

## NEW MATERIALS FOR COAL LIQUEFACTION

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### INTRODUCTION

Direct liquefaction is one of the alternatives currently under development for the production of clean burning fuels from coal. In the more advanced liquefaction processes, such as those of Gulf Research and Development, Hydrocarbon Research, Inc., and the Bureau of Mines (synthoil), coal is liquefied in the presence of a cobalt-molybdate catalyst at moderate temperatures (400°C) and high hydrogen pressures (2000-4000 psi). Extensive research is currently underway (1) to improve the performance of these catalysts. Properties of importance include activity (to reduce reactor size and pressure) activity maintenance (to increase life and regenerability) and selectivity (to minimize hydrogen consumption). The catalyst performs a number of functions such as cracking large aromatic molecules present in coal liquids and hydrogenation of certain cracked molecules with concomitant removal of heteroatoms such as sulfur, nitrogen and oxygen.

Because of the projected need for clean-burning liquid fuels and the technological complexity of existing liquefaction technology, first generation processes are likely to be based on existing catalyst technology. However, it is clear that there is room for substantial improvements in all aspects of the process, improvements that will require new catalytic materials and concepts. It is therefore timely to establish some of the ground rules which will guide the catalytic scientist and engineer in the choice of new materials to be tested as catalysts for coal liquefaction. This was the objective of a study recently conducted for the Electric Power Research Institute (2) and summarized in this report.

In this summary, the general criteria for the selection of materials for coal liquefaction catalysis are discussed first. This serves as a basis for a detailed analysis of a number of compounds and a preliminary assessment of the types of compounds that should be tested for coal liquefaction.

### CRITERIA FOR SELECTION OF MATERIALS

A discussion of new materials requires, in effect, a look at the enormous number of compounds that have been investigated in solid state and inorganic chemistry over the years. A number of the most important classes of compounds are shown in Table 1. They are formed by transition and alkaline earth metals and a small group of nonmetals from the upper right hand corner of the periodic table of the elements: boron, carbon, silicon, nitrogen, phosphorous, oxygen, sulfur and chlorine.

Considering the wealth of compounds represented by these various groups, it is interesting to note that relatively few have been tested for catalytic applications. Furthermore, it is difficult to choose a priori from this large number of materials those which would be applicable for study as liquefaction catalysts. The challenge in the selection sequence for new materials is therefore the identification of those constraints that have to be met by a compound in addition to its catalytic activity. Among the most important constraints for coal liquefaction are thermal and chemical stability.

Thermal stability takes into account the resistance of a given material to volatility, melting, sintering, and general mechanical failure. Temperatures which must be considered are both those for reaction and regeneration. The reaction temperatures for catalytic liquefaction processes are currently of the order of 400°C.

The regeneration scheme which is most likely to be applied to these process is controlled oxidation of the carbonaceous residues which are deposited on the surface of the catalyst. Although this is carried out with careful control of temperature, surface temperatures can frequently exceed 800°C. Continued use and regeneration brings about structural degradation of many materials at these conditions. Chemical stability relates to the chemical behavior of the materials in the environment of coal liquefaction and regeneration. Of primary concern in this respect is the stability of the catalyst in an H<sub>2</sub>S/H<sub>2</sub> atmosphere. In coal liquefaction, concentrations of H<sub>2</sub>S of 1-5 percent or higher are normal. Other reactive compounds that may affect stability are hydrocarbons, NH<sub>3</sub>, H<sub>2</sub>O, and O<sub>2</sub>. Except for oxygen used in regeneration, the effect of the other reactants is minimal compared to that of H<sub>2</sub>S.

In spite of the lack of catalytic information for many of the compounds shown in Table 1, the focus of a general survey such as the present one will be those materials containing cations that have shown catalytic activity. This is the reason for the emphasis on transition metals compounds. The thermal and chemical stability of these materials will now be discussed.

#### THERMAL STABILITY

The only compounds in Table 1 that are clearly excluded from further consideration because of poor thermal stability are the organometallic complexes. For example, Co<sub>2</sub>(CO)<sub>8</sub> decompose to the metal at temperatures as low as 150°C, unless the CO pressure in the system is greater than 600 psi (3). By contrast, some of the compounds in Table 1 can withstand temperatures that are among the highest of any material. For example, TaC melts at about 3980°C (4) and TiB<sub>2</sub> melts at 2980°C (5). In spite of this high thermal stability, the chemistry of these compounds changes with temperature and the stable stoichiometry at the synthesis temperature may be quite different from that at the temperature of operation. This is illustrated quite dramatically by a compound that has been considered for hydrogenation and desulfurization, VS<sub>4</sub> (6). An examination of a simplified phase diagram for this material reveals that above 300 to 400°C VS<sub>4</sub> decomposes to sulfur and the next stable stoichiometry, V<sub>5</sub>S<sub>8</sub> (7) (although there are indications that V<sub>3</sub>S<sub>5</sub> may also be formed (8)). It is therefore unlikely that at operating conditions VS<sub>4</sub> is the actual catalyst.

A diagram of temperature vs. composition is not complete without a specification of pressure. In the case of the V-S system the pertinent parameter is the pressure of sulfur or, equivalently, a sulfur containing compound such as H<sub>2</sub>S. The behavior of compounds in the presence of H<sub>2</sub>S depends on the chemical stability of the compound and is discussed in the next section.

#### CHEMICAL STABILITY

The two conditions that are most critical in coal liquefaction are the high H<sub>2</sub>S concentration and the need (unless alternate methods are discovered) to use oxygen to regenerate the spent catalyst. Before these two conditions are discussed, it is of interest to explore the behavior of compounds in the presence of the "parent" non-metallic element, namely the free energy of formation. For convenience, all the comparisons are made at 700K (which is comparable to current coal liquefaction temperature). Thermodynamic calculations are based on the latest published data and have been discussed in detail elsewhere (2). An extremely useful simplification, proposed by Searcy (9), allows direct use of heats of formation in the absence of values for the entropy change. This permits considerable extension of the published data and leads to some interesting conclusions concerning potential new materials for coal liquefaction catalysis.

### Free Energy of Formation

By comparing free energies of formation it is possible to make a qualitative evaluation of the relative stability of various compounds. This in turn can be used to predict the behavior of these compounds in certain chemical environments.

The free energies of formation of a number of compounds were examined in detail (2). Representative examples are shown in Tables 2 and 3. The following general observations are of interest for the present study:

- a. Oxides are the most stable compounds of the groups that were examined. In effect, the following stability trends are observed:

oxides >> nitrides > carbides  
oxides > sulfides  
oxides >> borides, silicides, phosphides

One consequence of these trends is that most compounds are expected to be thermodynamically unstable in an oxidizing environment such as encountered in catalyst regeneration.

- b. In general, the stability of a family of compounds decreases with increasing group number in the periodic table. Group VIII oxides, for example, are the least stable of the transition metal oxides. However, the extent of this decrease is not the same for all groups of compounds. It is most severe for nitrides and carbides, least severe for silicides. In general, the following order of stability change is observed:

nitrides, carbides >> oxides > sulfides > silicides

This difference is manifested in the variation in stability of members of one group of compounds (such as oxides) in the presence of the same environment. In H<sub>2</sub>S, for example, titanium oxide (Group IV) is stable. Cobalt oxide (Group VIII), on the other hand, is not.

- c. Thermodynamic information on borides is limited to the Group IV elements Ti, Zr and Hf. For these elements borides are more stable than silicides. From the similarity in many of the physicochemical properties of borides and silicides, it is expected that this behavior will continue throughout the periodic table. The behavior of silicides in H<sub>2</sub>S can therefore be used as a guide to the stability of borides in this environment.

### Stability in the Presence of H<sub>2</sub>S

The high H<sub>2</sub>S concentrations present during coal liquefaction imposes a most severe constraint on the choice of catalytic materials. Levels as high as 1-5% H<sub>2</sub>S can be expected. From the thermodynamics of sulfide formation it is found that most materials are unlikely to survive in this environment (2). Thus, at any reasonable process conditions, metals, alloys, organometallic complexes, carbides, and many oxides and nitrides can form the respective sulfide. However, as indicated earlier, the behavior of individual transition metals depends on their position in the periodic table. Some representative examples are shown in Table 4. In general, the following is observed:

- a. While oxides and nitrides of Group IV are stable in H<sub>2</sub>S, those of higher groups can form the sulfide.
- b. Conversely, while borides and silicides of Group IV are thermodynamically unstable in H<sub>2</sub>S, those of group VIII are expected to survive even in severe H<sub>2</sub>S environments.

- c. Many of the metals that are in the region of intermediate stability (Groups V, VI and VII) are likely to form complex compounds, such as oxysulfides, in the presence of  $H_2S$ . Formation of these compounds is a sensitive function of the  $H_2S$  pressure in the system.

It should be emphasized that the above statements are based on thermodynamic information only. No conclusions can be drawn concerning the kinetics of the respective transformations. However, the thermodynamic analysis does provide a guideline for the expected behavior of a system under the most adverse conditions.

#### CONCLUSIONS

Before a new material is tested for catalytic coal liquefaction, its chances of survival in the liquefaction environment should be examined. The presence of  $H_2S$  poses the most severe problem. A large number of compounds that may ordinarily be considered promising candidates sulfide in this environment. It is therefore fruitless to spend considerable effort in the testing of these materials. Compounds that are expected to resist sulfidation include a number of oxides, nitrides, borides and silicides. Among these there are a number of interesting compositions that have not been tested for catalytic liquefaction to-date. Examples are  $Mg_2Mo_3O_8$ , which has  $Mo_3$  clusters and has been found to exhibit hydrogenation activity intermediate between metals and oxides (10), the perovskite-like Nowotny nitrides such as  $Ni_3AlN$ , and the borides of the group VIII metals such as  $CoB$  and  $NiB$ . Serious consideration, of course, should also be given to the large number of sulfides that have been synthesized and characterized over the last few years, (an example is  $Al_{0.5}Mo_2S_4$ , which also contains  $Mo_3$  clusters (11)) and to sulfo-compounds such as oxysulfides which are likely to be formed by many of the compounds of intermediate stability. Some of these are being uncovered only recently, including  $Ta_2S_2C$  (12) which is capable of forming intercalation compounds and also retains the layered structure that is characteristic of a number of currently used hydrotreating catalyst.

If an alternative to oxidative regeneration is not found, even some of the sulfur resistant materials mentioned above will not be viable candidates for catalytic coal liquefaction unless they exhibit unusual activity maintenance and therefore require no or infrequent regeneration. It was observed earlier that a number of the compounds under consideration are likely to be thermodynamically unstable in an oxidizing environment. It is therefore important to consider how they will be resynthesized to the stoichiometry that is catalytically active. Sulfides, and oxysulfides, of course, present no problem. Carbides and even nitrides may be feasible. The use of  $PH_3$  or  $B_2H_6$  to resynthesize borides and phosphides is probably impractical. This further restricts the best candidates for catalytic liquefaction unless more economical reagents or means for resynthesis are developed. It should be mentioned that even among those classes of materials which may endure oxidative regeneration (e.g. carbides, nitrides, oxides, sulfides, oxysulfides and mixed systems) numerous compounds exist which are of interest for exploration as future generation liquefaction catalysts.

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TABLE 1  
REPRESENTATIVE CLASSES OF COMPOUNDS

Oxides	Simple	$Al_2O_3, MoO_3$
	Complex	$Mg_2Mo_3O_8$
Sulfides	Simple	$V_5S_8$
	Complex	$Al_{0.5}Mo_2S_4$
Carbides	Simple	WC
	Complex	$Pt_3SnC$
Nitrides	Simple	$Co_3N_2$
	Complex	$V_3Zn_2N$
Borides	$MoB, Co_{21}Hf_2B_6$	
Phosphides	$Co_2P$	
Silicides	$Mo_3Si$	
Alloys and Inter-metallic Compounds	Ni-Cu, ZrPt <sub>3</sub>	
Organometallic	$Co_2(CO)_8$	
Molten Salts	$ZnCl_2$	
Solid Acids	Zeolites, Clays	
Solid Bases	$CaO, NaNH_2$	

TABLE 2  
STANDARD FREE ENERGIES OF FORMATION ( $-\Delta G_f^0$ ) OF  
REPRESENTATIVE OXIDES, SULFIDES, CARBIDES, & NITRIDES  
(In kcal/g-atom Non-Metal At 700 K)

	<u>Oxides</u>		<u>Sulfides</u>		<u>Carbides</u>		<u>Nitrides</u>	
Group IV	TiO	108	TiS	64	TiC	44	TiN	65
	TiO <sub>2</sub>	97	TiS <sub>2</sub>	39				
Group V	NbO	84	NbS <sub>2</sub>	47	NbC	34	NbN	42
	NbO <sub>2</sub>	79						
Group VI	MoO <sub>2</sub>	55	MoS <sub>2</sub>	33	MoC	3	Mo <sub>2</sub> N	2
	MoO <sub>3</sub>	45						
Group VIII	CoO	42	Co <sub>9</sub> S <sub>8</sub>	25	Co <sub>2</sub> C	-4	Co <sub>3</sub> N (unstable)	
			CoS <sub>2</sub>	19				

TABLE 3

STANDARD FREE ENERGIES OF FORMATION ( $-\Delta G_f^0$ ) OF  
REPRESENTATIVE BORIDES, SILICIDES, & PHOSPHIDES  
(In kcal/g-atom Non-Metal At 700 K)

	<u>Borides</u>		<u>Silicides</u>		<u>Phosphides</u>
Group IV	TiB	39	TiSi	31	a
	TiB <sub>2</sub>	22	TiSi <sub>2</sub>	16	
Group V	a		NbSi <sub>2</sub>	16	a
Group VI	a		MoSi	14	a
Group VIII	a		CoSi	19	CoP 29

a. Data unavailable

TABLE 4

EXAMPLES OF STABILITY IN THE PRESENCE OF H<sub>2</sub>S

	<u>Reaction</u>	<u><math>\Delta G^0_{700 K}</math></u> <sup>a</sup>
Oxides:		
Group IVB	TiO <sub>2</sub> → TiS	+22
Group VIB	MoO <sub>3</sub> → MoS <sub>2</sub>	-33
Nitrides:		
Group IVB	TiN → TiS	+22
Group VB	TaN → TaS <sub>2</sub>	- 7
Group VIB	Unstable Nitrides	<< 0
Silicides:		
Group IVB	TiSi → TiS	-18
Group VIIB	MnSi → MnS	-12
Group VIIIB	NiSi → NiS	+12

a. Free energy of sulfide formation at 700 K in kcal/g-atom non-metal. Negative free energy indicates a favored reaction.

REFORMATION OF INORGANIC PARTICULATES SUSPENDED IN COAL-  
DERIVED LIQUIDS AND IMPROVED SEPARATION\*

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For coal liquefaction processes, the separation of fine inorganic particulates from the organic product matrix represents an important technical problem. This problem is difficult because the matrix is viscous and many of the particles are in the micron and submicron size range. Separation methods and devices tried with some success in separating the particles have been: hydroclones, centrifugation, magnetic separation, solvent extraction, solvent fractionation, and filtration. These techniques suffer, however, in varying degrees from unsatisfactory operation, maintenance, throughput, and cost. To help correct these shortcomings, we have undertaken a study of techniques by which the fine particulates might be enlarged or better collected. Some progress toward that end has been described in the open and patent literature for solvent addition. In these works, two mechanisms by which solvent improves separation have been suggested: (1) the solvent may soften or dissolve a coating from the particles, permitting physical attractive forces to cause agglomeration; or (2) the solvent may cause phase separation--the heavier phase acting as a collection flocculant.

This paper consists of five parts. First, I will describe the laboratory sedimentation test used in this study. Second, I will discuss the effects of solvent dilution on settling. Our main thrust will come in parts three and four, where settling with heating and with the addition of chemical promoters will be presented. These areas have not (to our knowledge) been studied previously. In part five, I will describe the possible mechanisms and the roles that each may play.

The laboratory sedimentation tests were conducted in a vertical 18-inch-tall by 1-inch-diameter metal tube using unfiltered oil from the Solvent Refined Coal process. Normally, 175 grams of this oil containing suspended particles was placed in the tube. The sealed tube was quickly heated to test temperature and then cooled rapidly at the end of the test. The contents, as shown in slide 1, were then separated into 10 or 11 fractions for examination by filtration, microscopy, or chemical analysis. The filtration was achieved by the use of a laboratory technique that I have described in the July 1976 issue of I&EC Process Design and Development.

The sedimentation tests with solvent dilution, using toluene or SRC recycle solvent as the diluent, gave comparable results with appreciable

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improvement in settling at 20% dilution. In slide 2, data are shown for settling at 310°C for 1 hour with 5, 10, and 20% dilution with recycle solvent; the ash for the 20% dilution is approaching the EPA requirement of 0.15% in the top 70% of the sedimentation tube. The role of particle agglomeration appears well-substantiated here since the agglomerates formed can be observed by optical microscopy to contain as many as 100 of the particles. Calculations of effective particle size from the settling rates indicate that the settling particles are a minimum of 53 microns in diameter whereas 90% of the particles in the starting test are less than 1 micron in diameter.

