075	011	BENCH						1.64	29.70	43.00										
18	71076	011	BENCH						1.65	23.32	31.99										
19	71078	011	BENCH						1.54	23.28	39.30										
20	71079	011	BENCH						1.66	21.63	34.84										
21	71105	011	BENCH						1.54	24.96	46.08										
22	71185	011	BENCH						1.65	26.90	38.04										
23	71187	011	BENCH						1.54	28.74	38.42										
24	71060	011	CHANNEL						2.44	30.17	28.91										
25	71061	011	CHANNEL						2.15	28.34	28.53										
26	71055	011	CHANNEL						2.46	28.38	35.22										
27	71056	011	BENCH						2.75	28.35	39.87										
28	71080	011	BENCH						1.93	23.82	46.26										
29	71108	011	BENCH						1.72	21.87	41.02										
30	71184	011	CHANNEL						1.51	27.01	33.12										
31	71186	011	BENCH						1.97	24.76	34.45										
32	71188	011	BENCH						1.71	40.79	22.14										
33	71189	011	BENCH						0.53	27.59	38.86										
34	71068	09	CHANNEL	1.12	10.23	16.87	36.53	64.75	1.53	23.93	26.90										
35	71069	09	BENCH	1.81	9.89	20.09	43.16	74.95	1.97	20.29	38.25										
36	71071	09	BENCH	0.86	16.11	20.36	23.51	60.84	1.95	26.03	40.10										
37	71072	09	BENCH	0.87	12.38	25.04	19.47	57.76	1.96	28.14	36.48										
38	71073	09	BENCH						1.82	26.02	33.88										
39	71089	09	CHANNEL						1.45	23.58	35.33										
40	71090	09	CHANNEL						1.48	21.27	38.51										
41	71091	09	BENCH						2.07	29.07	48.73										
42	71092	09	BENCH	0.45	10.61	25.63	41.88	78.57	1.22	19.79	39.95										
43	71094	09	BENCH	0.61	10.01	26.64	17.12	54.38	2.31	19.04	32.39										
44	71095	09	BENCH	0.56	12.10	34.26	35.56	82.48	2.00	19.76	42.41										
45	71096	09	BENCH						1.85	25.64	34.91										
46	71097	09	CHANNEL	0.71	11.73	19.81	20.20	52.45	1.65	20.99	36.40										
47	71098	09	CHANNEL	0.70	11.20	21.59	13.67	47.16	1.70	21.42	32.10										
48	71100	09	BENCH	0.65	10.74	26.31	40.30	78.00	1.65	24.78	43.53										
49	71102	09	BENCH						1.59	24.74	36.90										
50	71104	09	BENCH						1.43	25.40	35.28										
51	71144	09	BENCH	0.86	11.86	25.29	5.37	43.38	2.19	23.47	32.71										
52	71146	09	BENCH	0.96	13.98	24.37	13.04	52.35	2.52	26.34	29.11										
53	71149	09	BENCH	0.76	10.02	16.53	23.22	50.53	2.42	22.74	26.39										
54	71154	09	BENCH	0.57	13.33	19.90	32.49	66.29	1.41	27.15	39.42										

LIQUEFACTION DATA OF WESTERN KENTUCKY COALS

0	KCERL #	11 PREASPHALTENE 427 C	12 CONVERSION 427 C	13 GAS 445 C	14 OIL 445 C	15 ASPHALTENE 445 C	16 PREASPHALTENE 445 C	17 CONVERSION 445 C
1	71106	29.16	94.72	2.99	30.82	45.26	12.85	91.92
2	71107	22.32	93.12	3.19	31.10	40.39	19.42	94.10
3	71074	9.96	80.00	2.31	35.52	44.48	11.14	90.45
4	71083	16.20	87.81	2.68	34.13	48.10	11.05	95.87
5	71065	4.86	80.88	2.21	34.99	38.17	6.95	82.32
6	71109	23.99	93.28	2.58	32.83	42.57	18.63	94.61
7	71081	29.58	94.58	2.78	31.39	43.06	17.94	95.17
8	71110	19.32	86.31	2.54	39.14	33.42	12.62	87.72
9	71064	24.60	94.73	3.15	32.68	41.71	18.19	95.73
10	71066	12.97	89.07	2.14	36.12	39.68	15.72	93.66
11	71077	31.53	92.16	2.54	29.89	37.59	21.67	91.69
12	71063	25.72	89.75	2.63	30.48	39.97	13.90	86.98
13	71082	13.27	84.45	2.39	34.80	35.60	20.78	93.57
14	71057	28.70	91.41					
15	71058	23.43	92.35					
16	71059	21.66	89.53					
17	71075	20.34	90.68					
18	71076	34.77	91.73					
19	71078	31.27	95.39					
20	71079	33.45	91.58					
21	71105	20.82	93.40					
22	71185	26.80	93.39					
23	71187	26.74	95.44					
24	71060	30.98	92.50					
25	71061	33.15	92.17					
26	71055	20.24	86.30					
27	71056	13.30	84.27					
28	71080	23.82	95.83					
29	71108	31.83	96.44					
30	71184	22.09	83.73					
31	71186	24.86	86.04					
32	71188	23.81	88.45					
33	71189	17.66	84.64					
34	71068	37.00	89.36	2.88	32.13	35.50	17.21	87.72
35	71069	17.39	77.90	2.85	23.91	33.65	19.61	80.02
36	71071	22.38	90.46	3.01	38.40	31.30	20.51	93.22
37	71072	24.48	91.06	2.86	25.20	38.25	20.73	87.04
38	71073	30.56	92.28					
39	71089	27.76	88.12					
40	71090	27.16	88.42					
41	71091	11.88	91.75					
42	71092	24.57	85.53	2.31	26.08	37.34	17.30	83.03
43	71094	38.71	88.45	2.97	27.43	39.52	19.53	89.45
44	71095	26.80	90.97	2.56	31.80	40.09	18.18	92.63
45	71096	27.36	89.76					
46	71097	22.61	81.65	2.44	31.11	32.56	21.97	88.08
47	71098	28.09	83.31	2.44	29.79	33.89	18.37	84.49
48	71100	16.21	86.17	2.89	44.42	31.45	12.48	91.24
49	71102	29.17	92.40					
50	71104	30.07	92.18					
51	71144	21.72	80.09	2.86	32.57	33.58	10.90	79.91
52	71146	26.61	84.58	2.92	15.11	54.86	10.11	83.00
53	71149	20.00	71.55	2.72	31.77	29.00	7.21	70.70
54	71154	28.44	96.42	2.24	34.74	40.44	12.85	90.27

APPENDIX 2. LIQUEFACTION DATA OF WESTERN KENTUCKY COALS

0	KCERL	0	1	SEAM	2	SAMPLE TYPE	3	GAS 105 C	4	OIL 305 C	5	ASPHALTENES 105 C	6	PREASPHALTENES 105 C	7	CONVERSION 105 C	8	GAS 427 C	9	OIL 427 C	10	ASPHALTENE 427 C
55	71155	19			BENCH		0.44		10.05		22.01		11.82		44.32		1.52		20.64		39.95	
56	71159	19			BENCH		0.48		14.60		26.87		27.64		69.59		1.36		28.09		39.02	
57	71170	19			CHANNEL		0.57		12.20		20.26		9.65		42.60		1.77		28.01		29.62	
58	71173	19			BENCH		0.58		11.57		31.09		10.72		53.94		1.40		36.81		33.40	
59	71070	19			BENCH												1.79		30.14		33.50	
60	71150	19			BENCH												2.32		30.14		27.02	
61	71152	19			CHANNEL												2.36		25.50		29.47	
62	71153	19			CHANNEL												1.43		22.77		36.52	
63	71161	19			CHANNEL												1.61		26.16		34.72	
64	71165	19			BENCH												2.11		26.44		30.92	
65	71169	19			BELT												2.32		30.59		32.85	
66	71172	19			BENCH												1.75		24.20		39.12	
67	71156	19			BENCH												1.78		29.03		32.72	
68	71157	19			BENCH												1.53		22.42		37.11	
69	71158	19			BENCH												1.40		28.25		28.92	
70	71101	19			BENCH												1.97		13.57		50.43	
71	71103	19			BENCH												1.99		27.34		32.88	
72	71147	19			CHANNEL												2.27		23.97		35.02	
73	71171	19			BENCH												1.92		27.12		39.27	
74	71099	19			BENCH												1.71		27.57		36.57	
75	71175	19			BENCH												1.84		23.25		42.09	
76	71162	19			BENCH												1.74		31.23		40.35	
77	71163	19			BENCH												1.70		29.28		43.10	
78	71164	19			BENCH												2.25		27.11		31.79	
79	71166	19			BENCH												2.08		27.00		40.03	
80	71167	19			BENCH												1.95		26.39		41.54	
81	71168	19			BENCH												1.99		24.92		40.75	
82	71093	19			BENCH												3.10		23.54		32.52	
83	71176	19			BENCH												2.23		26.84		42.10	
84	71148	19			BENCH												2.22		29.03		36.76	
85	71151	19			BENCH												2.33		29.41		32.57	
86	71174	19			BENCH												1.75		23.96		33.11	
87	71142	19			CHANNEL												2.44		26.79		30.74	
88	71143	19			BENCH												2.38		24.28		36.57	
89	71067	012			CHANNEL		1.01		13.98		15.16		55.90		86.00		1.72		28.86		32.52	
90	71084	012			BENCH												1.70		27.91		42.00	
91	71085	012			BENCH		0.44		11.04		31.05		8.96		51.89		1.81		20.96		39.92	
92	71086	012			BENCH												1.71		24.09		30.48	
93	71087	012			BENCH												2.04		25.07		31.37	
94	71088	012			BENCH												1.82		33.67		41.26	
95	71190	012			CHANNEL												1.93		27.60		41.52	
96	71191	012			BENCH												1.58		35.38		32.66	
97	71192	012			BENCH												1.87		25.34		38.70	
98	71193	012			BENCH												1.81		28.95		34.82	
99	71194	012			BENCH												1.90		32.06		38.72	
100	71195	012			BENCH												1.83		26.39		38.17	
101	71138	AMOS			CHANNEL												1.71		18.51		21.49	
102	71139	AMOS			BENCH												1.78		22.16		24.39	
103	71141	AMOS			BENCH		0.70		12.09		15.35		17.52		45.66		1.64		21.78		37.96	
104	71181	AMOS			CHANNEL												1.70		20.93		33.94	
105	71182	AMOS U			BENCH												1.57		23.08		29.58	
106	71183	AMOS L			BENCH												1.70		20.58		30.83	
107	71177	FOSTER			CHANNEL		0.57		11.86		19.40		23.74		55.37		1.49		22.07		33.82	
108	71178	FOSTER U			BENCH												1.69		24.47		34.46	

APPENDIX 2. LIQUEFACTION DATA OF WESTERN KENTUCKY COALS

0	KCERL	11 PREASPHALTENE 427 C	12 CONVERSION 427 C	13 GAS 445 C	14 OIL 445 C	15 ASPHALTENE 445 C	16 PREASPHALTENE 445 C	17 CONVERSION 445 C
55	71155	20.54	82.65	2.46	27.14	42.73	13.93	86.26
56	71159	20.95	89.42	1.94	37.38	38.42	13.56	91.30
57	71170	25.23	84.63	1.82	30.89	40.14	13.03	85.88
58	71173	18.09	89.78	2.53	31.12	42.32	13.88	89.85
59	71070	29.60	95.11					
60	71150	31.17	90.65					
61	71152	32.59	89.92					
62	71153	25.74	86.46					
63	71161	28.11	90.60					
64	71165	32.96	92.43					
65	71169	28.53	94.29					
66	71172	19.63	84.70					
67	71156	25.72	89.25					
68	71157	21.37	82.43					
69	71158	35.51	94.16					
70	71101	27.92	93.89					
71	71103	32.95	95.16					
72	71147	30.26	91.52					
73	71171	21.20	89.51					
74	71099	16.08	81.93					
75	71175	16.97	84.15					
76	71162	18.40	91.72					
77	71163	15.32	89.48					
78	71164	21.61	82.76					
79	71166	23.91	93.02					
80	71167	19.73	89.61					
81	71168	27.58	95.24					
82	71093	31.16	90.32					
83	71176	24.33	95.50					
84	71148	16.37	84.38					
85	71151	25.42	89.73					
86	71174	34.02	92.84					
87	71142	26.61	86.58					
88	71143	21.33	84.56					
89	71067	25.38	88.48	2.34	35.73	28.51	24.22	90.80
90	71084	10.05	81.66					
91	71085	22.97	85.66	2.56	31.40	36.19	19.15	89.30
92	71086	36.10	92.38					
93	71087	35.36	93.84					
94	71088	8.70	85.45					
95	71190	8.01	79.06					
96	71191	23.90	93.52					
97	71192	27.09	93.00					
98	71193	28.14	93.72					
99	71194	12.66	85.34					
100	71195	13.22	79.61					
101	71138	49.92	91.63					
102	71139	45.58	93.91					
103	71141	25.39	86.77	2.45	33.13	35.49	20.39	91.46
104	71181	24.99	81.18					
105	71182	25.35	79.58					
106	71183	27.25	80.38					
107	71177	28.26	85.64	2.20	27.42	38.64	17.33	85.59
108	71178	34.12	94.74					

APPENDIX 2. LIQUEFACTION DATA OF WESTERN KENTUCKY COALS

0 KCERL #	1 SEAM	2 SAMPLE TYPE	3 GAS 385 C	4 OIL 385 C	5 ASPHALTENES 385 C	6 PREASPHALTENES 385 C	7 CONVERSION 385 C	8 GAS 427 C	9 OIL 427 C	10 ASPHALTENE 427 C
109	71179	FOSTER M BENCH						1.82	22.00	34.75
110	71180	FOSTER L BENCH	0.67	11.17	18.46	20.08	50.38	1.60	22.38	41.59