Keeping in mind that with 20% solvent dilution, adequate clarity can be approached by settling for 1 hour at 310°C, let us turn to part two. What can be done with heat alone? In slide 3, data are plotted that represent the results of a series of sedimentation tests conducted at temperatures of 100 to 350°C and for times of 1 to 21 hours. The filtration improvement factor is a term describing the relative filterability of the third fraction from the top; a factor of 1 is no improvement, whereas a factor of 20 or more indicates clarity meeting EPA standards. Little settling was found after 18 hours at 100 and 150°C. At 200 and 250°C, settling was more rapid and clarity was reached before 18 hours. At 310°C in 3 hours and at 350°C in 1 hour, the results were good. At higher temperatures, settling was poor because of decomposition. Therefore, 300 to 350°C appears to be the best working range. Settling at 350°C seems at least as good as with 20% solvent dilution at 310°C. The effects upon the particles may be considerably different since both the size and distribution of particles apparently change upon thermal treatment. Slide 4 shows particles in the starting oil at 24,000 magnification. Some of the particles are only 0.01 micron in diameter; the larger particles are rough on the edges, which suggests that they may be composed of smaller particles. Slide 5 reveals a similar magnification of the particles after treatment at 300°C for 1 hour; few particles less than 1 micron in size remain and the surface edges appear to be smooth.

With evidence that significant changes in particle size and form occur during a 1-hour thermal treatment, it follows that, during that treatment, the rate of transport of particles or their components must be appreciable and that the transport rate might usefully be increased by changing the system properties. We limit considerations here to additions of promoters in such small quantities that their economic recovery may not be required. Such candidate promoters were selected from two different groups: (1) organic materials which had previously been used to change properties of colloids and suspensions and (2) inorganic materials (particularly inexpensive ones) which could change the charge or chemical form of the particle surface. Initial scouting tests were made with 4,000 ppm of the additive for 70 minutes or less at 280°C. Additional testing at other conditions followed in cases where positive improvement was found.

Of the 34 organic and 25 inorganic candidate materials tested, four organic and nine inorganic appear to give some improvement. The best organic additive tested was Tretolite sample 771-119; at concentrations

of 4,000, 2,000, or 500 ppm, the ash found in the top fraction was less than 0.05%, which represented results that were 5 times better than control tests. Three other organic additives supplied by Tretolite Division of the Petrolite Corporation of St. Louis, Missouri, appeared to cause lesser improvement. The next slide shows the results of three pairs of sedimentation tests using the 771-119 additive at 4,000 ppm. The control was run before each additive test, with the six tests being made in a single sequence to minimize experimental variations. Significantly lower ash contents are noted for fractions 1 through 7 for the additive tests; larger ash contents are shown for the bottom fraction (as expected).

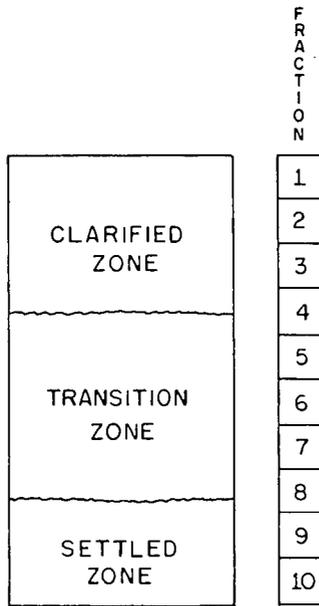
For the three additive tests, the ash content in the first 3 fractions was low, gradually increasing up to the 7th fraction and then sharply rising thereafter. Two of these runs were for 48 minutes, and 1 run was for 30 minutes. These figures include the time required for bringing the sample to test conditions; therefore, the actual operating time was less than the times shown. Each fraction represents about 3.5 cm in depth; thus, the settling rate for the smallest particle appears to be about 20 cm (or nearly 8 inches per hour).

Of the inorganic additives selected, aluminum sulfate, ammonium sulfate, and ammonium hydrogen sulfate appeared as effective as any organic additive tested. Aluminum phosphate appeared to perform better at temperatures near 340°C, while ammonium monohydrogen phosphate seemed to be less effective. Phosphoric acid, phosphoric anhydride, and sulfuric acid appeared to be most effective at higher concentrations such as 10,000 ppm but also seemed to be effective at temperatures as low as 200°C--phase separation in the matrix material and possibly flocculation were noted even at this low temperature.

These laboratory data indicate that, through heat treatment in the presence of a small amount of a promoter, settling takes place in less than 1 hour and, therefore, does meet clarity standards. Other arrangements, such as to couple settling with a polishing step, may be useful. The effect of heat upon settling has been confirmed in a larger-scale system, and the effect of additives is still being studied. These results will be reported at a later date.

Turning now to another consideration, the next slide tabulates some possible mechanisms which may promote settling. Since a wide range of particle types and compositions exist in a suspension in a variable matrix, several settling mechanisms may be operating simultaneously. Agglomeration is known to occur both after solvent dilution and upon the application of heat. The extent to which charge, melting, or chemical conversion occurs to promote agglomeration has not yet been established. Electron-microscope studies of before and after heat treatment indicate that particle reformation does occur. It implies some solubility of the organic species in the matrix organic materials at the test conditions, which is not particularly surprising in view of the polar components of the organic matrix. None of the promoters, when used alone, appear to flocculate and gather up particles as we would expect to observe in aqueous systems; however, some of the additive tests,

particularly those with phosphoric acid, phosphoric anhydride, and sulfuric acid seem to cause a small amount of a matrix phase to separate out and collect particulates. The normal changes in viscosity that are induced by temperature or by dilution with solvent are significant but do not account for the measured settling rates. Phase separations, as a result of treatment, can affect viscosity and, subsequently, the settling rates.



- Generally:
1. Clarified zone contains particles less than  $5\mu$  and has a total solids concentration much less than the UFO.
  2. Transition zone contains a few particles up to  $15\mu$  and varies from a low concentration to that of the UFO.
  3. Settled zone contains nearly all large dark particles and has a concentration much greater than UFO.

Fig. 1 Settling zone identification.

ANALYTICAL RESULTS FOR SETTLING OF PROCESS RECYCLE DILUTED,  
UNFILTERED OIL FROM THE SRC PROCESS

CONDITION	FRACTION NO.	ASH (WT %)	SULFUR (WT %)
1 HR AT 310°C, 5% DILUTION	1	1.67	0.63
	4	1.52	0.70
	7	1.44	0.67
	11	3.32	0.70
1 HR AT 310°C, 10% DILUTION	1	1.12	0.59
	4	0.72	0.60
	7	1.22	0.67
	10	3.49	0.75
1 HR AT 310°C, 20% DILUTION	1	0.33	0.50
	4	0.24	0.54
	7	0.03	0.54

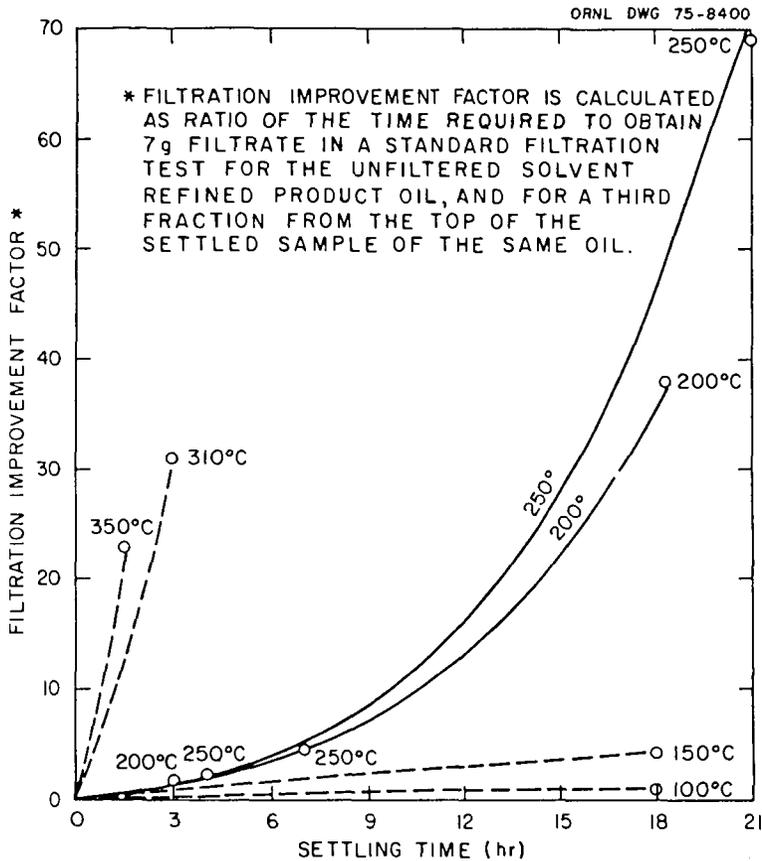


Fig. 3. Improvement in filterability as a function of settling time and temperature.



24,000 X

UNFILTERED SRC OIL

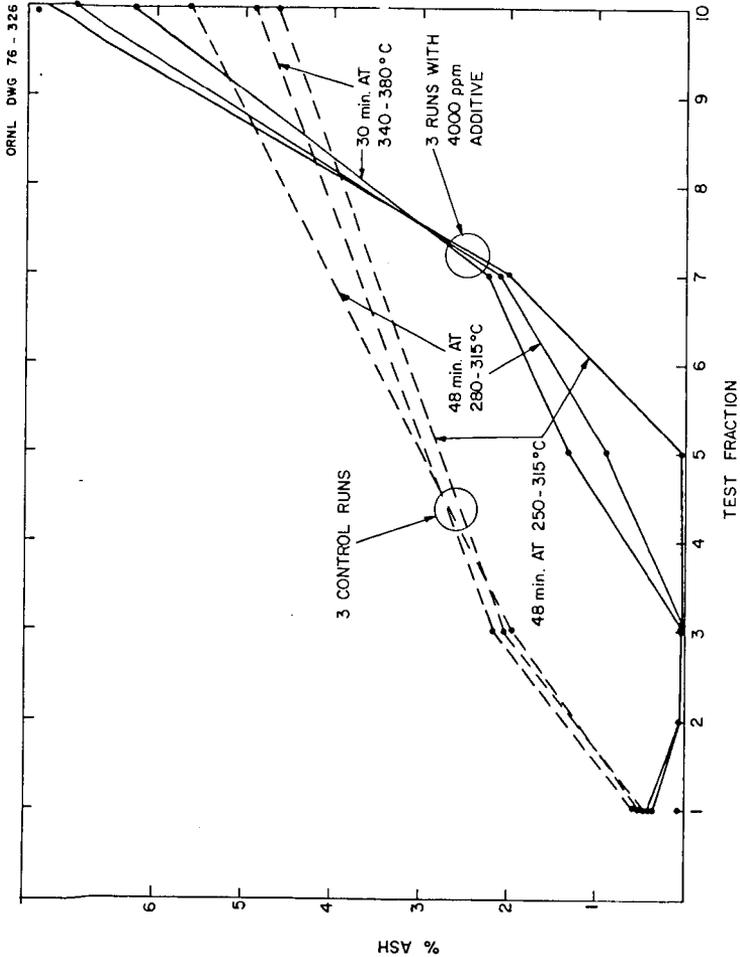
0.4μ



24,000 X

HEAT TREATED UNFILTERED SRC OIL

0.44



COMPARATIVE SETTLING TESTS

POSSIBLE EVENTS LEADING TO MORE RAPID SETTLING

INITIAL EVENTS

NEUTRALIZATION OF ZETA POTENTIAL  
MELTING AWAY OF HARD ORGANIC SURFACE LAYER  
CHEMICAL CONVERSION OF SURFACE  
PHASE SEPARATION

FINAL EVENTS

AGGLOMERATION  
PARTICLE ENLARGEMENT THROUGH RECRYSTALLIZATION  
FLOCCULATION

## THE ROLE OF SOLVENT IN THE SOLVENT REFINED COAL PROCESS

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### INTRODUCTION

The coal-derived liquid used to produce a pumpable liquid slurry feed to hydro-generation systems is commonly referred to as slurry oil or pasting oil. The role of this material, other than as a transport medium, has been neglected until the last few years. The pasting oil used in Bergius Catalytic Hydrogenation consisted of fractions collected at various points in the downstream process. Some of these products of carbonization and/or distillation, were catalytically hydrogenated before being used. No specific analyses were made which provided information about a chemical basis for understanding hydrogen donor capability. Necessary solvent qualities that contribute to or enhance coal conversion, hydrogenation or desulfurization were not quantified. Pott-Broche used a hydroaromatic middle oil generated from coal or tar hydrogenation as their pasting oil and were able to achieve conversions of about 80% at pressures in the 1500-3000 psig range.

More recently processes that depend upon the hydrogen donor capacity of the process solvent have been developed. Among these are the Consol Synthetic Fuel Process (CSF), Pamco Solvent Refined Coal Process (SRC), and Exxon Donor Solvent (EDS) Process.

The CSF and EDS processes depend upon special solvent production through fractionation and subsequent hydrogenation. The SRC process does not employ solvent preparation other than fractionation.

Interest has grown in the role of solvent in these three processes as bench scale and small pilot plant investigations have intensified. The application of analytical techniques toward identifying donatable hydrogen was described by R. P. Anderson (1). More recently donor reactions for desulfurization were described by G. Doyle (2).

The Exxon (EDS) process in operation since 1975 at the one-ton-a-day scale depends heavily upon knowledge of solvent quality and the ability to control it (3). A proprietary solvent quality index was reported by Exxon. A minimum quality index reported to be a function of liquefaction conditions was related to conversion and claimed to improve handling qualities of the products.

This work reports some rather dramatic bench scale coal processing data. Major effects are attributed to identifiable slurry solvent properties.

### THE ROLE OF SOLVENT

In conjunction with a process study undertaken at HRI under Electric Power Research Institute Research Project 389 to investigate SRC process operability and product yield structures for several coals of commercial interest, a preliminary analysis of the role of solvent upon coal conversion was carried out. The purpose of this project was to screen coals prior to their testing at the 6 T/D SRC pilot plant at Wilsonville, Alabama. The operation of this plant has been jointly funded by EPRI and Southern Services, Inc. Catalytic, Inc. is

<sup>1</sup> Hydrocarbon Research, Inc. Trenton, New Jersey

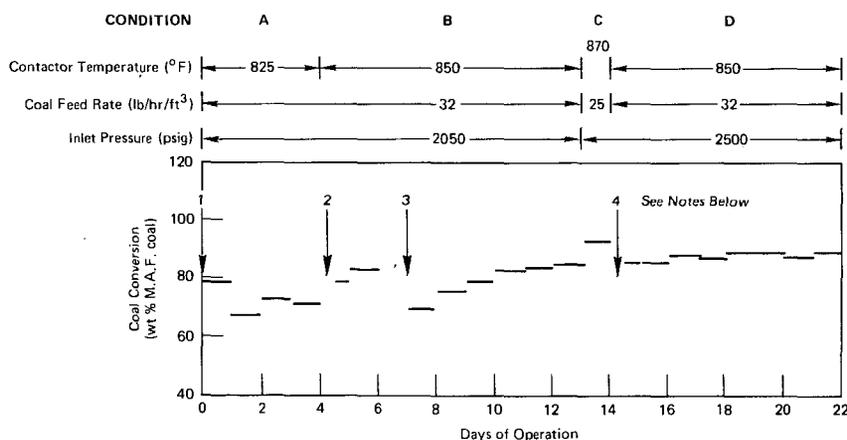
<sup>2</sup> Electric Power Research Institute, Palo Alto, California

the plant operator. The study was undertaken with two sub-bituminous coals, Wyodak coal and Black Mesa coal, and one bituminous coal, Illinois No. 6 coal from the Monterey Mine. The proximate and ultimate analyses of these three coals are summarized in Table 1. All of the work described here was done in a continuous bench-scale noncatalytic unit with a reactor having a volume of 1000 cc. This unit has been described previously in EPRI reports 123-1-0, 123-2, and 389-1 (4, 5, 6, 7).

The solvent was characterized by its tetralin to naphthalene ratio as determined by gas chromatographic analysis, and the  $H_{\beta}$  value by NMR measurement.  $H_{\beta}$  represents hydrogen on carbon atom at  $\beta$ -position of the aromatic ring (excluding methyls).

#### Effect of Tetralin Content of Solvent Upon Coal Conversion - Wyodak Coal Study

During the SRC processing of Wyodak coal it was observed that under steady operating conditions, there was a gradual but persistent change in coal conversion with the operating time. A plot is presented below to show process conditions and coal conversion vs. days of operation. This experimental program was carried out under four conditions as shown. The startup solvent and recycle solvent were characterized by tetralin content and tetralin to naphthalene ratio.