0 KCERL #	11 PREASPHALTENE 427 C	12 CONVERSION 427 C	13 GAS 445 C	14 OIL 445 C	15 ASPHALTENE 445 C	16 PREASPHALTENE 445 C	17 CONVERSION 445 C
109	71179	21.97	80.54				
110	71180	13.09	78.66	2.37	28.23	44.67	15.89
							91.16

APPENDIX 3. LIQUEFACTION DATA OF MACERALS

0 MACERAL	1 BRECKINRIDGE PARENT	2 BRECKINRIDGE DEMINERALIZED	3 BRECKINRIDGE BITUMINITE	4 71077 PARENT	5 71077 DEMINERALIZED	6 71077 VITRINITE	8 71071 PARENT	9 71071 DEMINERALIZED
1 0385C								
2 GAS	0.92	0.63	0.66	0.65	0.69	0.77	0.86	1.29
3 OIL	11.32	11.92	8.80	11.12	17.13	14.52	16.11	13.21
4 ASPHALTENE	12.09	10.30	5.94	23.85	19.54	10.38	20.36	23.13
5 PREASPHALTENE	13.44	18.25	12.22	31.35	6.13	6.03	23.51	22.41
6 IOM	62.23	58.90	72.38	33.03	56.51	68.30	39.16	39.96
7								
8 CONVERSION	37.77	41.10	27.62	66.97	43.49	31.70	60.84	60.04
9								
10								
11								
12 0427C								
13 GAS	1.71	1.49	2.82	1.64	1.56	1.66	1.95	3.38
14 OIL	31.07	37.36	31.02	24.33	29.67	21.79	26.03	24.25
15 ASPHALTENE	29.05	25.19	30.33	46.29	32.58	32.29	40.10	37.30
16 PREASPHALTENE	10.43	8.25	5.13	19.75	16.50	7.06	22.38	27.47
17 IOM	27.74	27.71	30.70	7.99	19.69	37.20	9.54	7.60
18								
19 CONVERSION	72.26	72.29	69.30	92.01	80.31	62.80	90.46	92.40
20								
21								
22								
23 0445C								
24 GAS	2.06	3.82	1.53	2.54	2.10	2.19	3.01	4.62
25 OIL	52.15	68.19	58.40	29.59	38.53	28.51	38.40	32.39
26 ASPHALTENE	31.36	14.81	28.17	37.59	33.93	29.23	31.30	36.27
27 PREASPHALTENE	5.94	6.43	6.78	21.67	4.82	2.22	20.51	18.29
28 IOM	8.49	6.76	5.12	8.31	20.62	37.85	6.78	8.43
29								
30 CONVERSION	91.51	93.24	94.88	91.69	79.38	62.15	93.22	91.57

APPENDIX 3. LIQUEFACTION DATA OF MACERALS

0 MACERAL	10 71071 VITRINITE	12 71094 PARENT	13 71094 DEMINERALIZED	14 71094 VITRINITE	16 71095 PARENT	17 71095 DEMINERALIZED	18 71095 VITRINITE
1 #385C							
2 GAS	1.61	0.61	1.40	1.06	0.56	0.44	0.72
3 OIL	9.86	10.01	9.75	7.86	12.10	12.31	8.10
4 ASPHALTENE	23.64	26.64	26.40	16.34	34.26	28.18	21.92
5 PREASPHALTENE	17.67	17.12	12.39	25.41	35.56	25.73	23.43
6 IOM	47.22	85.62	50.06	49.33	17.52	33.34	44.83
7							
8 CONVERSION	52.78	54.38	49.94	50.67	82.48	66.65	55.17
9							
10							
11							
12 #427C							
13 GAS	3.14	2.31	2.94	2.38	2.00	3.57	2.27
14 OIL	21.61	35.04	20.44	18.24	19.76	22.28	19.99
15 ASPHALTENE	31.40	32.39	34.88	34.76	42.41	41.64	33.90
16 PREASPHALTENE	39.61	38.71	30.60	39.31	26.80	24.71	40.98
17 IOM	4.24	11.55	11.14	5.31	9.03	7.80	2.86
18							
19 CONVERSION	95.76	88.45	88.86	94.69	91.97	92.20	97.14
20							
21							
22							
23 #445C							
24 GAS	3.93	2.97	3.97	3.39	2.56	3.99	3.37
25 OIL	29.05	27.43	27.25	46.79	31.80	29.75	26.79
26 ASPHALTENE	33.78	39.52	41.63	20.12	40.09	41.28	37.63
27 PREASPHALTENE	28.22	19.53	15.74	23.47	18.18	16.62	27.83
28 IOM	5.02	10.55	11.43	6.23	7.37	8.36	4.38
29							
30 CONVERSION	94.98	89.44	88.57	93.77	92.63	91.64	95.62

TECHNOLOGY ASSESSMENT AND FORECASTING

October 1, 1985 - December 31, 1986

Syracuse University

Barry Bozeman
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Title: Task VI. Technology Assessment and Forecasting

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Period: October 1, 1985 - December 31, 1986

THE EFFECTS OF SUPPORT HIATUS ON DIRECT COAL LIQUEFACTION DEVELOPMENT*

The purpose of this concluding chapter is to distill the information provided by each of the perspective chapters--economic policy, technological, and generally, historical--and draw broad conclusions. These conclusions represent, in a sense, a synthesis of the various perspectives taken.

A number of assumptions were made about the role of these conclusions in the study. First, as mentioned above, it was assumed that the conclusions should have considerable breadth. Each of the preceding chapters presents conclusions and there is no wish to present merely a summary of the conclusions drawn previously. Yet, at the same time, it is desirable that the conclusions presented here encompass the major points presented in the preceding chapters. Naturally, any synthesis requires subsidiary knowledge. Finally, the focus is on conclusions that have some potential policy relevance. Had the purpose of this study been purely historical the conclusions presented might be somewhat different and might focus a bit more on the role of unique events. But the concern here is to provide conclusions that seem a valid reading of the history of DCL development but, at the same time, have implications for public policy.

There are six chief conclusions presented or, more accurately, five conclusions and one overarching theme. It is perhaps useful to summarize these conclusions before discussing them in more detail.

*This is the summary chapter from a 10 chapter volume giving the results of a retrospective technology assessment for direct coal liquefaction that will be issued as a supplement to this report.

1. **Pioneering Processes Cannot be Assessed Like Conventional Technologies.** Problems in management of plants, in engineering, in equipment maintenance have been viewed as extraordinary, but in fact they should be expected and accepted as routine. Standards of technical efficiency applied to pioneering processes and plants require different standards.