#### NOTES

1. Startup solvent contained 2.8% tetralin, and 0.24 tetralin to naphthalene ratio.
2. About 3000 to 5000 grams of the startup solvent were added during the period of interruption.
3. Wyodak coal operations solvent generated during preceding periods, containing about 1% tetralin, was used for startup.
4. Startup solvent was hydrogenated anthracene oil, containing 1.3% tetralin and 0.76 tetralin to naphthalene ratio.
5. Unconverted coal is defined as the benzene insoluble organic component of dry filter cake. This value is obtained by filtering the slurry product in the bench-scale filter at 300°F, and extracting the cake with benzene to quantify the benzene insoluble content. The dry filter cake value is corrected by subtracting the benzene insolubles present in the 975°F+ oil. Coal conversion in this paper is derived from unconverted coal by using a forced ash balance for bituminous coal or a SO<sub>3</sub> free ash balance for subbituminous coal.

An examination of the operating data revealed that with the startup solvent containing 2.8% tetralin (Condition A), Period 1 gave 79% coal conversion which dropped to 68% during Period 2 as tetralin content decreased to 1.1%. These changes indicate that tetralin content, like coal conversion, is dictated by process conditions. High tetralin content therefore may not by itself sustain good coal conversion under unfavorable process conditions.

The effect of the tetralin content of the startup solvent was more fully demonstrated under Condition B, Periods 5 and 6 which yielded higher conversion, 82%, than Period 8 did. These two intervals were at the same operating conditions, but were interrupted by a shutdown caused by unit plugging. Period 8 was started with the vacuum distillate which comprised the internally generated slurring oil containing only about 1% tetralin, and Period 5 was preceded with an addition of 3,000 to 5,000 grams of the startup solvent containing 2.8% tetralin to the unit loop with a total holdup of 11,000 grams, resulting in an increase in the tetralin content which, in turn, raised the coal conversion.

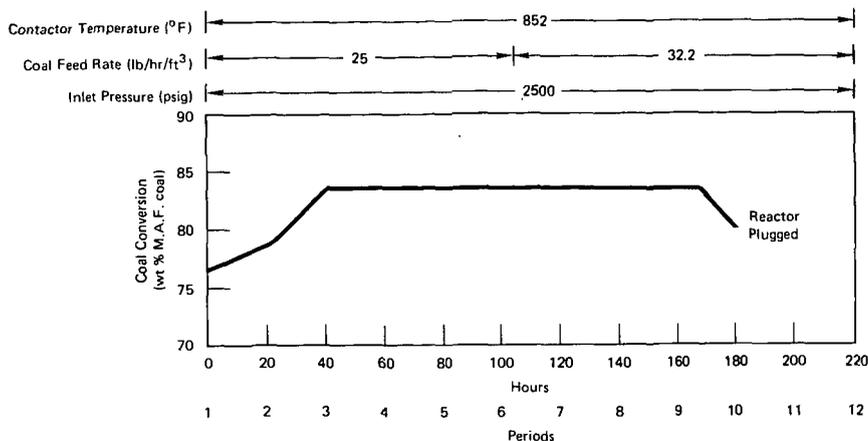
The gradual, but persistent, increase in coal conversion observed during Periods 8 through 13 was rather unique in that it had not been observed before. This was probably caused by the use of a poor startup solvent produced from preceding periods at lower reactor temperatures, which did not contain any tetralin. The solvent from Period 13 had a tetralin content of 1.3%. The bench unit has a rather large holdup capacity; at 15% solvent production, it takes about six days to displace 70% of the startup solvent. These observations further indicate that the hydrogen donor content of the solvent as well as coal conversion is controlled by the process conditions.

Condition D used hydrogenated anthracene oil as the startup solvent. Raw anthracene oil, a coal tar product, was hydrogenated to increase its hydrogen content from 5.5 to 7.2% in a separate operation prior to its use in this work. The hydrogenated anthracene oil has a higher initial boiling point (426°F) than all the other solvents used during this study. Hence, its tetralin (boiling point - 405°F) content is only 1.3%. However, its exceedingly high tetralin to naphthalene ratio, 0.76, indicates that it would be a good donor solvent if it contained other high boiling hydroaromatics with donor capability. Condition D was at higher pressure than Condition B, 2500 psig vs. 2050 psig. Hence, Condition D was expected to yield higher coal conversion than Condition B. The use of hydrogenated anthracene oil as startup solvent did result in a high initial conversion of 86%. The coal conversion only increased slightly to 88% in contrast to the steady increase from 70% to 85% under Condition B which used a poor startup solvent possessing a tetralin to naphthalene ratio of about 0.16. The high initial conversion and slight increase in conversion observed under Condition B leads to a conclusion that the hydrogenated anthracene oil is a better donor solvent than the other startup solvent and recycle solvent because it contains high concentrations of hydrogen donors other than tetralin.

#### The Effect of Other Hydrogen Donors - Black Mesa Coal Operation

Solvent analyses for the Black Mesa and Monterey coal operations are summarized in Table 2. A plot is presented below to show process conditions and coal conversion.

The Black Mesa coal operations led to a rather significant deduction. The startup solvent obtained from the Wilsonville SRC unit on another coal contained 4.2% tetralin and a tetralin to naphthalene ratio of 0.35. These values were much higher than those of the bench unit recycle solvent, which contained 1.6 to 2.5% tetralin and a tetralin to naphthalene ratio of 0.12 to 0.23. However, the coal conversion steadily increased from 77 to 83.5% and then remained at this level.



An examination of the H-NMR data in Table 2 discloses that  $H_{\beta}$ , a measure of the hydroaromatics content of the recycle solvent, increased steadily from 16.5 to 21.6% from Period 1A to Period 7/8. Since the tetralin (one of the hydroaromatics) content of the startup solvent is higher than the recycle solvent, the increase in  $H_{\beta}$  represents an increase in other hydroaromatics through the displacement of the startup solvent. These observations indicate that the solvent produced from the hydrogenation of Black Mesa coal contains other hydrogen donors which are more reactive towards Black Mesa coal than tetralin.

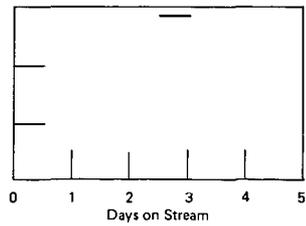
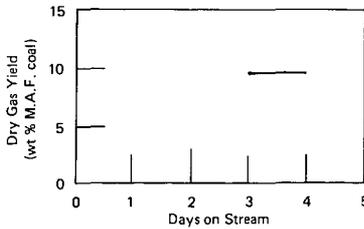
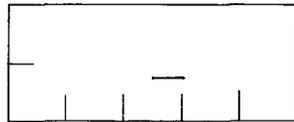
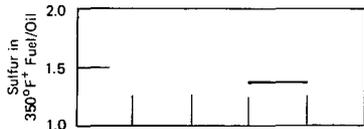
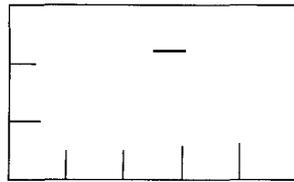
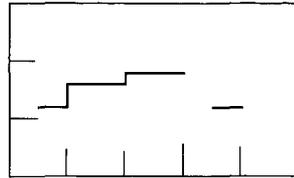
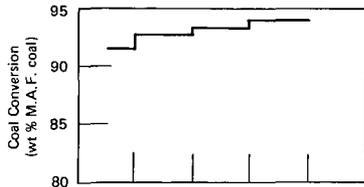
#### The Effect of Solvent Quality Upon Coke Formation - Monterey Coal Operation

Wilsonville started operation on Illinois No. 6 Monterey coal in August 1975. Since the Monterey coal had a higher organic sulfur content (2.8%) than the Illinois No. 6 coal from Burning Star Mine which had been used previously, the dissolver temperature was raised from the previous 835°F level to 855-890°F at 1,700 psig in an attempt to produce SRC meeting the sulfur specification of 0.96 weight percent. There was an indication of solids buildup in the dissolver during these runs. This was confirmed by flushing out 400-500 pounds of solids from the dissolver, which has a total volume of 20 cubic feet. Later, extensive plugging of transfer lines around the dissolver occurred with substantial coke accumulation in the lower half of the dissolver. The plugging forced a shutdown of the plant. HRI was retained by EPRI to carry out bench unit SRC experiments under conditions similar to Wilsonville's. Experiments were carried out at 1500 psig, 840 and 868°F contactor temperatures. The coking problem was demonstrated and duplicated in the bench-unit operation at the higher temperatures.

Table 3 summarizes solvent analyses together with certain pertinent operating data. The recycle solvents contained more hydroaromatics than the startup solvent from the Wilsonville SRC plant, as shown by the higher tetralin/naphthalene ratio and higher NMR H measurements of the recycle solvents. Hence, the recycle solvents from these two runs should be better solvents than the Wilsonville solvent. This assumption was supported by the slight, but steady, increase in coal conversion during these two runs. Plots are presented below to show coal conversion, hydrogen consumption, sulfur content of 380°F+ fuel oil, and dry gas production.

Run Number 177-117  
 Contactor Temperature (°F) 840  
 Coal Feed Rate (lb/hr/ft<sup>3</sup>) 25  
 Inlet Pressure (psig) 1500

177-118  
 868  
 25  
 1500



The hydrogen consumption was higher at high contactor temperature, 5.1 vs. 4.1 W % as expected. However, the high hydrogen consumption was accompanied by unfavorable product distribution as follows:

1. Low coal conversion, 89.5% at high temperature vs. 94% at low temperature.
2. High C<sub>1</sub>-C<sub>3</sub> dry gas production, 13.3% vs. 7.8%.
3. A deterioration in solvent properties, as shown by the low tetralin to naphthalene ratio, 0.36 vs. 0.5, and low H<sub>g</sub> value, 16 vs. 19%.
4. High Coke Formation: The run at 840°F was operated for 83 hours without reactor plugging. The run at 868°F was operated for 78 hours then terminated by reactor plugging. The reactor was filled with a hard plug of solids between the middle of preheater to a length of 9 feet out of reactor length of 13 feet. In addition, it was observed that the extensive coke formation was accompanied by a doubling of the filtration rate of the slurry product.

These phenomena lead to the following hypothesis: Coal hydrogenation is promoted by the hydrogen donors present in the solvent. When the process conditions result in a deterioration of donor capability of the solvent, thermal cracking gets ahead of hydrogenation, which can lead to coke formation.

#### COKE FORMATION

##### Characterization of Coke

Two coke samples taken from the Wilsonville dissolver after operations on Illinois #6 coal from Monterey Mine (8) were sent to Pennsylvania State University for optical characterization. One was a fine-grained material and the other was a much coarser grain size. Penn State reported (9) that the fine-grained sample was composed of insoluble particles surrounded by a layer of anisotropic carbon. The most common constituents of the nuclei are semi-coke and calcite, both of which are present in feed coal. The shell of anisotropic carbon is deposited on these nuclei in the SRC process with this coal. Fine-grain anisotropy and extinction characteristics are indicative of a uniform, onion-like deposition, i.e., concentric layers surrounding a nucleus. The coarse-grain sample exhibited agglomeration of the fine-grained deposit and there was a coarsening of anisotropy of the carbonaceous shell. These domains or mosaic structures are recognized as the more traditional optical texture of coalesced mesophase.

The immediate cause of sedimentation of the particles in the reactor was the growth of anisotropic carbon on to the undissolved materials. These insolubles consist of a semi-coke contaminant, mineral matter and undissolved macerals (generally fusinitic material). The resulting adhesion of particles forms a coke-like sediment. Operation conditions and optical texture of the bonding anisotropic carbon suggest that its growth from the solution was by a mechanism of growth of nematic liquid crystals, thus resulting in mesophase formation which then leads to a non-plastic semi-coke.

Coke analyses from both Wilsonville and HRI operations with Illinois No. 6 Monterey coal are summarized in Table 4.

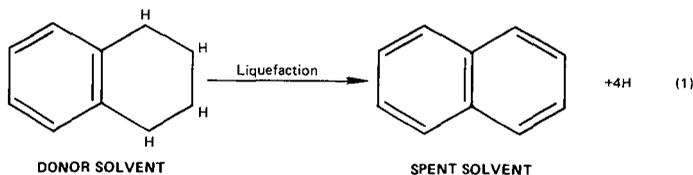
Most of the solids recovered from the dissolver and various parts of the Wilsonville unit such as the high pressure letdown valves and the blowdown tank were similar in composition. These compositions are represented by a UCC (undissolved carbonaceous cresol insolubles) to ash ratio of around 2 with the

exception that the solids which deposited at the vapor-liquid interface contained much more cresol-insoluble carbonaceous material than the others. The solids recovered from the HRI bench units had a much higher ash content than those from the Wilsonville unit. The higher ash content of coke together with the shorter time of HRI operation coincides with Penn State's characterization of coke as a uniform, onion-like carbon deposition surrounding a nucleus of mineral matter.

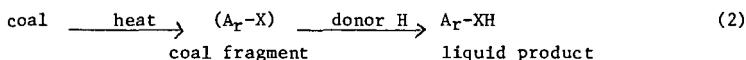
The H/C atomic ratios of all coke deposits (including the solids deposits at the vapor-liquid interface) were quite consistent, about 0.50. This is significantly lower than the H/C atomic ratio of the Monterey Mine coal, 0.78, and the unconverted coal, 0.73. There was no difference in the H/C atomic ratio between the coke accumulated over short periods of time (three to four days in the HRI unit) and long periods of time (more than one month in the Wilsonville unit). The consistency of the H/C of coke under these circumstances leads to the postulation of a reprecipitation mechanism, without any significant carbonization after the coke deposition.

#### Mechanism for Coke Formation

The SRC process as practiced at Wilsonville uses a recycle solvent (350° to 750°F) for transporting the coal into the reactor and for promoting the dissolution and the conversion of coal. Reaction (1) illustrates the ability of a donor solvent molecule to release donor hydrogen during liquefaction using tetralin as an example of a donor solvent molecule.



Reaction (2) represents the free radicals formed by thermal cracking of the coal "molecules" accepting donor hydrogen to form liquid product.



X = C, O, S, or N

When there is a deficiency of donor hydrogen the coal fragments recombine to form coke.



The presence of solid particles, such as mineral matter, acts as nucleus upon which the reprecipitation of coal fragments occurs.

#### SUMMARY AND CONCLUSIONS

A preliminary study of the effect of solvent upon SRC process performances was undertaken. The startup solvent and makeup solvent have a significant effect upon coal conversion. However, the use of a good startup solvent does not sustain good process performance under unfavorable process conditions and vice versa. Hydroaromatics, measured in part by Hg from NMR analysis, other than tetralin also possess hydrogen donor capabilities. These hydroaromatics could be better donors than tetralin. This conclusion was reached during a process study of the Black Mesa coal, a subbituminous coal. At the same hydrogen pressure, an increase in reactor temperature resulted in higher hydrogen consumption, lower coal conversion and high dry gas (C<sub>1</sub>-C<sub>3</sub>) production. The poor process performances were accompanied by a deterioration in solvent properties (as shown by the lower tetralin to naphthalene ratio and lower Hg value) and significant amount of coke formation. These findings support a hypothesis that coke formation results when thermal cracking gets ahead of hydrogenation which is promoted by the hydrogen donors present in the solvent.

#### ACKNOWLEDGEMENTS

The work described here was done as part of Electric Power Research Institute Research Project (RP) 389. The purpose of the work was to generate process operability, yield structure and hydrogen consumption data for candidate feed coals to the Utility Industry Solvent Refined Coal Test Unit at Wilsonville, Alabama.

The stimulating discussions and solvent analysis provided by Dr. D. D. Whitehurst and Dr. T. O. Mitchell (whose work was carried out as part of EPRI Research Project 410) are sincerely appreciated.

Analysis of coke from the Wilsonville unit was carried out under EPRI Research Project 366 at the Pennsylvania State University.