2. **DCL is Best Viewed as Government Sheltered High Technology Development (not industry development).** Direct coal liquefaction (DCL) development policy has been premised on government-business partnership and the building up of DCL as market-competitive industry. DCL should be developed whether or not industry is interested and should be rationalized in national security/energy security terms. Short or intermediate-term competitiveness with the price of oil should be a less relevant consideration. Policies should be similar to those used to build the computer industry: overspecification of performance at cost-plus, guaranteed purchase for government stockpiles, procurement-based incentives.

3. **Information Management Should be Improved.** Currently several DCL technologies have developed to the point that are considered commercial. Yet at the same time they are not commercially viable in a market driven environment. They cannot and through incremental improvements they will not overcome the factor of two differences in the price of commercial fuel. If DCL is constrained to operate in a market driven environment only basic new developments will save the concept of liquid fuels directly from coal. One key is to use current information more effectively and to encourage cross-fertilization among DCL researchers and others working on separate but potentially relevant problems.

4. **Resources have been Spread too Thin: Small Increments Spread Out Over Multiple Projects.** Limited resources have been spread too thin. The result is that not enough attention has been given to sustained development of the strongest candidate technologies.

5. **Invest in Contingency Planning.** DCL policy has typically been developed in the context of the immediate events -- current crisis, current energy availability, current federal budgetary climate. DCL and synfuels generally require longer-range thinking and contingency planning.

Overarching Theme: The Hiatus Effect. The constant changing of policy and the on-again-off-again nature of support for DCL have undermined development efforts. DCL development requires some long-run, sustained development activity.

1. PIONEERING PROCESSES CANNOT BE ASSESSED LIKE CONVENTIONAL TECHNOLOGIES

Throughout the development of DCL two points have been particularly troublesome: (1) it has never been "competitive" with the price of oil; (2) pilot plant, demonstration, and maintenance costs have been "excessive." In the ensuing section we consider the problems with the competitiveness criterion; here we suggest that the excessive operational costs have been misinterpreted.

The government experience in developing high technology in synthetic fuels has not paralleled the high technology development role in space or defense. Consider the case of computer technology. Many observers seem to feel that the federal government played a central role in early and intermediate development of computers "overspecification" of quality control and materials standards, by procurement policies guaranteeing sales and, most relevant to the present point, by maintaining expectations appropriate to the state-of-the-science at a given point in development.¹ One might argue that the federal government could afford a more tolerant attitude about the technical efficiency and pay-off of computers because of their enormous commercial potential. But this would be an inaccurate interpretation of the early history of government support for computers -- early forecasts implied that the world market for mainframe computers would never exceed an installed base of 500.²

In any discussion of DCL it is important to remember that not a single full-scale plant has ever existed in the U.S. Nonetheless, evaluative standards for pilot plants have sometimes been almost as demanding as one would expect for a fully-developed, commercialized technology. While there have, indeed, been instances of cost-overruns, inefficiency, and dominance of pork barrel politics, many of the pilot plants have perhaps been judged by an unduly harsh standard. In development of novel defense technologies it has been traditionally assumed that one standard of efficiency is required for judging production and another for prototype development. In the case of DCL this seems not to have been the case. In large measure, this rigidity has to do with the fact that the concern, throughout the history of DCL development, has been with the establishment of an industry rather than just the establishment of the technology (see argument below).

In some respects the most important object lesson for the development of coal liquefaction is the South African SASOL plants. Early on, the South Africans picked a viable technology (presumably they could have picked among several), invested heavily with no expectation of quick return, nourished the technology, were patient with early operational problems, and supported the cost of the resultant fuel. This same option was, theoretically, open to the U.S. but the U.S. chose instead to provide for much more limited development of a variety of technologies, none with sustained effort. The experiences with many of the pilot plants constructed in the U.S. have not, in fact, been that different from the early experiences of the South Africans with the SASOL plants. But the South Africans committed to the technology with the result

that it had long-term pay-off. While there are several problems with the South African analogy,³ one point is clearly relevant: DCL development requires considerable tolerance for the early technical and operational problems associated with pilot plants.

2. DCL IS BEST VIEWED AS GOVERNMENT SHELTERED HIGH TECHNOLOGY DEVELOPMENT

In our view the attempt to develop a DCL-based industry has been well-intentioned but, in some respects, misguided. At this point, and into the immediate future, synthetic fuels options of virtually every variety are best viewed from the standpoint of energy security. DCL is not presently important from a market standpoint but it is important as a public good, in the same sense that national defense is provided as a public good. It is impossible to put a price on the value of national defense and it is not reasonable to seek to match the provision of national defense services and products to a competitive market. The public goods characteristics of DCL are considerable. Energy security has enormous "spill-over effects;" it defies conventional pricing and confers benefits not easily captured in full by investors and producers. For all of these reasons, reliance on a strategy of industry development and price competition is wrongheaded.

This is not to say that government should seek a monopoly over DCL and become the primary developer. Industry is needed to produce DCL but not for the sake of developing a product that rises or falls in a competitive market. DCL development is not unlike nuclear submarine development. The ludicrousness of requiring defense contractors to market nuclear submarines to private consumers is clear enough. However, there has been no hesitation in expecting that DCL should deliver products that will be marketed chiefly to private consumers. The problem is that the chief value at this point is not to any particular set of consumers but to all consumers, and that value is not just fuel but energy security.

We agree with the prevailing opinion of experts interviewed for this project that DCL support should be aimed at producing energy reserves and that the government should guarantee the price at a level somewhat commensurate to the value of the product to energy security. From this perspective, the price of oil is not crucial. If we assume that oil is scarce, or even finite, then it only remains to judge the collective value of energy security. In our view, that value is quite high, far exceeding the cost of the price of oil. Supports for development of DCL should consider these shadow prices and guarantee a price adequate to ensure industry participation.

3. INFORMATION MANAGEMENT SHOULD BE IMPROVED

There are sound arguments for accelerating scientific investigations pertinent to DCL, but there is also a need to make more effective use of current research. The concern about information management is of two types.

Support for DCL research has been discontinuous. One of the many negative impacts of discontinuous development has been the loss or inefficiency in the production of knowledge. There are avoidable start-up costs associated with some projects. Few of the projects begun in the past several years have been radical departures so disconnected from previous work as to have little relevance to it. In some instances this has led to a degree of "re-learning" and stymied progress. To be sure, much of the relevant work is published and unpublished papers are much better documented and stored than in the past. What is lost, however, is not so much the basic knowledge produced but the "know how" requisite for DCL research, development, and demonstration. Persons working on projects develop valuable ad hoc approaches to solving technical problems, they develop decision heuristics and they develop expertise with equipment and ancillary resources. This knowledge is rarely conveyed in formal information sources and, thus, is either lost or diminished by on-again-off-again project support. This problem is a small piece of the hiatus effect discussed below and the solution is, conceptually, straightforward: some level of sustained effort.