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TABLE 1

ANALYSIS OF FEED COALS

	<u>Wyodak</u> <u>Coal</u>	<u>Black</u> <u>Mesa Coal</u>	<u>Illinois No. 6</u> <u>Monterey Coal</u>
Proximate Analysis (dry basis) wt.%			
Ash	7.04	10.10	10.11
Volatile Matter	46.48	42.57	40.85
Fixed Carbon	46.48	47.33	49.04
Ultimate Analysis (dry basis) wt.%			
Carbon	67.78	69.81	69.71
Hydrogen	4.97	4.79	4.56
Sulfur	0.80	0.33	4.52
Nitrogen	0.65	1.04	1.17
Ash	7.04	10.10	10.11
Oxygen (by difference)	18.76	13.93	9.89
Sulfur Forms (dry basis) wt.%			
Pyritic Sulfur	0.15	0.17	1.23
Sulfate Sulfur	0.01	0.00	0.14
Organic Sulfur (by difference)	0.51	0.20	2.78
Total Sulfur	0.67	0.37	4.15
Mineral Analysis (ignited Basis) wt.%			
P <sub>2</sub> O <sub>5</sub>	0.35	0.13	0.34
SiO <sub>2</sub>	27.91	46.99	50.25
Fe <sub>2</sub> O <sub>3</sub>	5.30	5.33	18.66
Al <sub>2</sub> O <sub>3</sub>	15.75	16.96	18.15
TiO <sub>2</sub>	1.10	0.96	0.87
CaO	19.00	18.00	4.25
MgO	5.60	2.24	0.86
SO <sub>3</sub>	22.84	6.17	3.29
K <sub>2</sub> O	0.48	0.81	1.92
Na <sub>2</sub> O	0.72	1.69	1.17
Undetermined	0.95	0.72	0.24

TABLE 2

## SRC OPERATIONS ON BLACK MESA COAL AND MONTEREY COAL

## SOLVENT ANALYSIS

Run Number 177-	Startup Solvent From Wilsonville		Black Mesa Coal		Recycle Solvent		Monterey Coal	
	119-1	-2B	-5	-7/8	117-4	118-3B		
Reactor Temperature, °F (estimated)	847	845	838	841	835	863		
Inlet Pressure, Psig	2500	2500	2500	2500	1500	1500		
Coal Feed Rate, Lbs/Hr/Ft <sup>3</sup>	21.4	25	25	32.2	25	25		
Coal Conversion, W % of M.A.F.F. Coal	77.1	79.2	83.0	83.3	94.0	89.5		
Hydrogen Consumption W % of M.A.F.F. Coal			2.94	2.84	4.1	5.1		
Simulated Distillation (VPC)								
Boiling Point, °F	284	293	302	266	320	302		
IBP, °F	10.3	15.3	11.7	13.2	14.8	15.0		
IBP-403°F, W %	4.2	1.6	2.5	2.5	5.2	4.1		
405°F (Tetralin)	12.1	13.2	10.9	11.5	10.0	11.3		
412°F (Naphthalene)	50.2	47.8	52.3	48.7	49.3	46.0		
413-642°F	9.9	7.2	6.6	8.2	5.3	6.3		
644°F (Phenanthrene/Anthracene)	13.4	14.8	16.0	15.9	15.4	17.3		
646°F-EP	797	833	824	824	824	860		
EP, °F	16.3	14.8	13.4	14.0	15.2	15.4		
Tetralin + Naphthalene	0.35	0.12	0.23	0.22	0.52	0.36		
Tetralin/Naphthalene								
Proton Distribution (H-NMR) /l/								
Har (9-6 ppm)	52.9	54.2	50.3	48.2	48.0	54.6		
Hα (3.5-2 ppm)	24.2	24.2	23.7	23.9	27.0	24.5		
Hβ (2-1.1 ppm)	17.5	16.5	20.5	21.6	18.3	16.4		
Hγ (1.1-0.4 ppm)	5.4	5.1	5.5	6.3	6.7	4.5		

/l/ H<sub>α</sub> represents aromatic hydrogens, H<sub>β</sub> benzylic hydrogens including methyls, H<sub>γ</sub> hydrogens on carbon atoms at β-positions of aromatic rings, and H<sub>γ</sub> hydrogens in aliphatic methyl groups.

TABLE 3

## SRC OPERATIONS ON ILLINOIS NO. 6 MONTEREY MINE COAL

## SOLVENT ANALYSIS

	Startup Solvent From Wilsonville	Recycle Solvent	
		117-4	118-3B
Contactor Temperature, °F (Estimated)		839	863
Inlet Pressure, psig		1500	1500
Coal Feed Rate, Lbs/Hr/Ft <sup>3</sup>		25	25
Coal Conversion, W % of M.A.F. Coal		94.0	89.5
Hydrogen Consumption, W % of M.A.F. Coal		4.1	5.1
		0.66	0.57
Simulated Distillation (VPC), Boiling			
Boiling Point, °F			
IBP, °F	284	320	320
IBO-403°F, W %	10.3	14.8	15.0
405°F (Tetralin)	4.2	5.2	4.1
412°F (Naphthalene)	12.1	10.0	11.3
413-642°F	50.2	49.3	46.0
644°F (Phenanthrene/anthracene)	9.9	5.3	6.3
646°F-End Point	13.4	15.4	17.3
End Point, °F	797	824	860
Tetralin + Naphthalene	16.3	15.2	15.4
Tetralin/Naphthalene	0.35	0.52	0.36
Proton Distribution (H-NMR)*			
H <sub>ar</sub> (0-6 ppm)	52.9	48.0	54.6
H <sub>ar</sub> (3.5-2 ppm)	24.2	27.0	24.5
H <sub>β</sub> (2-1.1 ppm)	17.5	18.3	16.4
H <sub>r</sub> (1.1-0.4 ppm)	5.4	6.7	4.5

\* H<sub>ar</sub> represents aromatic hydrogen, H<sub>α</sub>, benzylic hydrogen including methyls, H<sub>β</sub>, hydrogen on carbon atoms once removed from aromatic rings (excluding methyls), and H<sub>r</sub>, hydrogen in aliphatic methyl groups.

TABLE 4

ANALYSIS OF COKE DEPOSITS

Coal Feed	Wilsonville Operation				HRI Operation		
	Monterey		Burning Star		Monterey		
Date Sampled	8/28/75	8/31/75	9/4/75	9/5/76	4/7/75	4/8/75	
Sample No.	9464	9343	9440	9457	--	--	--
Run No.	--	--	---	--	--	177-117	177-118
Location	Let Down Valve LV-415	Low Pressure Flash at Pump	Flushing- Top of solids dissolver vapor liquid interface	Bottom of dissolver 6' cone	Dissolver solids flushout	Dissolver solids hydro-	Dissolver Middle section Bottom Section
Ash, W %	31	34	35	19	33	52.26	28.99
UCC(1), W %	64	58	63	75	66		
Cresol Soluble, W %	5	8	2	7	1		
UCC/Ash	2.06	1.71	1.80	3.89	2.00		
Benzene Insoluble, W %	--	--	--	--	--	19.18	44.75
Benzene Soluble, W %	--	--	--	--	--	28.56	26.26
Benzene Insoluble/Ash	--	--	--	--	--	0.37	1.54
Sulfur, W %	1.68	1.41	1.80	0.79	0.55		
Sulfide	0.14	0.10	0.18	0.13	0.33		
Pyritic	0.11	0.50	0.12	0.16	0.09		
Sulfate	0.64	1.52	0.57	0.62	1.34		
Organic							
Elemental Analysis, W %							
C	60.83	56.12	56.95	73.55	69.09	42.99	Benzene-Insoluble Solids
H	2.53	2.14	2.27	3.02	2.02	1.86	34.40
N	1.03	1.09	1.02	1.15	1.00	0.73	55.26
Cl	0.78	0.96	0.96	0.36	0.10	0.05	--
O (by difference)	0.79	2.06	2.28	0.84	2.95	0.91	--
S, total	2.57	3.54	2.67	1.70	0.87	5.24	5.61
Ash	31.47	34.63	34.86	19.28	24.07	48.62	28.99
H/C Atomic Ratio	0.50	0.46	0.48	0.49	0.51	0.52	0.47

(1) Undissolved carbonaceous cresol insolubles

DEACTIVATION OF CO-MO CATALYST  
DURING H-COAL® OPERATIONS

Cecilia C. Kang and Edwin S. Johanson

Hydrocarbon Research, Inc.  
P. O. Box 1416  
Trenton, N. J. 08607

The H-Coal® Process has been under development for over ten years and has been supported by government and industry. Work has been carried out on bench-scale units handling about 25 pounds of coal per day and in a Process Development Unit (PDU) handling 3 tons per day. Some fourteen coals, including bituminous, subbituminous, lignite and brown coal have been tested without difficulty.

In the H-Coal Process, coal is dried, pulverized, and slurried with coal-derived oil for charging to the coal hydrogenation unit. The heart of the process is the unique reactor design shown in Figure 1. The coal-oil slurry is charged continuously with hydrogen to a reactor containing a bed of ebullated catalyst wherein the coal is catalytically hydrogenated and converted to liquid and gaseous products. In the ebullated bed the upward passage of the solid, liquid, and gaseous materials maintains the catalyst in a fluidized state. The relative size of the catalyst and coal is such that only the unconverted coal, ash, liquid and gaseous products leave the reactor while the catalyst remains therein. Catalyst can be added and withdrawn continuously so a constant activity can be maintained. The reactor provides a simple means of controlling reactor temperature and an effective contact between the reacting species and the catalyst, permitting a satisfactory degree of reaction at reasonable operating pressure. The liquid product from the reactor is a synthetic crude oil which can be converted to gasoline and furnace oil by conventional refining processes. Alternately, under milder operating conditions, a clean fuel gas and low sulfur fuel oils may be produced. The relative amounts of these products depend on the desired sulfur level in the heavy fuel oil.

In September 1974, Hydrocarbon Research, Inc. received an 8.1 million dollar first phase contract to design a nominal 600 ton per day pilot plant to demonstrate the H-Coal Process. The contract is jointly funded two thirds by Government and one third by industry. At the present time two oil companies and Electric Power Research Institute are the industry representatives.

The proposed pilot plant will be located at Catlettsburg, Kentucky, adjacent to the Ashland Oil Refinery. It is designed for two modes of operation, (1) to process 633 tons of coal per day to produce 1,920 barrels of fuel oil with less than 0.7 W % sulfur from coal

containing more than 3 W % sulfur (fuel oil mode), or (2) to process 210 tons of coal per day to produce 740 barrels per day of synthetic crude (syncrude mode). The design basis for the fuel oil mode of operation is based on bench-scale experimentation. The current laboratory program has been directed towards confirming in the PDU the design basis for the pilot plant.

#### H-COAL CATALYST

The H-Coal Process uses a commercial Co-Mo catalyst developed originally for desulfurizing the petroleum residua. The Co-Mo catalyst selectively hydrocracks the carbon-sulfur bonds to release the sulfur as hydrogen sulfide and to terminate the carbon bond by hydrogenolysis without cracking of the carbon-carbon bond. Bituminous coal and subbituminous coal are characterized by the fact that they are mainly composed of condensed aromatic rings and oxygen-containing functional groups:  $-COOH$ ,  $-OCH_3$ ,  $-OH$ , and " $>C=O$ ". These first three functional groups are all terminal groups, but the so-called "carbonyl group" (" $>C=O$ ") exists as an oxygen bridge linking the condensed aromatic rings together. Efficient coal liquefaction with minimum hydrogen consumption can be achieved if the " $>C=O$ " linkage is selectively hydrocracked. Since the organic functional groups containing oxygen or sulfur behave similarly, the use of Co-Mo catalyst for coal liquefaction and desulfurization has given reasonably good performance.

HRI has accumulated nearly 50,000 hours of process evaluation and optimization in bench scale and process development units. While the H-Coal Process development is in an advance stage in most respects, catalyst evaluation and development has not kept pace with overall program progress. A proposal for improving the current Co-Mo catalyst has been submitted to the Energy Research and Development Administration. It is anticipated that an approval from ERDA will be received soon.

#### CATALYST DEACTIVATION

Critical examination of available analytical data on fresh and used catalysts has disclosed that three common causes for catalyst deactivation, namely, carbon deposition, sintering, and metal deposition contributed to the deactivation of the Co-Mo catalyst. Their relative detrimental effects on the catalyst vary with the rank of coal being processed and the processing conditions.

Catalyst deactivation curves in terms of hydrogen consumption and sulfur content of fuel oil are presented in Figures 1 & 2. These curves were derived from HRI's recent PDU operation with Illinois No. 6 coal from Burning Star Mine and were included in a paper presented at the 68th AIChE Meeting, November, 1975.<sup>(1)</sup> The deactivation curves are characterized by a steep initial deactivation followed by a gradual decline. The shape of the curve is typical of most catalyst deactivation curves.

A discussion is given below with respect to the magnitude of carbon deposition, sintering, and metal deposition on the Co-Mo catalyst and the relative importance of these three factors in contributing to catalyst deactivation.

## CARBON DEPOSITION

The used catalysts contained 10 to 35% carbon. In operations in the normal range of conditions the used catalyst contained 10 to 20% carbon. No consistent trend has been observed between the magnitude of carbon deposition on catalyst and the rank of coal feed. Although the lower rank coals (e.g. Wyodak Coal) and lignites tend toward the lower end of the range, while higher rank coals (e.g. Pittsburgh Seam Coal) tend toward the higher end of this range. For purposes of illustration, Table I summarizes the carbon content of used catalyst from a number of bench unit experiments on Pittsburgh Seam Coal. The extent of carbon deposition reaches a certain level within a few days time and does not increase with further operations. Low pressure operations at 800 psi hydrogen pressure or lower invariably yielded carbon deposition of over 22% on used catalyst. Experiments carried out with catalyst after regeneration indicate that carbon deposition contributes significantly to initial catalyst deactivation.

Table I

### CARBON CONTENT OF USED CATALYSTS

Coal Feed	----- Pittsburgh Seam -----				
Coal Processed, Lb.	760	102	805	2246	2602
Catalyst Age, Hours	503	59	463	1474	263
Hydrogen Partial Pressure, psig	800	-----1800-----			
Used Catalyst, % C	26.5	19.0	13.6	20.7	20.0

## SINTERING

The Co-Mo catalysts used in the majority of experiments are supported on gamma alumina. Gamma alumina is thermally unstable, particularly in the presence of steam. Literature data are available on the effect of steam on sintering of alumina. For the purpose of illustration, the effect of temperature and steam on the sintering of a nickel on gamma alumina catalyst<sup>(2)</sup> is shown in Figure 4. The presence of steam not only causes an initial drop in surface area during the first sixty hours but also enhances the long term slow rate of decline.

An examination of the available analytical data on fresh, used, and regenerated catalysts indicates that catalyst sintering occurred after an extended run of thirty days using Illinois No. 6 coal wherein the H<sub>2</sub>O: H<sub>2</sub> in the reactor outlet gas is about 1: 8. An eleven day operation under similar conditions did not cause any noticeable sintering of catalyst. Sintering was quite pronounced after a forty nine day operation using partially dried coal containing 20% moisture, resulting in a H<sub>2</sub>O: H<sub>2</sub> ratio of 1: 2 in reactor outlet gas. Catalyst sintering could be the cause for the observed high deactivation rate of the wet Wyodak coal operation in comparison to a similar experiment using more completely dried Wyodak coal containing only 2% moisture.

## METAL DEPOSITION

Some typical analysis of coal ash composition and major catalyst contaminants are shown in Tables 2 and 3. Table 4 presents a semi-quantitative analysis of a typical used catalyst by emission spectrometry. The relative level of metal contaminants on the catalyst was not in the ratio characteristic of the ash composition of the coal. Metal contaminants act as a physical barrier between the reactants and active sites of the catalyst. When any metal contaminant increases with catalyst age, it usually is the prime factor in causing catalyst deactivation. The common metal contaminants on the used catalyst are titanium, iron, calcium and sodium. Bituminous coal, such as Pittsburgh Seam and Illinois No. 6, deposits appreciable amounts of titanium and low amounts of calcium and sodium; subbituminous coal, such as Wyodak, usually deposits higher amounts of sodium and similar amounts of calcium in comparison to the bituminous coal. The range of iron deposition is similar from various ranks of coal.

Table 2  
COMPOSITION OF COAL ASH

Coal	Wyodak	Illinois No. 6
Ash, W %	9.73	9.95
<u>Composition of Ash, W %</u>		
Phosphorus Pentoxide	0.61	0.06
Silica	33.64	45.74
Ferric Oxide	3.80	16.18
Alumina	17.08	18.95
Titania	1.16	0.95
Calcium Oxide	18.50	9.50
Magnesium Oxide	4.70	0.94
Sulfur Trioxide	18.04	4.52
Potassium Oxide	0.71	1.79
Sodium Oxide	0.80	0.43
Undetermined	0.95	0.94

Table 3  
CONTAMINANTS ON USED CATALYSTS

Coal Feed	Wyodak	Illinois No. 6
Catalyst Age, lb. Coal/lb. Catalyst	781	2644
<u>Oil-Free Catalyst, Analyses, W %</u>		
Carbon	13.67	10.9
Sulfur	5.13	4.6
Iron	1.73	1.5
Titanium	0.03	5.11
Sodium	1.46	0.42
Calcium	1.04	0.24

Table 4

EMISSION SPECTROMETRY ANALYSIS OF A TYPICAL USED CATALYST

Analysis of Oil-Free (Benzene-Extracted) +20 Mesh Extrudates

<u>Element</u>	<u>Approximate W % Metal</u>
Aluminum	10
Antimony	0.02
Arsenic	0.2
Barium	Not detected
Beryllium	0.01
Boron	0.7
Calcium	0.3
Chromium	0.05
Cobalt	1
Copper	<0.01
Gallium	0.05
Germanium	0.3
Iron	1
Lead	0.01
Magnesium	0.2
Manganese	0.08
Molybdenum	5
Niobium	~0.01
Nickel	0.3
Silicon	0.2
Titanium	3
Vanadium	0.2
Zinc	0.1
Zirconium	0.05

It is observed that among the metal contaminants identified so far, titanium deposition from the bituminous coal increased with catalyst age. Recent analyses of benzene-insoluble and benzene-soluble components of the residua derived from Illinois No. 6 coal show that the benzene-insoluble portion of the residuum contains about the same amount of titanium as present in the M.A.F. coal, 900 ppm, and the benzene-soluble portion of the residuum contains only about 5% of the titanium as present in the coal. Thus it is quite logical to deduce from these data that titanium exists in a form of organometallic complex in the bituminous coal. This deduction is further supported by the knowledge that titanium is just below vanadium with respect to the strength of the ligand-metal bonds and stable vanadium porphyrin exists in petroleum. It should be noted that very little titanium was deposited on the catalyst when Wyodak coal was processed, even though Wyodak coal contains about the same amount of titanium as Illinois No. 6 coal. Further work is needed to establish whether the benzene-insoluble residuum from the Wyodak coal contains any significant amount of

titanium. It is also observed that only about one-twentieth of the titanium present in the Illinois No. 6 bituminous coal deposited on the catalyst.

Scanning electron micrograph of spent catalysts showed that titanium penetrated to a depth of approximately 10% of the radius of the 1/16" extrudate, and iron was found in clusters on the surface of the extrudate. The way that titanium deposition concentrates in the periphery of the catalyst extrudate is expected to be more detrimental in reducing the effective diffusion of 'coal molecule' into the catalyst pore than if the titanium were distributed uniformly throughout the whole extrudate.

When bituminous coal, such as Illinois No. 6, was processed and was liquified, metal deposition appeared to cause the gradual but steady deactivation of catalyst.

#### CATALYST ATTRITION

The magnitude of catalyst attrition in the ebullated bed reactor is well defined by the rotating drum attrition test developed by HRI. By applying this test, HRI has successfully chosen a commercial catalyst which showed satisfactory attrition resistance during recent PDU operations. Catalyst recoveries are summarized in Table 5. About 93 W % catalyst (by Mo balance) was recovered after 814 hours operation, processing 2,687 lb. coal/lb. catalyst. The increase in weight of the catalyst was consistently greater than the total weight of the major contaminants determined. These and other data obtained with different coal feeds indicate the possibility of the presence of other major contaminants. Deposition of alumina appears to be another major contaminant as shown by a few analyses comparing the Al to Mo ratio of fresh and used catalyst.

Table 5

#### CATALYST RECOVERY FROM PDU OPERATIONS

Run	A	B	C	D
Catalyst Age				
Hours	814	535	475	272
Coal Processed, Lb/Lb Catalyst	2687	3061	2451	1509
Catalyst Recovery, W %				
Gross Weight	139.0	140.6	133.8	156.4
Gross Weight less major Contaminants determined	103.5	102.3	100.0	112.2
Molybdenum Balance	92.7	96.8	96.4	97.6

## SUMMARY AND CONCLUSIONS

Critical examination of available analytical data on fresh and used catalysts disclosed that three common causes for catalyst deactivation, namely, carbon deposition, sintering, and metal deposition, contributed to the deactivation of the Co-Mo catalyst used in the H-Coal<sup>®</sup> Process. Their relative detrimental effects on the catalyst vary with the rank of coal being processed and the process conditions.

The used catalyst contained 10 to 35% carbon. The extent of carbon deposition is affected more by process conditions than by either coal feed or catalyst age. Low pressure operations at 1000 psig or lower yielded high carbon deposition of over 22%.

The Co-Mo catalyst is supported on gamma alumina. The pronounced effect of steam on sintering of gamma alumina at temperatures below 1000°F is well known. Operations with subbituminous coal such as Wyodak coal caused much more pronounced catalyst sintering than those using bituminous coal such as Illinois No. 6 coal. The high oxygen and high moisture content of Wyodak coal (in the event of incomplete drying) give rise to a relatively high H<sub>2</sub>O/H<sub>2</sub> ratio in the process gas, which caused rapid catalyst deactivation through sintering.

Major metal contaminants found on the catalyst are titanium, iron, calcium, and sodium, and in some cases also aluminum. The magnitude of titanium deposition on catalyst from bituminous coal feed increased with catalyst age. Titanium deposition was concentrated to a depth of approximately 10% of the radius of spent 1/16" extrudate, whereas iron was found in clusters on the extrudate surface.

It is concluded that the initial catalyst deactivation is caused by carbon deposition in the case of bituminous coal. Both carbon deposition and sintering contribute to the initial catalyst deactivation with subbituminous coal feed. Titanium deposition from the bituminous coal causes a gradual decline in catalyst activity.

Commercial Co-Mo catalysts have shown different magnitude of catalyst attrition in the ebullating bed reactor. HRI developed a rotating drum attrition test which defines the attrition resistance of the catalyst under H-Coal processing conditions. HRI successfully chose a commercial catalyst which showed satisfactory attrition resistance during recent extended PDU operations at gas and coal rates at the design values for the pilot plant being built at the present time.

## ACKNOWLEDGEMENT

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# EBULLATED BED REACTOR

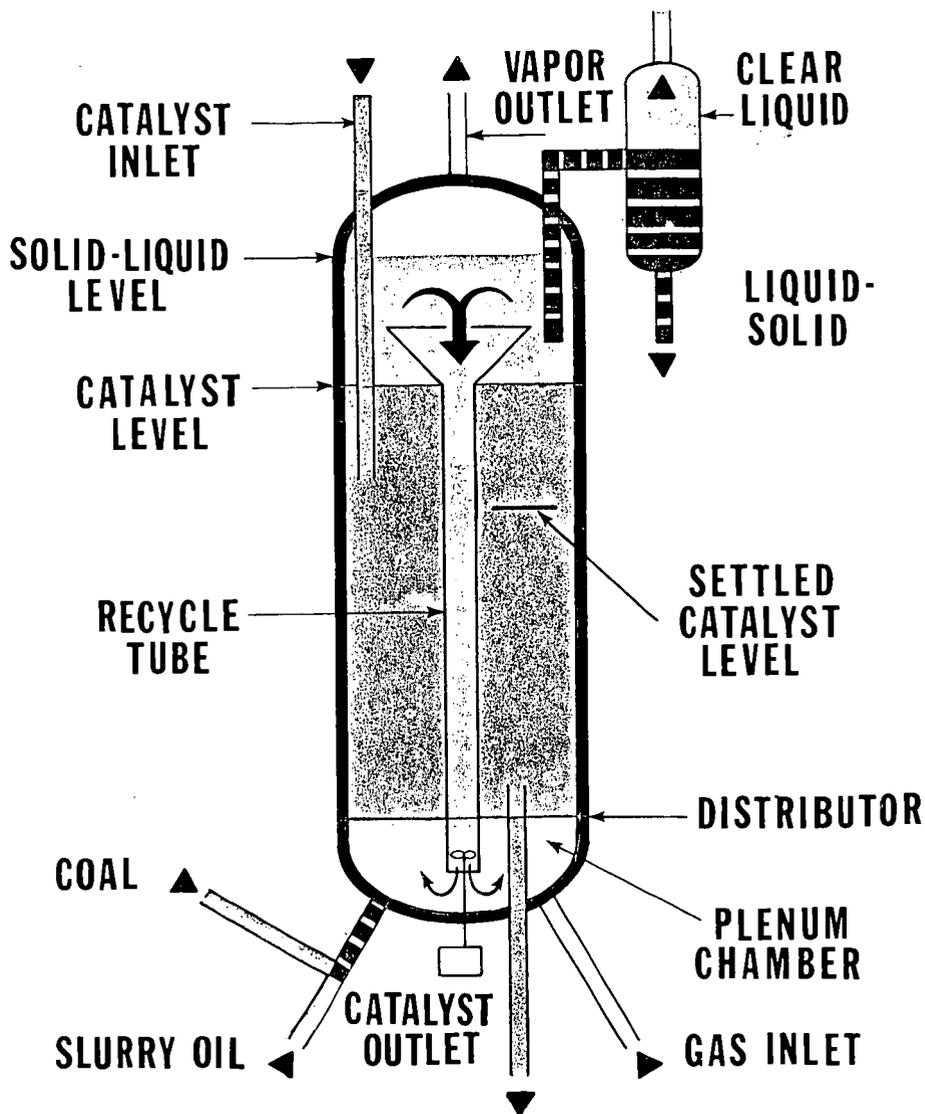


Figure 1

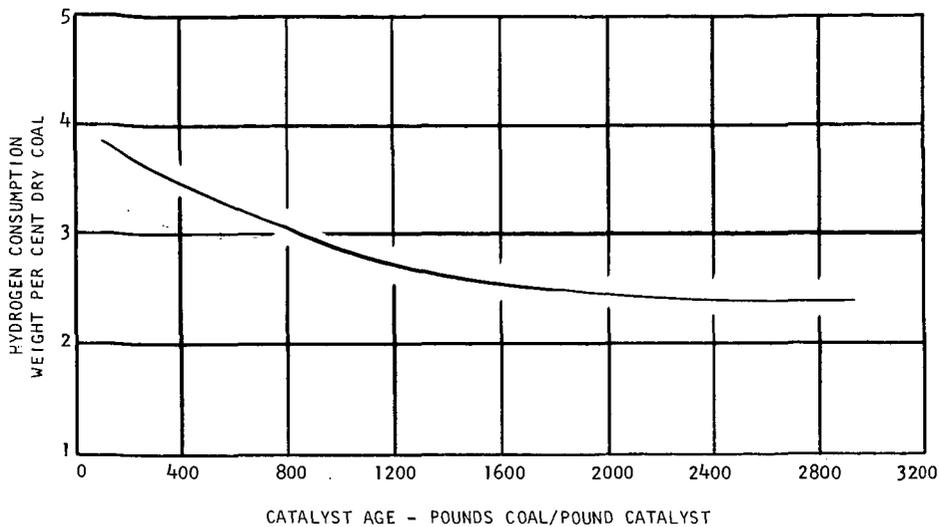


Figure 2 Decline in Hydrogenation Activity of Catalyst

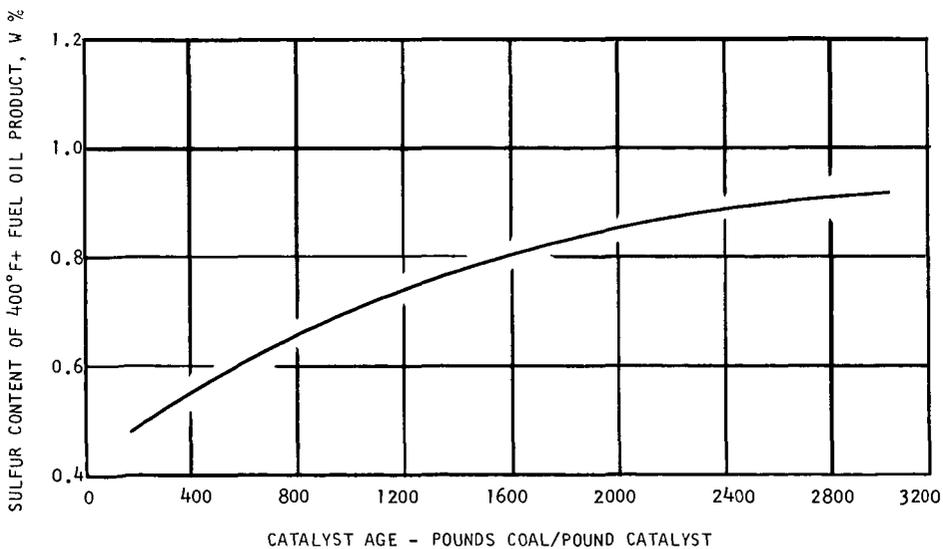
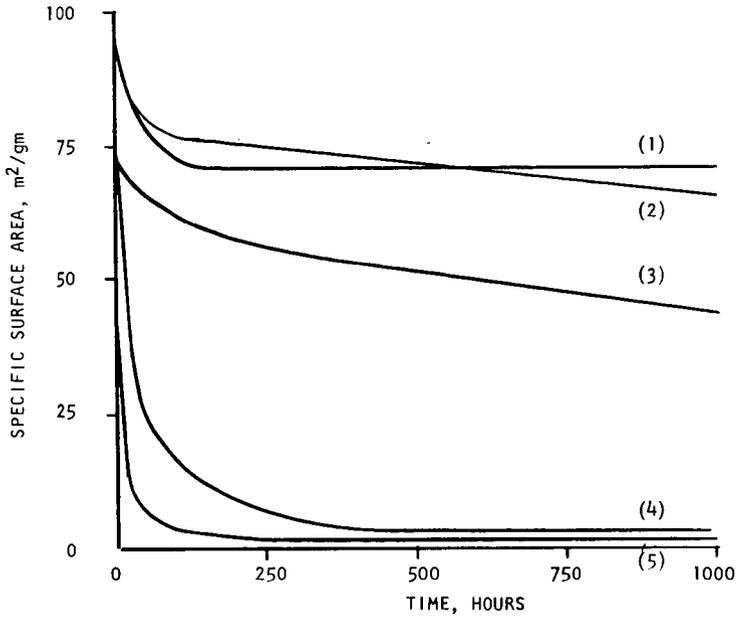


Figure 3 Decline in Desulfurization Activity of Catalyst



- (1) 800°C, only H<sub>2</sub>
- (2) 400°C, H<sub>2</sub>O:H<sub>2</sub> = 9:1
- (3) 500°C, H<sub>2</sub>O:H<sub>2</sub> = 9:1
- (4) 600°C, H<sub>2</sub>O:H<sub>2</sub> = 9:1
- (5) 800°C, H<sub>2</sub>O:H<sub>2</sub> = 9:1

Figure 4

Effect of Temperature and Steam  
On Sintering of Gamma Alumina Catalyst

## Filterability of a Coal-Derived Liquid

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### INTRODUCTION

All coal liquefaction processes must somewhere face the problem of separating unliquefied coal and the mineral matter that entered the process with the coal, from the liquid stream that contains the product. One of the major advantages of the Synthoil process now being developed by ERDA, as reported by Yavorsky et al (3), is that it is quite tolerant of imperfections in the solids removal step, as both the product and the recycle stream are acceptable with as much as 10 pct undissolved material. However, a number of major advantages will be obtained when the present solids removal system is improved or replaced:

(1) Although Synthoil ash values are low--in an experiment reported by Yavorsky et al (4) a Kentucky coal containing 16.9 pct ash yielded a product oil with 1.5 pct, which represents excellent quality for a furnace designed to accept coal--reduction to below 0.1 pct will obviate the inclusion of electrostatic precipitators in the furnace, thus reducing capital costs in product utilization.

(2) An ash content in the final product of less than .005 pct will meet specifications for gas turbine fuel, (1), thus greatly expanding the area of interchangeability between Synthoil and scarce petroleum products.

(3) Reduction in the amount of organic insolubles will further reduce the sulfur content of the product, since the residual sulfur is concentrated in this component.

(4) Alternate systems, even if they should not improve the quality of the product, may yield substantial reductions in operating and capital costs.

Solids separation from coal liquefaction products is a difficult step because of the small particle size (2), variously estimated at mean diameters from 5 to below 0.5 micrometers, wide particle size distribution, from 25 micrometers down to colloidal size, low density difference between particle and liquid, physicochemical affinity between particle and liquid, and high liquid viscosity. We have examined the problem of improving product quality with centrifugation and with three approaches to filtration: (1) a bench filter consisting of a small pressure vessel with a perforated closure to support a 1.4-inch-diameter (0.0107 sq ft) filter medium of cloth, screen, filter paper or "precoat", a powder frequently used industrially as an easily renewable filter medium; (2) a tubular unit in which 0.7 sq ft of cloth filter medium in the form of a bag or sock is supported on a perforated steel tube so that the cloth can withstand high pressure differentials; and (3) a rotary drum pressure filter with 4.7 sq ft of filter surface, capable of operation as either a cloth filter or precoat filter. All three units are operable at 200° C and 200 psig.

Although there was some overlap, each unit was assigned different functions in the research. This paper describes the work with the bench filter. The bench filter was used to establish basic principles in Synthoil filtration that would be applicable

to the engineering of the various commercial forms of filters. With the bench filter we have shown that filtration is a feasible approach to ultra-low-ash Synthoil, that non-Newtonian behavior of Synthoils must be considered in analyzing Synthoil filtration, that the filter medium which is initially installed in the filter controls the initial flow rate and the length of time required to build up a cake of the Synthoil residue (during which time the quality of the filtrate may be poor), after which flow rates and product quality are relatively independent of the initial medium and depend mostly on the quality and integrity of the cake. Tests with a precoat medium showed that a sharp demarkation could be obtained between the precoat and filter cake, indicating that a continuous system could be operated with good filtration and economic use of the precoat material.