Another information management problem has nothing to do with the hiatus effect. Cross-fertilization of scientific knowledge may be quite important to the development of DCL. The experts interviewed for this project reached no consensus as to the most likely locus and type of breakthroughs that might be expected for DCL. However, at least some believed that DCL will progress from either a basic science base or from knowledge, basic or applied, developed for some purpose other than use in DCL. Presently there is effective management of information clearly relevant to DCL. The challenge is to deal with information that is produced by persons unconcerned about DCL but may nonetheless be vital to the development of DCL. Case histories in invention and innovation have shown consistently that major contributions are often made by scientists and technologists far removed from the field that is advanced.⁴ DCL research currently is more insular than it need be. There is a need to broaden the net cast for information. This can be accomplished in a number of ways but one of the most effective is to expand the informal information networks of which DCL researchers are a part. The formal information channels currently in place appear adequate, but the informal information channels and "invisible colleges" of DCL researchers seem less well developed than for many scientific areas. Steps need to be taken to expand the coverage and use of informal scientific and technical information networks relevant, or even potentially relevant, to DCL.⁵

4. RESOURCES HAVE BEEN SPREAD TOO THIN: SMALL INCREMENTS SPREAD OUT OVER MULTIPLE PROJECTS

In an assessment of the Sasol development experience, Olliver concludes with the observation "...it is just as well that Sasol plunged ahead with a big plant; if it had been cautious and dabbled with a pilot plant, the problems and the change in the outlook for oil would probably have killed the project, and there would be no process in the world that could, if needed, be relied upon to produce

oil from coal without many years of development."⁶

The U.S. approach has been small-scale support of multiple projects rather than large-scale support of one or two major projects. While we are not prepared to argue that it has been a mistake to hedge bets and to continue to develop multiple technologies, we are prepared to argue that the failure to commit to one or two (in addition to small-scale investments in several) is the best explanation of why no plant currently exists.

There are a number of reasons for the tendency toward multiple small-scale development. In the first place, it was never assumed during any of the growth periods for DCL that funding would dry up so completely so quickly. Just as important, the politics of pork barrel almost always dictate that more is better. Few federal programs and projects are not subject to the demands of distributive politics. More to the point, the chief political currency of DCL projects, especially at early stages, is regional economic impact. It is usually easier politically to provide for many small-scale regional impacts than for one or two projects with gigantic impacts. Indeed, sometimes relatively small-scale regional economic impacts are more desirable than gigantic ones because they are beneficial but less disruptive. Thus, purely from the standpoint of distributive politics, it is "rational" to provide as many projects as practically feasible given a particular level of investment.

There are many DCL technologies that "work." The trade-offs for each vary -- some are not so cheap, others are not so clean, still others are less proven -- but several seem at least equal to the processes used for years in the Sasol plants. It would seem to make sense to choose one or two of the best currently available technologies and provide a sustained developmental effort while continuing to support other approaches at a, relatively, quite modest level.

5. INVEST IN CONTINGENCY PLANNING

The events influencing DCL development have been, from one perspective at least, unpredictable. However, it can also be argued that the possible scenarios affecting DCL have been and are presently knowable. As mentioned above, few people in the early and mid-1970's would have predicted that there would soon be an oil glut and that the need for a DCL alternative would seem so much less compelling. But the discontinuities and rapid change associated with the DCL economic and policy environments need not wreck havoc to the extent they have in the past.

Contingency planning is one key to dealing with an environment likely to continue as unstable and volatile. Contingency planning, properly implemented, could smooth some of the disruptions caused by changes in course. Naturally, more stable policies would be welcome, but it is best to proceed as if policies will not be stable. Contingency planning might provide a set of workable development alternatives for any of a variety of specified environmental conditions. While contingency planning would, in principle, provide

considerable benefits in rationalizing DCL developmental efforts, it must be underscored that contingency plans are useful only to the extent that they are taken seriously and implemented. Perhaps the best approach to formulating contingency plans for DCL development is through some forum drawing together researchers, industry and policy-makers to advise on most appropriate directions given various levels of resources and national need. Only if all major parties to DCL development participate in contingency planning is there any strong likelihood that contingency plans will be implemented during periods of major environmental change. Moreover, the most likely benefit of a thorough-going contingency planning effort is not the direct product, which may or may not be implemented, but the exercise itself. One failure in DCL policy has been the inability of policy-makers and other actors to anticipate some of the major environmental shocks that have affected DCL development. The very process of anticipating possible changes might itself prove valuable. This report, providing a retrospective assessment of DCL development, might well be the first step in a more formal multi-party contingency planning effort.

THE HIATUS EFFECT AND DCL

With the demise of the Synthetic Fuels Corporation in 1985,⁷ the 90 percent reduction of federal synthetic fuel research funding since 1981, and the post-1982⁸ shutdown of the major synthetic fuels research labs in industry, the United States ended its third major⁹ synthetic fuels technology development thrust this century without having demonstrated a single process configuration at a commercial scale.

It is fair to assume that the development problems associated with DCL in the U.S. is at least partially explained by the economics of oil, the sectoral coordination problems described by Viotor and the politics of the energy crisis.¹⁰ The explanation as to why these problems became more pervasive in the case of synthetic fuels technology (SFT) development than in the case of other macro-engineering technologies is needed if an improved understanding of large-scale technology development processes is to be developed and if the potential of SFT is to be more accurately assessed.

In addition to these broadly-discussed problem areas associated with DCL development, there was the major problem of discontinuous scientific and engineering activity associated with the technology. In effect, DCL development in the U.S. has experienced several major hiatuses where little research, development, or demonstration was carried out or where insufficient time and effort were devoted to the technology. These hiatus periods were the product of inconsistent public policy¹¹ and under-investment in basic research by industry and government and had the result of limiting the potential of DCL as a fuel replacement option.

Given the fact that the U.S. has just entered its third major technology development slowdown, it is important that the potential effect of these periods on the future of DCL be understood prior to the initiation of any future research development and demonstration

(RD&D) program.

DCL processes, as conceptualized in the periods of U.S. development, were not competitive given the price of oil and the market economics of large oil/energy companies. The result was that each effort to develop commercial DCL ended in failure.

Recent analyses by the Rand Corporation¹² indicate that a critical variable in the success of any process-oriented technology is the continuous support of a RD&D program over an extended period of time. Discontinuous support or breaks in the process development cycle, labeled the hiatus effect, was viewed as the most critical factor in determining the success probability of process type technologies, such as DCL. Furthermore, an analysis of information/knowledge survival rates, both in private firms and the government, suggests that information and knowledge regarding process technologies, such as DCL, is often lost during periods of non-R&D activity. This loss factor appears to be a function of the extent to which new demonstration and pilot plant data are produced on a continuous basis. Another important factor identified by the Rand team is the importance of person-to-person knowledge transfer in this type of R&D effort. Apparently, after an R&D team is dismantled and assigned new duties the loss rate of knowledge is very high.

In addition to the effect of hiatus periods on the loss of information and knowledge important to the development cycle¹³ Hess concluded that the improvement of plant performance in process oriented technology is a function of continuous incremental improvements. Using the SASOL I experience, it is estimated that it takes 4-5 years to eliminate basic performance problems in innovative pioneer plants. According to Hess "this suggests that, for an innovative technology, a second plant potentially faces fewer startup difficulties if its design does not begin until after the pioneer plant has had at least 5 years operational experience."¹⁴ Given this initial time investment, the Rand study further concludes that an additional 10 to 15 years of pioneer plant operation is frequently required. Any hiatus period in this 20 year cycle will significantly diminish the potential of any improvements to reduce the process cost and potentially limit the viability of the technology.

In a related study,¹⁵ Lieberman found that continuous and higher levels of R&D expenditures accelerate the rate of process improvement. Discontinuous R&D, it is speculated, has the effect of reducing and limiting the rate of process improvement using patents only in the area of coal liquids production. Figure I details the change in the patents rate after the 1974 and 1980 funding patterns changes and illustrates the drastic changes in patent productivity in these periods.

Regarding the overall effect of hiatus periods in the R&D process, Myers and Arguden¹⁶ concluded that time, as opposed to people, facilities or information storage systems, was the critical variable in determining the decay rate of process oriented knowledge. Their consensus seemed to be that delays in the 20 year cycle would

require reinitiation of the development effort after each extended hiatus.

While the effects of periods of hiatus on the production of basic knowledge is difficult to measure, it is known that funding pattern reduction does affect the rate and direction of knowledge production.¹⁷ Given this reduction in the rate of production and the fact that loss in the rate of knowledge production can result in a dissemination problem, it is speculated that periods of research hiatus result in excessive research duplication and reinitiation. These reinitiation efforts are often time-consuming and lead to substantial delays in technology development processes. Beyond the knowledge losses, there is the more general effect of reduced funding limiting the search for potentially new processes which might be based on the findings of the basic research.

In sum, the hiatus effect on technology development is one of a reduction in the ability of a process to develop along standard cost-reducing routes. The process development cycle appears to be about 20 years for significant cost reductions to occur and for technical risk to be reduced to levels which will permit investment.

Additional hiatus effects include a reduction in the rate of production of new knowledge and thus, a reduction in the probability of developing new pioneer process configurations.

DCL DEVELOPMENT AND THE HIATUS EFFECT

The development of DCL appears to have historically been done in a rush in response to a critical national need. As early as the 1920s, German coal hydrogenation RD&D efforts were carried out with great haste, almost in a crisis environment. It was only 1925 when Pier¹⁸ obtained a good quality gasoline from coal and this was only at the bench scale. By September 1926, a plan to construct a 100,000 ton/year processing plant at Leuna had been developed and was announced.¹⁹ Completed after a monumental effort in 1927, the plant was fraught with technical difficulties and cost overruns. Production never reached more than 70,000 tons at the Leuna plant (before 1929) and according to the developers (I.G. Farber)²⁰ the plant was so expensive that more R&D was needed before moving ahead with any other plants. Despite arguments to shut down Leuna and put a moratorium on R&D, development continued. This continued effort was carried out as a means of potentially developing raw materials to aid in the balance of payments problem Germany faced at the time.

Changes in the petroleum market between 1926 and 1930 forced the process developers to focus on development of internal markets and ultimately after 1933 development for the support of Weimar government policies, including rearmament. Thus, the development of the eleven additional coal hydrogenation plants (between 1936 and 1943) for the production of synthetic gasoline "flourished in an environment of rearmament and autarky."²¹

From a technology development perspective, the German experience between 1927 and 1944 could be classified as a first

generation technology demonstration. Unfortunately, the plants were never intended to be competitive on the world market and perhaps more importantly, they were not based on a sound knowledge base. These German plants were also never fully developed in the sense that they lacked a systematic research development and demonstration history over the 20 year time frame suggested by Rand. Yes, they did operate but very inefficiently and with numerous technical difficulties.

In the period between 1945 and 1948, American efforts to capitalize on the German first generation SFT knowledge were launched in response to a perceived oil supply crisis.²² This plan, however, was based on several incorrect assumptions, not the least of which was the effect of the knowledge loss rate in transferring the German technology base to the U.S. after the war. These included:

- 1) the assumption that the German technology was sound because it had worked, when in fact, from an economic perspective, it was not viable;
- 2) the assumption that the empirically developed German hydrogenation process could easily be adapted to U.S. coal characteristics.

American policy in the 1940s had embarked on the path of demonstrating an uneconomical technology that lacked the science base necessary for improvements. The result was an economically unsuccessful four year operation of the hydrogenation pilot plant in Louisiana, Missouri.

In the case of the Louisiana, Missouri pilot plant, the hiatus effect begins to significantly impact the SFT process. There had been only limited U.S. R&D on hydrogenation since the 1920s with only 3 to 4 years of significant research before the beginning of the 1949 demonstration.²³ Thus, the U.S. data base was limited and the German data base was certainly spotty at best. Beyond the research base inadequacies, the pilot plant was only operated for four years before complete shutdown. According to the Rand studies, this would have been an insufficient time period to further develop the technology and lower the costs. Following the shutdown of the plant in 1953, with the exception of some small scale industrial efforts, the U.S. SFT development program entered a 10 year period of minimal research and development. Such a period of hiatus would indicate that in 1963, when the Office of Coal Research (OCR) began the development of three liquefaction demonstration projects, that the technology development process had returned almost to square one.

The result was that once again, as was the case in 1929 with the Leuna plant and in 1949 with the U.S. project, the demonstration projects were overwhelmed by cost overruns and economic efficiency problems. By 1974 when the political cry for SFT development began in response to the Arab oil embargo, no demonstration project of the OCR had yet been economically successful.

In 1974, out of panic and in an attempt by OCR to protect its bureaucratic status, a major demonstration project was funded. Known as Coalcon, the project suffered immediately from cost overruns and technical failure. In fact, it is not unfair to conclude that the decision to proceed with the Coalcon project was a grievous error. It was a known fact that the SFT option was not ready for demonstration prior to embarking on the \$237 million project.²⁴ There existed no continuously developed data base and no stockpile of basic knowledge from which to make design decisions for the plant. The insufficient development time frame associated with the German technology, the lack of continuous R&D support resulting from the hiatus of 1953 to 1963, and the inadequate development efforts of OCR between 1963 and 1974, doomed this project to failure from the start. The knowledge or technology base just wasn't there for any demonstration plant effort in 1974.

Given the hiatus periods in the DCL development history (see Table I) and the time frame associated with the successful development of process oriented technologies, the 1974 Coalcon decision, the 1976 Synthetic Fuels Commercial Demonstration Program, and the 1980 Synthetic Fuels Corporation efforts could have been economically successful only if the 1949 U.S. program had continued annually to the point where by 1969 a second plant could have been operated for 15 years. At this point, the knowledge may have existed for the development of a potentially cost-effective industry.

Unfortunately, the DCL process was plagued by periods of non-development and the push after 1974 was for commercialization of the technology, not for the needed R&D. The presence of the hiatus periods in the DCL development cycle made the commercialization goals set in 1976 and 1980 unobtainable.