#### Experimental Procedures

The basic piece of equipment is shown in figure 1. It consists of a perforated plate to support the filter medium screwed to a steel case which can be pressurized with nitrogen to drive the filtrate through the medium. A top opening provides for insertion of a thermocouple. The assembled unit can be inserted in a vertical 2-inch-diameter tube furnace for operation at elevated temperature. The experiments that were conducted in this equipment can be subdivided into five groups listed in table 1. Groups I, III and IV used a standardized feed (designated FB-36) which

TABLE 1.- Experimental series in filtration

Group	Table No.	Feed	Filter Material
I	2	FB-36	Filter paper 41H
II	3	Varied	Other sheet materials
III	4	FB-36	Precoat on paper
IV	5	FB-36, 38	Precoat on 100-mesh screen
V	-	Varied	Varied

was a very viscous Synthoil product, almost solid at room temperature, that had been produced at 3,000 psi and 435° C from a Western Kentucky coal and contained 5.7 pct ash and 1.0 pct sulfur. These high values of viscosity, ash and sulfur represent what we expect to be the most difficult filtration parameters that would be met in the Synthoil process. Group II used other feeds in addition to FB-36.

The first group of experiments consisted of filtering FB-36 through a standard laboratory filter paper (Whatman 41H)\* at various temperatures, pressures and filter cake thicknesses, and measuring flow rates and quality of product. In Group II the Whatman 41H paper was replaced by other sheet filter materials. A major industrial filtration technique is the use of rotary filters with "precoats" in which the filter medium is a layer of granular material such as diatomaceous earth. In the third group of experiments, two such materials were used as a layer on top of filter paper and in the fourth group, the precoat materials were used on top of an open screen (100 mesh), without paper as a second medium. In both these groups the variables included coarseness of the precoat material and the thickness of the precoat as well as those variables measured in the previous groups. The fifth group comprised experiments in which the feed materials were other than FB-36. These data are not constituted into a separate table but are incorporated into the other tables.

\* Appearance of commercial or trade names does not imply endorsement of the products by the U.S. Government or ERDA. Such names are used only for identification.

The initial experiments on filter paper, for which the data in table 2 are

TABLE 2.- Effect of pressure and temperature on Synthoil filtration through filter paper 41H

Feed: FB-36, Ash 5.7%, Sulfur 1.0%

Run No.	07	08	10
Temperature, ° C .....	185	178	180
Pressure, psig .....	200	200	150
Filtrate, grams .....	17.5	20.0	20.0
Cake, grams .....	4.3	4.5	4.7
Initial <sup>1</sup> filtration rate, 1b-ft <sup>2</sup> -hr <sup>1</sup> .....	4.72	4.91	2.40
Final <sup>1</sup> filtration rate .	2.30	1.54	1.19
Ash, initial <sup>1</sup> filtrate, pct .....	0.21	0.27	0.18
Ash, final <sup>1</sup> filtrate, pct .....	.08	.06	.08
Sulfur, initial <sup>1</sup> filtrate, pct .....	.50	.50	.43
Sulfur, final <sup>1</sup> filtrate, pct .....	.50	.45	.44

<sup>1</sup> "Initial" is first 10 grams, "final" is last ten grams or less if 10 grams is not available.

typical, established several facts. (1) For material as viscous as FB-36, temperatures greater than 165° C and pressures of 150 psig or more were necessary to attain a filtration rate through the paper that was experimentally practical in the sense of collecting analyzable quantities of 10 to 20 grams in less than three hours. (2) The flow rate is quite sensitive to temperature, as shown by comparison between tests 07 and 08 wherein a 7° C increase causes a 49 pct increase in "final" flow rate. The comparison is made between "final" conditions because, as will be verified later, "initial" conditions are subject to many more rapidly changing and partially uncontrolled variables such as changing temperature and changing resistance. (3) Flow rate is dependent on pressure. A 25 pct pressure decrease between runs 08 and 10 produced a 23 pct "final flow" rate decrease despite a 2° C temperature increase. (4) Ash removal was at least 95 pct of the input ash, and removal improved to 98.6 pct as the cake built up. (5) The sulfur content on the other hand was rapidly reduced to 50 pct of the input sulfur, but was not further reduced with cake buildup.

The effects that have been described are indicative of some of the differences between coal liquefaction products and other materials that are usually subject to filtration. The inability to reduce the sulfur content below some apparently fixed level implies that part of the sulfur in Synthoil is present in a colloidal or soluble component. The temperature sensitivity of the flow rate is a reflection of viscosity changes in the fluid. A series of viscosity measurements were made using a rotational type of viscometer. For a Newtonian, or normal liquid, the shear stress vs rate-of-shear relation is a straight line passing through the origin, and the ratio of shear

stress to rate of shear, which is the viscosity, is a constant that changes only with temperature. The relation demonstrated in figure 2, in which the curves do not pass through the origin, shows that the FB-36 feed material was non-Newtonian and that the effective viscosity is a function of flow rate and diameter of the flow channels (pores in a filtration medium) as well as temperature. This leads to a non-linearity of filtration rate with pressure drop when all other parameters are constant. The degree of non-linearity increases with lower flow rates, a factor which must be considered in all data extrapolation. Another complication in filtering a coal liquefaction material is that two insoluble components are actually being removed--the inorganic matter, which is measured as ash, and the insoluble organic matter, or incompletely converted coal. The two components have different particle size distributions, different affinities for the filter medium and different requirements with respect to product quality specifications. Since the principle use of the Synthoil product is as a fuel, the incombustible (inorganic) content of the filtrate is the measure of product quality; however the total material removed as cake (organic plus inorganic) is the major factor controlling the separation process, as will be shown in the next section. Furthermore, the solubility of the organic matter in the feed may be expected to increase with temperature, so that the temperature may affect not only viscosity but also the amount of cake functioning as a filter medium in the filtration process, and consequently will affect both filtration rate and filtration quality.

#### Effect of Filtration Septum - Group II

In the second group of experiments, three different feed materials were filtered, each through two different filtering sheet materials or septa. One septum of each pair was the 41H Whatman filter paper used throughout the Group I experiments. The others were of different constructions and are described in table 3, which also lists the results of the tests. In the table the value for initial filtrate rate is given as measured and also (in parentheses) corrected to the value that would have been expected if the flow rate were proportional to pressure and if the initial pressure were 200 psi, which is the value for the final period of all runs but 38. This calculation is necessary to make the values of initial and final filtration rates more comparable. Experimentally the initial pressures had to be set much lower than the final values to keep the initial flow rates from being too high to measure conveniently.

In table 3 the most notable observation is that for the run pairs 08/09 and 40/41 the initial flow rates and filtrate clarity (pct ash) are highly disparate, whereas the final conditions are quite similar. For example, tests 08 and 09, which were with the same feed material, had initial corrected flow rates that differed by a factor of 168 whereas the final rates differed by less than 2. Initial ash contents of the filtrates differed by a factor of 19, and final values by 2. It may be hypothesized from this that initial flow rates and clarity were controlled by the properties of the septum that was used, but that the final filtering medium was the same regardless of the septum and was essentially the filter cake itself. The influence of the septum, therefore, was (a) to control the clarity of the initial filtrate (which could be recycled later, if this clarity was below specification), (b) to control the time required to build up a filter cake of sufficient thickness to become an effective filtering medium. In short batches, filtered without recycling, the septum will also affect the amount of cake that is removed and formed into the filtering medium, and affect therefore, both the average and final product clarity.

In table 3 the observations for pairs 38/39 are not as marked as those for the other two pairs, but this constitutes support for the filtering sequence suggested above. Measurements of several filter cakes showed that 10 grams of cake corresponded to a thickness of about 0.6 mm. Therefore, because of the low solids content in the feed, the total weight of cake deposited during runs 38 and 39 would be only a few micrometers thick, which based on later estimates of particle size, would correspond to only a few particle diameters and therefore provide a rather ineffective filtering medium even at the end of the run.

#### Use of "Precoat" as a Filter Medium - Groups III and IV

Industrial filtration is performed with many different devices, but considerations of particle size, concentrations and expected scale of operations in a coal liquefaction industry suggest use of a rotary drum filter, operated in a "precoat" mode. In this mode, a layer of a granular material, frequently a diatomaceous earth or a derivative thereof, is deposited on a perforated rotating cylinder which is partially immersed in the material to be filtered. A pressure differential between the outside and inside of the drum drives the liquid through the cylinder wall and the solids are deposited on or within the layer of precoat. As the drum rotates, the deposit is brought into contact with a knife blade. The blade advances at a rate which is set to remove the cake along with as much of the precoat material as may be obstructed by penetration of the cake.

The next phase of the filtration program was an exploration of the parameters of "precoat" filtration vis-à-vis rates and product clarity of other septa that have been illustrated in tables 2 and 3. In the Group III experiments, as shown in table 4, two different grades of a commercial calcined diatomaceous earth were deposited from an oil suspension on grade 41H filter paper. Comparison of the results for runs 07 and 08 in table 2 with those for runs 15 and 11 in table 4, which pertained to the same pressure, temperature and amount of cake, shows that the superposition of precoat on filter paper caused the initial flow to be increased considerably and the initial ash to be decreased; the final flow rate was decreased with approximately equal ash removal from the filtrate. The precoat retains some of the initial solids without building up a substantial cake, so that the filtrate is cleaner than the initial filtrate without the precoat, although the flow rate is higher. Ultimately a cake builds up, pressure drop increases and product clarity improves, but only to a level equivalent to that of the same cake formed without precoat. This observation provides further support for the hypothesis advanced in the previous section that the effective filter medium is not the original septum but the layer of cake that is filtered from the feed.

Table 4 also permits comparisons between (a) grades of precoat, (b) different amounts of the same grade, (c) different amounts of feed and therefore of cake, and (d) different temperatures. The table shows no significant correlation between any of these variables and the quality of the product, which is again confirmation of the hypothesis that the ash removal is primarily a function of the deposited cake, rather than of the substrate.

The fact that the amount of cake has no obvious effect on quality (compare, for example, pairs 11/12 and 15/27) implies that once the cake is formed, the solids separation is performed at the surface of the cake rather than within its depth. A consistent observation is that for each pair of runs that is identical except for amount of charge (11/12, 13/14, etc.), the final filtration rate is less for the greater charge. That is, the approximately doubled thickness of cake causes the flow rate to be cut approximately in half. This observation, in conjunction with the observation that the extra cake does not contribute to improved product

TABLE 3.- Effect of filter medium on Synthoil filtration

Run No	08	09	38	39	40	41
Pressure, psig .....	200	.1-200	.1-40	20-200	50-200	.2-200
Temp., ° C .....	178	179	21	21	85	90
Feed .....	FB-36	FB-36	FB-39cfcg	FB-39cfcg	FB-39unc	FB-39unc
Viscosity @ temp., cp .....	85	85	151	151	8.4	6.8
Filter medium .....	Wh41H	SFYC	Wh41H	Wh42	Wh41H	LC
Wt of filtrate, grams .....	20	22.4	132.4	142.3	93.3	67.2
Wt of cake, grams .....	4.5	4.0	0.11	0.16	15.0	12.2
Avg filtrate rate, lb-ft <sup>-2</sup> hr <sup>-1</sup> .....	2.30	0.86	89.8	4.80	3.08	2.71
Initial filtrate rate (corrected to 200 psi) .....	4.91(4.91)	4.13(826)	22.1(4420)	3.61(361)	6.60(26.4)	.87(868)
Final <sup>2</sup> filtrate rate .....	1.54	0.88	1116.2	2.91	3.19	2.28
Pct ash, feed .....	5.7	5.7	0.012	0.012	7.4	8.9
Pct ash, initial <sup>2</sup> filtrate ..	0.27	5.1	.009	.008	0.01	1.9
Pct ash, final <sup>2</sup> filtrate ....	.06	0.13	.010	.007	<.01	0.04

1 Wh41H--Whatman filter paper, grade 41H (a rapid grade).

Wh42--Whatman filter paper, grade 42 (very retentive).

SFYC--Cloth, cotton non-woven (Eimco-Envirotech SFYC 17521116)

LC--A proprietary resin treated mat (Lainyl Clartex, Lainiere de Sclessin s.a., Belgium).

2 "Initial" is first 10 grams, "final" is last 10 grams, or less if 10 grams is not available.

TABLE 4.- Use of supported "precoat" as a filter medium  
Support: Wh-41-H filter paper

Run No.	11	12	13	14	16	17	15	27
Pressure, psig .....	200	200	200	200	200	200	200	200
Temperature, °C .....	170-179	164-171	160-179	180	182	183	182	185-178
Viscosity, centistokes ...	88.7-63.7	111-85.4	130-63.7	61.4	57.2	55.2	57.2	51.4-66.0
Precoat material <sup>1</sup> .....	C545	C545	C545	C545	C545	C545	Hyflo	Hyflo
Precoat weight, grams .....	1.2	1.2	1.2	1.2	3.6	3.6	1.5	1.5
Feed .....	FB-36	FB-36	FB-36	FB-36	FB-36	FB-36	FB-36	FB-36
Filtrate, grams .....	21.1	43.8	21.8	40.9	22.9	46.8	22.2	50.5
Cake, grams .....	4.7	9.5	4.7	8.8	6.4	9.4	5.4	10.0
Initial <sup>2</sup> filtrate rate, corrected to final press., lb-ft <sup>2</sup> -hr <sup>-1</sup> .....	5.51	24.9	13.7	13.9	25.6	60.5	12.1	38.4
Final <sup>2</sup> filtrate rate .....	1.83	0.91	2.80	1.07	9.02	2.19	1.82	1.02
Pct ash, initial <sup>2</sup> filtrate.	0.23	0.38	0.43	0.83	0.57	0.07	0.12	0.11
Pct ash, final <sup>2</sup> filtrate ..	.03	.07	.08	.22	.05	.01	.08	.04

<sup>1</sup> Precoat: C545 - Johns-Manville Celite 545, Nominal relative flow rate: 2,160  
Hyflo - " " Hyflo Super-Cel, Nominal relative flow rate: 500

<sup>2</sup> See footnote, table 2.

clarity, leads to the conclusion that a continuous system should be operated with the minimum cake thickness required to give good clarity. Since, however, a finite cake layer is required for acceptable clarity, the cake-on-precoat layer should not be cut so deep as to remove the entire cake layer, thus preserving all the precoat.

"Initial" flow rates are less meaningful because they are not instantaneous values but are values integrated over one-half to one-third the total filtration time during that interval when pressures, temperatures (and therefore viscosities), and cake formation are all changing. In all cases the "initial" flow rate for the larger amount of feed was greater than for the smaller amount; this is probably not of fundamental significance but is a reflection of the longer interval to reach equilibrium and perhaps indicates that the larger volumes may initially disturb the upper layer of the precoat material.

The effect of the larger amount of precoat (compare runs 16 with 13 or 17 with 14) is to cause a larger "initial" flow rate, which supports the hypothesis offered in an earlier paragraph that the porosity of the precoat delays the formation of a filtering cake. However, Hyflo (the less porous precoat as rated by the manufacturer) used in run 27 increased the flow rate over that measured in run 14, in which Celite 545, nominally a more porous precoat, was used. The difference in this case may be due to the fact that Hyflo and Celite 545 are somewhat different chemically, so that the flow resistance to water, as used in the manufacturer's criterion, may not follow the same patterns as resistance to Synthoil, if hydration, streaming potentials or other physicochemical forces are operative.

The last series of filtrations was made with the precoat material supported only on a 100-mesh stainless steel screen, i.e., unbacked by filter paper. Initial tests gave erratic results that could be explained by the sensitivity of the precoat layer to small disturbances in flows and pressures. Even the minor fluctuations in pressure caused by normal operation of a pressure regulator caused occasional rapid flow which disturbed the precoat layer and caused the feed to bypass the precoat, as disclosed by disassembling the filter unit and observing layers of Synthoil between the precoat and the wall of the filter tube. Successful filtrations were obtained by installing a needle valve between the pressure regulator and the filter to damp out sudden fluctuations and by maintaining close control on temperature changes. The data in table 5 were taken for five runs permitting comparison between two precoat materials and two different feed materials.

Because, for the unsupported precoat runs it was deemed necessary to increase temperatures and pressures very gradually, the conditions for the "initial" interval varied widely from run to run and these values are less comparable than are the "final" data. In all cases of good filtration, a line of sharp demarkation was found between the cake and precoat which implies that little penetration takes place into the precoat and that on a continuous filter, the cake could be removed without excessive loss of precoat.

The data in table 5 confirm the previously stated hypothesis that once a stable filter cake layer is formed, Synthoil filtration is independent of the substrate on which the layer is deposited. All the "final ash" analyses represent removal of 98.8 to 99.3 pct of the ash in the feed. The apparently wide variation in the absolute value of the ash analysis (.08 pct to .035 pct) reflects a sensitivity of the process to bypassing: if the filter actually reduces the ash content from 5.7 pct to .035 pct; and only 1.0 pct of the feed bypasses the filter action, the product will contain  $(.00035 \times 99) + (.057 \times 1) = .092$  pct ash, an increase of 2.5 times the true filtrate analysis.