So, in 1986, we find the U.S. DCL development process again in a period of curtailment. Again, some of the knowledge developed in the past is being lost and, again, when the SFT commercialization cycle begins in the future the nation will attempt to demonstrate a technology that is in reality not completely developed. The successful development of SFT, as shown by Steinberg²⁵ will require that the knowledge base be in place prior to any movement toward demonstration and commercialization of the projects.

CONCLUSION

The political decision to pursue the development of a national technology, such as DCL, requires substantial public sector and private sector coordination, as well as economics that will provide for investment and development. This is particularly true for technologies, which unlike space and military developments, must compete within the framework of an existing market. These criteria are nothing new and are well integrated into administrative and financial decision making. What is missing from the political decision making process is an assessment of the stage of development a given technology has achieved prior to its identification as a national objective. This fact is also nothing new,²⁶ but in the case of DCL it became a critical barrier to successful commercial development.

It is difficult to determine where DCL would be today if the government had supported a national, step-wise R&D program since it obtained the German technology base in 1945. It is also difficult to determine if SFT would have proven to be more viable if the initial German developers had pursued the technology with a stronger R&D base. Neither of these what-ifs will ever be known. The cost of sporadic government support and the premature attempts to commercialize SFT do, however, have a cost. The cost includes the billions spent on research to date, as well as the estimate that we remain 15-25 years from being able to produce a science-based, developmentally sound DCL option which has any chance of operating at a level of efficiency that would permit commercialization.

The ultimate need for synthetic fuels seems a certainty. Given the current slowdown in the SFT technology development process and the fact that it is likely that there won't be a 15-25 year lead time to any long-term oil supply interruption, it is fair to conclude that inefficient SFT options will be our only means of meeting the need. The results will be expensive synthetic substitutes being produced from inefficient plants. Thus, the choice is to launch a realistic, long-term R&D program 15-25 years before the need for low-cost synthetic fuels, or proceed with the current state of the technology. Absent any attempt to mitigate the current slowdown, a commercially viable DCL option will not be available when needed.

Approximate Development Cycle for the Coal Liquefaction Option of Synthetic Fuels Technology

Slowdown Period III	1985	Reduction in Research and Development Program and Shutdown of Demonstration Program
Premature attempt to commercialize SFT	1980-1985	Organization and demise of the Synthetic Fuels Corporation
Premature Demonstration	1976-1980	Synthetic Fuels Commercial Demonstration Program
	1974-1977	Coal Con Demonstration Failure
Premature Development	1963-1974	OCR develops and operates 3 liquefaction pilot plants (projects racked by funding and development problems)
	1961	Office of Coal Research (OCR) established in the U.S. Deptment of the Interior. Small scale coal research/synthetic fuels research initiated.
Hiatus Period II	1952-1956	Carbide and Carbon Chemicals operates a 300 ton/day hydrogenation plant after 17 years of lab scale work.
	1953	U.S. Pilot Plant in Louisiana, MO shut down after running six American coals. Cost studies show process not competitive.
	1949	First U.S. Hydrogenation Pilot Plant began operation in Louisiana, MO.
Hiatus Period I	1945	New U.S. Bureau of Mines liquefaction lab erected at Bruceton, PA.
	1941-1944	12 million metric tons of synthetic liquids produced from first generation plants in Germany.
	1936	U.S. Bureau of Mines initiates experimental work on Coal liquefaction
	1936-1944	11 First generation plants built and operated by Germans
Premature	1927-1936	Operation of Leuna Liquefaction Plant
	1927	First Generation Hydrogenation Demonstration Plant built in Europe
	1920s	Germans discover 3 processes for coal conversion to liquid fuels.
	1924	U.S. Bureau of Mines Initiates Small Scale Coal Synthesis Research

REFERENCES

1. R. Rothwell and W. Zegveld, Industrial Innovation and Public Policy (London: Frances Pinter, 1981).
2. J.E. Schnee, "Government Programs and the Growth of High-Technology Industries," Research Policy, 5, 1 (17), 2-24.
3. Some ways in which the U.S. and South African experience diverge: the South African air quality standards are more lax, the South Africans' indigenous petroleum reserves are modest, South Africa has taken several steps to prop up the price for coal liquids.
4. J. Jewkes, D. Sawers, and R. Stillerman, The Sources of Invention, second edition, New York: Norton, 1969.
5. Specific strategies for building up informal communication networks are discussed in T. Allen, Managing Technology (Cambridge, Mass.: M.I.T. Press), 1977.
6. D. Oliver, Oil and Gas from Coal (London: Financial Times Business Information Ltd.), 1981, p. 127.
7. The U.S. Synthetic Fuels Corporation was abolished April 18, 1986 pursuant to the Consolidated Omnibus Budget Reconciliation Act of 1985 (Public Law 99-272). That law transferred the responsibility of monitoring current synthetic fuels projects to the Office of the Secretary of the Treasury. In addition, on April 19, 1986 the Secretary of the Treasury established the Office of Synthetic Fuels Projects to monitor technically and environmentally current federally funded synthetic fuels projects.
8. Research and development funding for synthetic fuels research dropped in constant 1974 dollars from a high in 1981 of \$377.6 million to a low level of projected funding of less than \$20 million total in FY 1986. The funding level is the lowest annual federal commitment to research and development activities related to liquefaction and gasification of coal since the 1960s. Essentially, the funding level for the research and development activities sponsored by the federal government has been returned to the pre-energy crisis level.
9. For a summary of the four major thrusts see M.M. Crow and G.L. Hager, "Political vs Technical Risk Reduction and the Failure of the U.S. Synthetic Fuel Development Efforts," Policy Studies Review, August 1985, vol. 5, no. 1, pgs. 145-152.
10. For an excellent summary of the politics surrounding energy technology in general and synthetic fuels specifically, see W.A. Rosenbaum, Energy, Politics and Public Policy, Washington, DC: Congressional Quarterly Inc., 1981.

11. For a good summary of the ebb and flow of public policy surrounding synthetic fuels technology development, see Joseph R. Rudolph and Sebrina Willis, The Politics of Technology, Public Policy and Administration: The Synthetic Fuels Adventure in Western Democracies, paper presented at the 1985 Annual Meeting of the American Political Science Association.
12. Hess, R.W. (1985, March). Potential Production Cost Benefit of Constructing and Operating First of a Kind Synthetic Fuel Plants. Report N-2274-SFC, Santa Monica: The Rand Corporation; Myers, C.W. and Arguden, R.Y. (1984, January). Capturing Pioneer Plant Experience: Implications for Synfuel Projects. Report N-2063-SFT, Santa Monica: The Rand Corporation; Hess, R.W. (1985b, March). Review of Cost Improvement Literature with Emphasis on Synthetic Fuel Facilities and the Petroleum and Chemical Process Industries. Report N-2275-SFC, Santa Monica: The Rand Corporation; Merrow, E.W., Phillips, K.E., and Myers, C.W. (1981, June). Understanding Growth and Performance Problems in Pioneer Process Plants. Report R-2569-DOE, Santa Monica: The Rand Corporation.
13. Hess, R.W. (1985, March). Review of Cost Improvement Literature with Emphasis on Synthetic Fuel Facilities and the Petroleum and Chemical Process Industries. Report N-2273-SFC, Santa Monica: The Rand Corporation.
14. Hess, R.W. (1985, March). Potential Production Cost Benefit of Constructing and Operating First of a Kind Synthetic Fuel Plants. Report N-2274-SFC, Santa Monica: The Rand Corporation, p. 2.
15. Lieberman, M.B. (1982). The Learning Curve Pricing and Market Structure in the Chemical Processing Industries, Ph.D. Thesis, Harvard University, Cambridge, Mass.
16. Myers, C.W. and Arguden, R.Y. (1984, January). Capturing Pioneer Plant Experience: Implications for Synfuel Projects. Report N-2063-SFT, Santa Monica: The Rand Corporation.
17. M. Crow and B. Bozeman, "R&D Laboratory Variation in the 1980's: Some Implications for Policy Analysts." Journal of Policy Analysis and Management, forthcoming; A.N. Link, "The Impact of Federal R&D Spending on Productivity." IEEE Transactions on Engineering Management, (1979) EM-29, 166-169.
18. Hughes, T.P. (1969, August). Technological Momentum in History: Hydrogenation in Germany 1898-1933. Past and Present, 44, pp. 106-133.
19. Donath, E.E. (1963). Hydrogenation of Coal and Tar in Chemistry of Coal Utilization (supplemental volume). H.H. Lowry (ed.), New York: John Wiley and Sons, Inc.

20. Hughes, T.P. (1969, August). Technological Momentum in History: Hydrogenation in Germany 1898-1933. Past and Present, 44, pp. 106-133.
21. Hughes, T.P. (1969, August). Technological Momentum in History: Hydrogenation in Germany 1898-1933. Past and Present, p. 130.
22. U.S. Congress, 1944; 1948.
23. Donath, E.E. (1963). Hydrogenation of Coal and Tar in Chemistry of Coal Utilization (supplemental volume). H.H. Lowry (ed.), New York: John Wiley and Sons, Inc.
24. Desai, U. and Crow, M.M. (1983, August). Failures of Power and Intelligence in Government Decision Making, Administration and Society, 5(2), 185-206.
25. Steinberg, G.M. (1985). Comparing Technological Risks in Large Scale National Projects, Policy Sciences, pp. 80-93.
26. Lambright, W.H., Crow, M.M. and Shangraw, R. (1984, May). National Projects in Civilian Technology, Policy Studies Review, 3(3-4), 453-459.

INTEGRATION AND DATABASE DEVELOPMENT

October 1, 1985 - December 31, 1986

University of Kentucky

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Title: Coal Liquefaction Infratechnology and Generic
Technology--Integration and Database Development

PI's: Frank E. Huggins
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Period: October 1, 1985 - December 31, 1986

The coal liquefaction technology database/network is viewed as one means to integrate activities of the various research groups involved in the OFFLS project. The database/network will enable the different groups to share and exchange information and will provide electronic mail for rapid communication and report transfer between groups. The database/network will be hosted at the University of Kentucky on an AT&T 3B20 mainframe computer in the school of Engineering. This computer, which uses UNIX as the operating system, has more than 1.8 Gbytes of memory and is currently accessible by modems from remote locations.

The structure of the database is shown schematically in figures 1 and 2. Within the database/network, facilities will exist for electronic mail, bulletin boards, file and report transfer, and the database. The items are briefly described below:

- (a) electronic mail: Anybody associated with the OFFLS program will have access to the electronic mail facilities for person-to-person communication.
- (b) bulletin boards: news and information of more general interest can be deposited on the bulletin boards, which will be accessible to all members.
- (c) file and report transfer: protocols will be established to facilitate the transfer of files between research groups and for submission of reports to the OFFLS office at UK.
- (d) database: it is hoped to collect many of the data generated in the OFFLS projects in a centralized database for perusal by all members. Such centralization should minimize duplication of effort, for example in routine analytical services, provide more timely knowledge of other OFFLS groups' work and promote the exchange of samples and techniques.

As indicated in Figure 2, the principal users of the database/network will be all investigators working on OFFLS projects at the different research centers. Secondary users might include DOE/PETC personnel, industrial affiliates and other sanctioned users; these latter users will have all access to network communications, but a somewhat restricted access to file transfer and database facilities. The principal users have been given the opportunity to detail their potential usage and requirements for the OFFLS database/network by means of a questionnaire that was distributed at the December 5th meeting of the OFFLS council at the Greater Pittsburgh Airport.

As also indicated in Figure 2, an added feature that will be explored is the linking of the CFFLS database with other coal-related databases. In this regard, we have held discussions with Dr. W. Peters, PETC, regarding the feasibility of linking up with the National Coal Data Center. This facility consists of various data subsets (e.g. the Penn. State University coal database, liquefaction technology database, combustion properties database, etc.) and resides in 2+ Gbytes of memory in a cluster of VAX computers. Options for real-time graphical depiction of data, including engineering diagrams and geographical maps, makes the database visually impressive. However, such graphics require that special terminals and high-speed direct lines would be necessary for remote tie-ins to be fully effective. Further work needs to be done on the feasibility of linking the two systems.

The database/network management team will consist of a coordinator (F. E. Huggins) and one or more graduate assistants (yet to be named) with input from CFFLS Director (G. P. Huffman) and from the AT&T 3B20 computer manager (L. S. Sendlein). For management purposes, three AT&T 6300+ personal computers have been ordered for interfacing with the 3B20 mainframe computer. These computers are basically IBM-PC compatibles, but also have the ability for context switching to UNIX, the resident operating system on the 3B20. The personal computers will connect to the 3B20 via modems until the UK campus-wide Ungermann-Bass network becomes fully operational.

Planned Work for 1987

In the coming year, the CFFLS database/network should move from conceptualization to at least partial implementation on the 3B20 at UK. In the first quarter, a graduate student will be hired and assembly of the three CFFLS on-campus AT&T personal computer interfaces to the 3B20 should be completed so that the student can start work on developing the software routines for implementing the database/network on the 3B20. In part, this software development will be directed by responses to the questionnaire from CFFLS principal investigators and by the restrictions required by the 3B20 manager. In subsequent quarters, software development will continue until the full system is deployed.

Figure 1: Planned Attributes of CFFLS Database/Network on AT&T 3B20 computer at University of Kentucky

Figure 2: User network envisaged for CFFLS Database/Network.

DOE/PC/80009-T20

COOPERATIVE RESEARCH IN COAL LIQUEFACTION
INFRASTRUCTURE AND GENERIC TECHNOLOGY DEVELOPMENT

DOE