TABLE 5.- Use of unsupported "precoat" as a filter medium

Run No.	29	32	33	34	37
Pressure, psig	100-150	28-200	30-100	30-100	15-50
Temperature, C	152-166	155-179	170-179	190-200	96
Viscosity, centistokes	179-103	159-63.7	88.7-63.7	43.2-30.9	63
Precoat, material <sup>1</sup>	Hyflo	C545	C545	C545	C545
Precoat weight, grams	6.0	6.0	6.0	6.0	6.0
Feed	FB-36	FB-36	FB-36	FB-36	<sup>4</sup> FB-38
Filtrate, grams	19.2	40.3	42.8	45.4	60.2
Cake, grams <sup>3</sup>	9.4	(7.4)	9.2	(10.0)	9.2
Initial <sup>2</sup> filtrate rate, corrected to 200 psig, lb-ft <sup>2</sup> -hr <sup>-1</sup>	4.72	11.0	28.3	47.7	72.1
Final <sup>2</sup> filtrate rate, corrected to 200 psig, lb-ft <sup>2</sup> -hr <sup>-1</sup>	2.87	1.35	1.84	2.65	114.0
Ash, initial, pct	0.16	0.73	0.10	0.12	0.03
Ash, final, pct	.04	.056	.067	.035	.08
Sulfur, initial, pct	.51	.70	.52	.41	.24
Sulfur, final, pct	.51	.53	.50	.47	.26

1 See footnote 1, table 4.

2 See footnote 2, table 2.

3 Cake weight in parentheses denotes indirect determination from measurement of cake thickness.

4 Ash = 8.6 pct, Sulfur = .37 pct.

The qualitative effect of temperature is apparent in table 5. Runs 32, 33, and 34 differ only in temperature, and the observed filtration rates for the three experiments increase as the viscosities decrease. Additional data is available for an analysis of the pressure drop flow relation, but since no direct measurements of the cake deposited are available except at the end of the run, and since flow rates were not measured but only total weights at various times, a number of assumptions must be made and only a simplified correlation can be attempted. We may assume that:

- (a) the flow rate,  $dW/d\theta$  is proportional to the driving force  $\Delta P$ , inversely proportional to the fluid properties incorporated in the measured viscosity,  $\mu$ , and inversely proportional to a cake property we define as a resistance  $R$ . This assumption may be restated as

$$dW/d\theta = k_1 \Delta P / (\mu R) \quad 1)$$

which may be used as a defining equation for  $R$  by setting  $k_1 = 1$ , from which

$$R = \Delta P / (\mu dW/d\theta). \quad 2)$$

As it is reasonable to assume that:

- (b) the resistance to flow will be inversely proportional to the cross-sectional area transverse to the direction of flow, Equation 2 can be somewhat generalized by stating the flow rate as flow per square foot or:

$$R = \Delta P / [\mu (dW/d\theta/A)] \quad 3)$$

The test procedures that were followed provide no mechanism for determining the amount of cake present at any instant during the filtration; we therefore make a third assumption:

- (c) the amount of cake is proportional to the amount of slurry that has been filtered.

Figure 3 is a graph of the resistance to flow through the filter cake and precoat of runs 32, 33 and 34, plotted as a function of the total weight of slurry filtered. Although the legend in the figure indicates an average temperature for each run, the resistance values were calculated for the measured temperature at the specific time. Figure 4 is a similar plot for earlier runs in which filter paper and not precoat was used. It is apparent that the resistance, as defined in terms of pressure drop and flow and as corrected for temperature effects by division by the viscosity, correlates well with the total weight of filtrate. If the abscissa were weight of cake, and all other cake properties were invariant, the curves of figures 3 and 4 would be straight lines, with the v-intercept equal to the resistance of the initial septum, i.e. the precoat or filter paper. The observed curvature could be due to any one or more of a number of factors which have been discussed earlier.

- (a) The weight of cake is not proportional to the weight of filtrate. This is, in fact, known to be the case, as the analytical results showed that more solids were removed from the last part of the filtrate than from the "initial" filtrate. However, changes in the weight of ash removed from the "final" filtrate are small so that the last half of the data should approximate a straight line.

- (b) Size distribution of the particles removed may change, so that more fines are removed that tend to plug or "blind" the passages in the latter part of the cake than in the former.
- (c) The cake may be compressible, so that its permeability is decreased as the pressure drop across it increases.
- (d) The non-Newtonian viscous behavior of the fluid, as demonstrated in figure 2, may be of sufficient magnitude that the changed shear rate in the latter part of the filtration may create a much greater effective viscosity than is used in the resistance calculation.

Each of the above possibilities presents a major challenge, the evaluation of which may lead to greatly improved filtration. However, even without resolving the reasons for the curvature of figures 3 and 4, important deductions can be made.

- (a) Resistance increases more than proportionally with the amount of cake. For a continuous system where the cake thickness can be controlled, the thickness should be held at the minimum value that will yield acceptable filtrate clarity.
- (b) Resistance per unit of cake increases much more rapidly when the initial septum is filter paper rather than precoat.

#### Varied Feeds - Group V

Although most of the tests discussed were made with the feed material designated as FB-36, several other materials were used. The results for these materials were entirely consistent with the results for FB-36 and they have been included in tables 3 and 5 (runs 37, 38, 39, 40, 41) wherein the only significant effect due to the feed is that feeds with lower ash content yielded products with less ash, although, for reasons discussed earlier in connection with table 3, the changes were not proportionate.

#### ADDITIONAL WORK

In parallel efforts, filtration studies have been carried on with larger scale equipment. In tests with a rotary drum filter, details of which will be published at a later date, we have utilized the principles advanced here of maintaining a thin, uniform cake of solids on top of a precoat layer. A recent run of 444 uninterrupted hours on stream, included a steady state period of 200 hours, during which an ash removal of at least 99.1 pct was maintained, with an average filtrate content of .09 pct ash.

#### CONCLUSIONS

Batch filtration is a technically feasible method of removing ash from a Synthoil product so that the only remaining problem is the mechanics of scaled-up continuous filters. Starting with a material containing 5.7 pct ash, analyses of less than 0.1 pct have been almost routinely attained using a commercial precoat material with no filter paper support. The nominal filter medium has little influence on the ultimate product clarity, as the true filter medium is the cake that is formed from the feed. The nominal filter medium affects the pressure drop, the time required to build up a functioning cake, and the number of precautions that are required to forestall possible system disturbances such as pressure variations during cake buildup. Filtration rates are very sensitive to temperature, but when cake resistances are divided by the measured viscosity, the temperature effect is properly accounted for.

In the batch filter tests reported here, two observations suggest that a continuous filter will be effective:

- (1) a clear demarkation usually exists between cake and precoat so that separation in a continuous unit should be simple with minimum cost in precoat;
- (2) adequate clarity is attained with a relatively thin cake layer whereas additional cake adds to the pressure requirement without major improvement in clarity.

Filtration of Synthoil causes a certain amount of reduction in sulfur, but beyond this point, improved filtration, as measured by ash reduction, does not improve sulfur reduction. Quantitative analysis and possible improvement of the filtration process requires further study into particle size distribution, cake compressibility, and the effect of the observed non-Newtonian flow characteristics of the fluid being treated.

#### NOMENCLATURE

W = weight of filtrate  
 $\theta$  = elapsed time  
 $\Delta P$  = pressure difference across filter  
 $\mu$  = viscosity  
R = resistance to filtrate flow  
 $k_1$  = constant  
A = area of filter normal to flow

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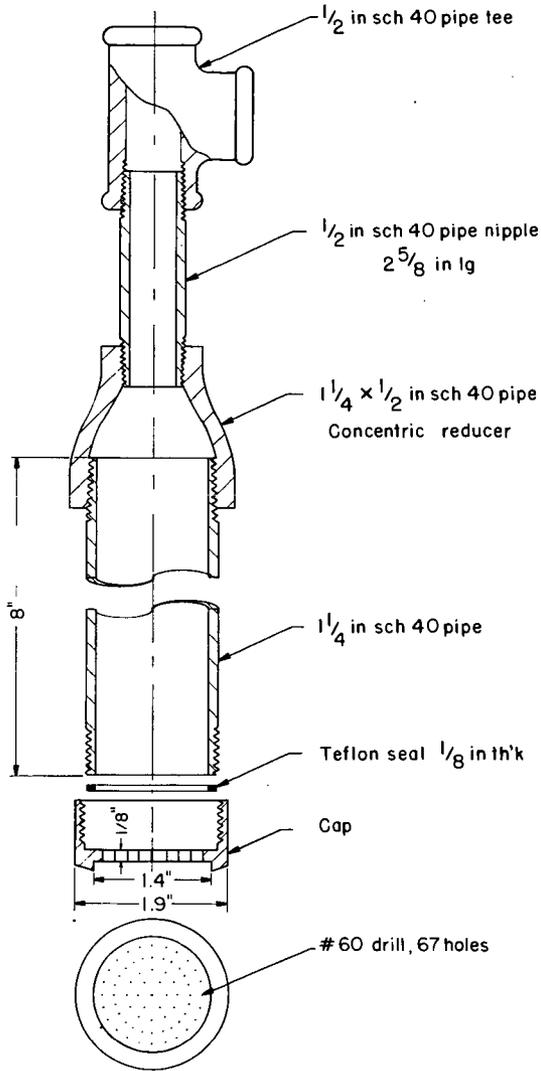


Figure 1—Small filter for use at elevated temperatures and pressures.

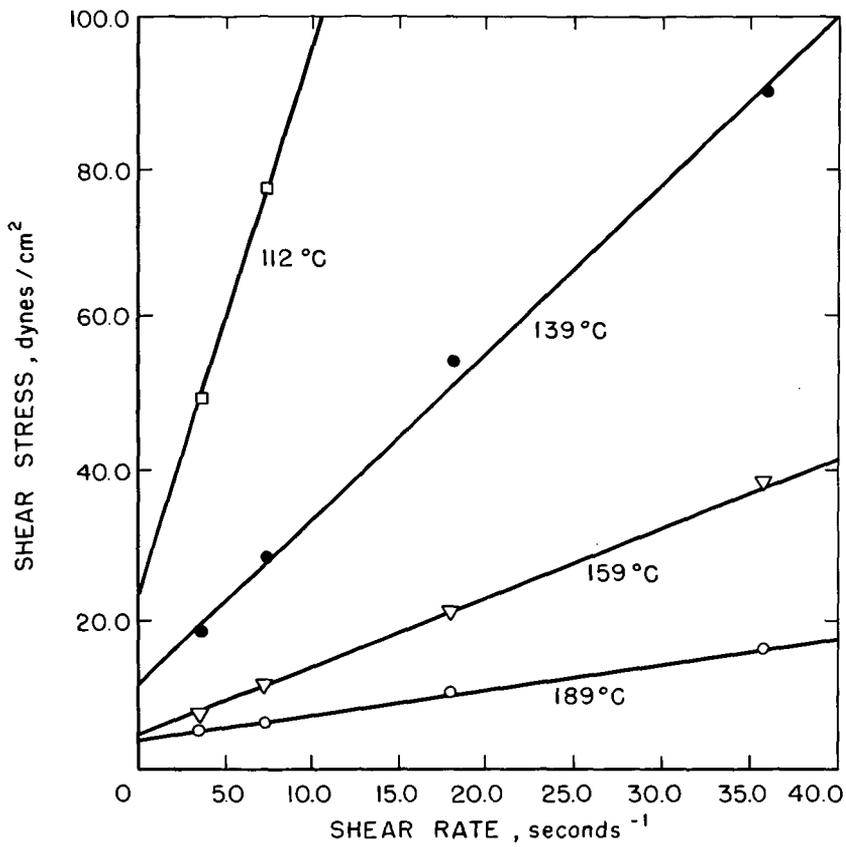


Figure 2 - Viscous behavior of FB-36.

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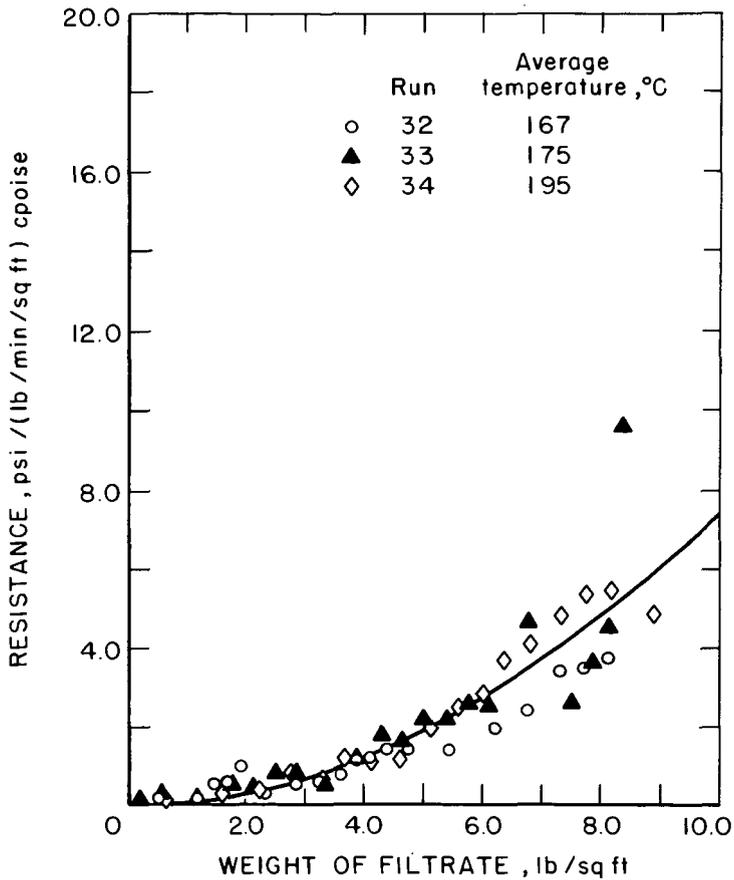


Figure 3 - Filtration resistance through filter cake and 6grams of C-545 precoat.

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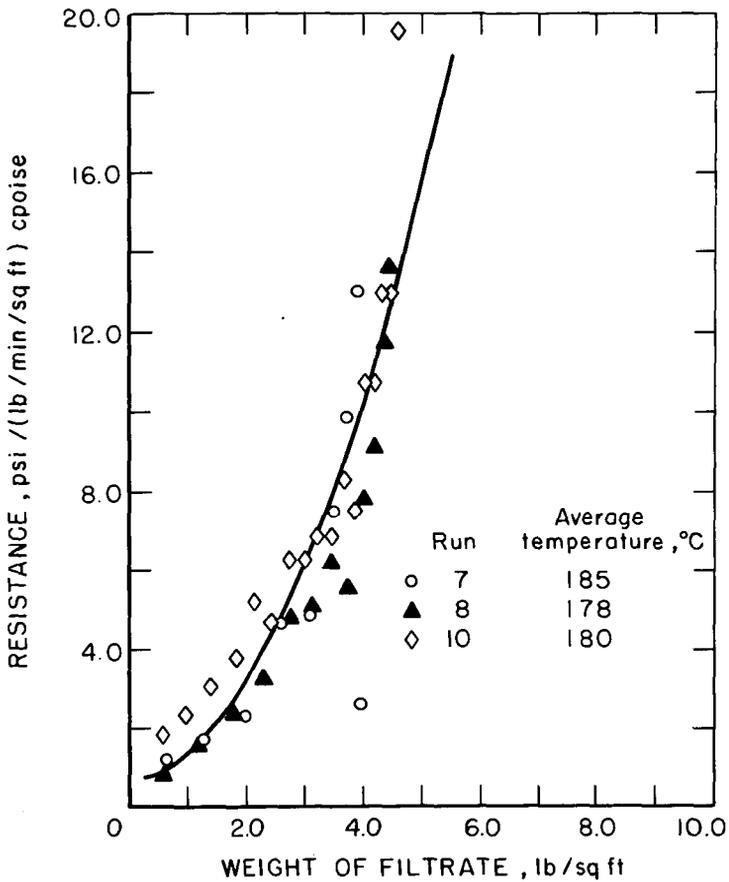


Figure 4 - Filtration resistance through filter cake and filter paper.

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## EFFECT OF COAL MINERALS ON REACTION RATES DURING COAL LIQUEFACTION

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### Introduction

Coal minerals represent a readily available, abundant, inexpensive source for catalytic agents for use in accelerating liquefaction and hydrodesulfurization reactions in coal conversion processes. Experimental evidence of the catalytic effect of coal minerals on hydrogenation has been reported.<sup>1</sup> In fact, there is a patented coal conversion process in which mineral residue is recycled because of its catalytic activity.<sup>2</sup> Yet the benefits of coal mineral catalysis has not been well established. The purpose of this paper is to demonstrate that certain coal minerals catalyze the hydrogenation and hydrodesulfurization of creosote oil, a coal-derived solvent used as a start-up solvent in the solvent refined coal (SRC) process; to show that, by accelerating hydrogenation of process solvent such as creosote oil, coal minerals catalysis accelerates indirectly the rate of liquefaction of coal solids; and to provide better insight as to the process advantages and disadvantages of coal mineral catalysis - more specifically, removal of coal minerals prior to hydrogenation/hydrodesulfurization, or recycle of coal mineral residue.

### Experimental

Reagents and Materials. Creosote oil (Table 1) used in these experiments was obtained from Southern Services, Inc., and is used as a start-up solvent at the SRC pilot plant located at Wilsonville, Alabama. Southern Services, Inc., obtained the oil, creosote oil 24-CB, from the Allied Chemical Company. The oil has a carbon-to-hydrogen ratio of 1.25 (90.72% C and 6.05% H), a specific gravity of 1.10 at 25°C, and a boiling point range of 175° to 350°C. Kentucky No. 9/14 coal mixture was crushed; and the -170 mesh fraction - having the screen analysis shown in Table 2, and the elemental analysis in Table 3 - was used in the experiments. Table 4 lists specifications of the individual coal minerals studied. Hydrogen and nitrogen gases were the 6000 psi grade supplied by Linde. All coal was dried overnight at 100°C and 25 inches Hg vacuum before use.

Procedures. Basically four different types of experiments were performed: 1) catalyst screening, 2) recycle of mineral residue, 3) hydrogenation and hydrodesulfurization of demineralized coal, 4) hydrogenation and hydrodesulfurization using prehydrogenated solvent.

1. Catalyst Screening. Catalyst or mineral preparation consisted of grinding, followed by screening to the respective size. Depending on the hardness of the catalyst, either a diamond grinder and/or a mortar and pestle was used. For each run: the charge consisted of 15 gms of catalyst, 100 gms of creosote oil, and an initial hydrogen atmosphere of 3000 psig.; reaction was carried out for two hours at 425°C and a stirrer setting of 2000 rpm. A heat-up rate of about 12 to 20°C per minute was used - requiring only about three minutes for heat-up within the zone in which significant reaction occurs<sup>3</sup> (above 370°C) and a total heat-up time of about 30-35 minutes. Prior to heat-up 400 psig of hydrogen was charged to the reactor (a 300 cc magnedrive autoclave from Autoclave Engineers, Inc.) and at reaction temperature more hydrogen was added to attain the desired initial hydrogen pressure of 3000 psig. Reaction temperature (425°C) was held constant within ±3°C.

Throughout each run total pressure was recorded periodically (Figure 1); and after exactly two hours of reaction, a gas sample was collected, and the autoclave contents were quenched to below 200°C within five minutes. After allowing the catalyst to settle for one hour, a liquid sample was collected for sulfur analysis.

Between consecutive catalysts screening runs, blank runs, having no catalyst present, were made to eliminate any "memory effect." As shown in Figure 2 about three blank runs were required following a run made with the Co-Mo-Al catalyst, which - having the highest catalytic activity of those agents considered - exerted the strongest memory effect.

2. Recycle of Mineral Residue. The reaction conditions used for all of these runs were 400°C, a stirrer setting of 2000 rpm, and an initial hydrogen pressure of 2000 psig. A 3:1 solvent-to-coal weight ratio (40 gm. of coal, 120 gm. of creosote oil) was used. Two runs were made to establish a base-line for comparison. Once completed, two more runs, each having a charge with a higher concentration of mineral matter, were made: In the first, solid residue from one of the base-line runs was added; and in the second, solid residue from the run with a higher mineral matter concentration was added, increasing further the mineral matter concentration. For each run, total pressure was periodically monitored (Figure 3); and final hydrogen partial pressure was measured. Final cresol soluble yields, y, were also determined (Table 5) where:

$$y = \frac{C - (R - A)}{C(1 - M)} \times 100$$

And C is the charge of moisture free coal; R, the recovered insoluble residue; M, the fraction of mineral matter in dry coal (0.12 for Kentucky No. 9/14 mixture); A, the mass of residue added.

To insure that solid residue was free of solvent prior to its use, after being filtered from the reaction mixture, it was washed with hot cresol and benzene, with clear benzene passing through the filter in the final wash.

Hydrogenation and Hydrodesulfurization of Demineralized Coal. Coal was slurred with water and partially demineralized by passing it through a high intensity magnetic separator - reducing its ash content by 64 per cent (as determined by ASTM D-271) and its total sulfur content by 25 per cent as determined by a Leco sulfur analyzer. The partially demineralized coal was then dried overnight under 25 inches Hg vacuum at 100°C; slurred with recycle solvent in a 3:1 solvent-to-

coal proportion; and reacted at 410°C, 1000 psig of initial hydrogen pressure, and a 1000 rpm stirrer setting for reaction times of 15, 30, 60, and 120 minutes. At the end of each reaction, a liquid sample of reaction product was collected; the total sulfur content and cresol soluble yield (Figure 4b) was determined using a Leco sulfur analyzer and Soxhlet extraction, respectively. Assuming, on the basis of prior experimental verification<sup>4</sup>, that the pyritic sulfur content (as determined by ASTM D2492-68) was reduced to the sulfide form (Fe<sub>7</sub>S<sub>8</sub>)<sup>8</sup> within fifteen minutes of reaction, the final organic content of each reaction mixture was computed (Figure 4a).

As a basis for comparison, a sample of the feed to the magnetic separator was collected. The coal in the sample was separated from the water by filtering; dried and reacted in the same manner as the demineralized coal. For completeness, coal that had not been exposed to water (as in the slurry feed tank to the magnetic separator) was also dried and reacted (Figure 4).

Hydrogenation and Hydrodesulfurization Using Prehydrogenated Solvent. To improve the hydrogen donor activity of the solvent, it was hydrogenated at 410°C for one hour in the presence of 15 per cent by weight of minus 150 mesh Co-Mo-Al catalyst (Comax-451, Laporte Industries) and an initial hydrogen pressure of 2500 psig. The hydrogenated solvent was then allowed to settle for 24 hours and doubly filtered to remove all the Co-Mo-Al catalysts: emission spectrophometric analysis, and also, outside analysis by Galbraith Laboratories, Inc., showed the Co and Mo content in the resulting hydrogenated solvent to be less than 1ppm and 10ppm, respectively. The hydrogenated solvent has a specific gravity of 1.05 at 25°C and a carbon-to-hydrogen ratio of 1.15 (91.56% C and 6.65% H). Comparative runs were then made in which hydrogenated solvent and untreated solvent were each reacted in a 3:1 solvent-to-coal ratio at 410°C for 15 minutes in the presence of a nitrogen pressure of 2000 psig, and also, in an initial hydrogen pressure of 2000 psig (Table 6).

## Results and Discussion

Using total pressure as a rough indicator of reaction rate, from Figure 1 some of the coal minerals definitely appear to provide catalysis for hydrogenation of the creosote oil. The upper and lower curves in Figure 1 represent the extreme behavior present with no catalyst and with a commercial Co-Mo-Al catalyst, respectively. The different mineral matter additives show evidence of catalytic activity, intermediate between these two extremes. Most interestingly, one of the more active catalysts is filter cake residue from the Wilsonville SRC pilot plant. Also, the catalytic activity of -325 mesh pyrite is higher than that of -80 +150 mesh pyrite - demonstrating that not only the composition of the mineral matter, but also its physical state, is of considerable importance in process applications.

Sulfur removal data for each of the catalyst screening runs are presented in Figure 5 and are in general agreement with the catalytic activity sequence evidenced by the total pressure data with two exceptions: Pyrite, despite its pronounced effect on total pressure, appears to be a relatively poor catalyst for hydrodesulfurization. High pressure liquid chromatographic analysis of the creosote oil after hydrogenation reveals that the concentration of dibenzothiophene, an organic sulfur constituent, decreases from  $1.271 \pm 0.03$  to only  $0.720 \pm 0.09$  per cent when pyrite is present; whereas it is reduced to  $0.888 \pm .05$  when no catalyst is present and to only trace amounts ( $< 0.04\%$ ) when Co-Mo-Al is present.<sup>5</sup> As stated earlier in the experimental section, pyrite is reduced rapidly during

hydrogenation to the sulfide form ( $\text{Fe}_7\text{S}_8$ );<sup>4,8</sup> some back-reaction by the  $\text{H}_2\text{S}$  generated during reduction of the pyrite may occur, and this reaction may be partly the reason why the presence of pyrite had such a poor effect on hydrodesulfurization of the creosote oil.<sup>12</sup> Secondly, iron, which had a much less effect on total pressure than that of pyrite, is second only to Co-Mo-Al in sulfur removal. However, the role of iron in sulfur removal during hydrogenation is probably more as a reactant than as a catalyst, in that it reacts with any  $\text{H}_2\text{S}$  produced or directly with sulfur in the oil to form sulfides. In fact, gas analysis showed little, or no  $\text{H}_2\text{S}$  to be formed during hydrogenation of the creosote oil in the presence of iron.

An indication of hydrogenation activity is shown in Figure 6 where the final hydrogen partial pressure is presented for each of the catalyst screening runs, as determined from gas analysis and total pressure. Again, the Co-Mo-Al is most effective for hydrogenation; however, iron pyrite and SRC solids residue also indicate relatively high activity. Prather et al.<sup>5</sup> show, using high pressure liquid chromatography, that the total concentration of the four major constituents in the creosote oil - naphthalene, acenaphthene, phenanthrene, anthracene - decreases the same during hydrogenation in the presence of pyrite as it does in the presence of Co-Mo-Al, and 22 per cent more than it does when no catalyst is present.

The results of experiments showing the effect of recycling filtered mineral matter from successive autoclave runs are shown in Figure 3; again total pressure is assumed to act as a rough indicator of reaction rates. Obviously continued recycle (higher concentrations) of mineral matter residue leads to increased reaction rates, as evidenced also by the resulting higher yields and decreasingly lower final hydrogen partial pressures (Table 5).

Further evidence that coal minerals catalyze liquefaction reactions are given in Figure 4, in that the rate of conversion for demineralized coal is much slower than that of untreated coal. In addition, soaking of the coal in water, or slurring with water, causes also a significant decrease in the rate of liquefaction. Some of the coal minerals - particularly sulfates - are soluble in water, and thus, are extracted by soaking the coal in water, as evidenced by the 0.12 per cent decrease in total sulfur content of the coal with soaking (Table 7), which is about the same as the per cent sulfur (0.13%) present in the sulfate form in the untreated coal. Yet, since exposure of the coal to water may affect the chemical characteristics of the coal in various ways other than removal of soluble minerals, further experimental study is needed to determine conclusively why slurring coal with water prior to hydrogenation decreases its rate of liquefaction.

Despite the significant effect of demineralization of the coal on its liquefaction behavior, its organic hydrodesulfurization activity remained practically the same (Figure 4a). Assuming that mostly pyrite was removed by the magnetic separator, then no significant difference in the organic hydrodesulfurization activity of the demineralized coal and that of untreated coal should result, and the results given in Figure 4a should be expected; for, as shown in Figure 5, pyrite has relatively little overall catalytic effect on hydrodesulfurization of creosote oil. Depending then on the composition of coal minerals - eg. high pyrite content, etc. - the relative effect of coal mineral catalysis can be significantly greater for liquefaction than for organic hydrodesulfurization. As a result, coal mineral catalysis during hydrogenation/hydrodesulfurization of coal may or may not be

advantageous, depending on process objectives and on composition of the coal minerals. To illustrate: If hydrogenation is limiting, for example, as may be the case in producing a synthetic fuel oil, then catalysis by coal minerals of hydrogenation reactions would be advantageous; and thus, so would recycle of coal minerals. On the other hand, if hydrodesulfurization is limiting and, as usual, minimum hydrogenation is desired, which is often the case in SRC and related processes, removal of coal minerals such as pyrite prior to hydrogenation/hydrodesulfurization would be advantageous; for, to attain the required amount of sulfur removal, more hydrogenation would occur when all the catalytic coal minerals are present than when no pyrite, and similar behaving catalytic coal minerals, is present. That is, in the presence of coal minerals such as pyrite, excess hydrogenation - more than that required to liquefy the coal so that mineral residue can be separated by filtration, etc. - would occur.

For coal particles to dissolve in a carrier solvent, i.e. liquefy, at temperatures of 385 to 450°C, either molecular hydrogen or hydrogen donor species must be available to transfer hydrogen to the coal.<sup>6</sup> A direct relationship exists between the degree of dissolution and hydrogen transfer: the more hydrogen transferred, the greater the liquefaction.<sup>7</sup> Coal mineral matter, being solid in form, most likely can not directly catalyze hydrogen transfer to coal solids either from molecular hydrogen dissolved in the carrier solvent or from hydrogen donor species. More reasonably, coal minerals can catalyze transfer of dissolved molecular hydrogen to the solvent - i.e. hydrogenation of the solvent. But, does hydrogenation of the solvent increase its hydrogen donor activity? If indeed it does, then the rate of liquefaction of coal slurried with prehydrogenated solvent should be greater than that of coal slurried with untreated solvent. To verify whether or not this is true, the conversion of coal solids obtained in the prehydrogenated solvent experiments were compared with those obtained with untreated solvent (Table 6). Apparently prehydrogenation of the solvent increases its hydrogen donor activity significantly, for the conversion obtained with the prehydrogenated solvent was 97 and 49 per cent higher than that obtained with untreated solvent in a nitrogen and a hydrogen atmosphere, respectively. Yet, practically the same amount of sulfur removal results when either prehydrogenated or untreated solvent are used. Apparently then, coal minerals serve to catalyze hydrogenation of the solvent, increasing its hydrogen donor activity, and thereby, the rate of hydrogen transfer to the coal, thus the rate of liquefaction.

Supportive evidence that coal minerals serve primarily to catalyze hydrogenation of the donor solvent is provided by Curran *et al.*;<sup>7</sup> they found that, in a nitrogen atmosphere, "... all attempts to accelerate hydrogen transfer to coal slurried in tetralin with contact type of catalysts of the hydrofining type (cobalt molybdate on alumina) or with cracking catalysts (silica-alumina) were unsuccessful." Whereas, in a hydrogen atmosphere - as shown here and by others<sup>1</sup> - the rate of liquefaction increases directly with increases in the concentration of coal minerals. The rate limiting step in liquefaction furthermore appears to be the transfer of dissolved molecular hydrogen to the donor solvent, with the transfer of hydrogen from the donor solvent to coal solids occurring rapidly.

### Conclusions

Certain coal minerals - particularly pyrite - catalyze hydrogenation of coal-derived solvents such as creosote oil and SRC recycle solvent. The rate limiting step in liquefaction of coal is the transfer of hydrogen to donor solvent, and the

rate of liquefaction increases directly with the concentration of coal minerals. Certain coal minerals also catalyze hydrodesulfurization of creosote oil - pyrite having a relatively insignificant effect on total hydrodesulfurization. The physical state, as well as chemical composition, of the coal minerals affect hydrogenation and hydrodesulfurization activity during coal liquefaction. Coal mineral catalysis of hydrogenation and hydrodesulfurization reactions occurring in coal conversion processes may or may not be advantageous, depending on process objectives and on composition of the coal minerals.

#### Acknowledgement

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TABLE 1  
Gas Chromatographic Analysis of Creosote Oil

Compound	Weight %
coumarone	.10
p-/cymene	.02
indan	.11
phenol	.12
o-cresol	.05
benzonitrile	.12
p-cresol	.37
m-cresol	.16
o-ethylaniline	.03
naphthalene	5.1
thianaphthene	.08
quinoline	.37
2-methylnaphthalene	1.3
isoquinoline	.30
1-methylnaphthalene	.38
4-indanol	.55
2-methylquinoline	.42
indole	.21
diphenyl	.49
1,6-dimethylnaphthalene	.39
2,3-dimethylnaphthalene	.19
acenaphthene	6.0
dibenzofuran	6.7
fluorene	10.3
1-naphthonitrile	.18
3-methyldiphenylene oxide	1.7
2-naphthonitrile	.14
9,10-dihydroanthracene	2.4
2-methylfuorene	.85
diphenylene sulfide	.52
phenanthrene	18.6
anthracene	4.3
acridine	.19
3-methylphenanthrene	.98
carbazole	2.2
4,5-methylenephenanthrene	2.5
2-methylanthracene	.24
9-methylanthracene	1.2
2-methylcarbazole	1.7
fluoranthene	5.5
1,2-benzodiphenylene oxide	.96
pyrene	2.6

Table 2. Screen Analysis of Bituminous Kentucky No. 9/14 Coal Mixture

Mesh Size of Screen	% Retention
170	1.23
200	1.92
230	1.09
270	4.30
325	17.94
400	10.86
-400	62.65
Total	99.99

Table 3. Chemical Analysis of Bituminous Kentucky No. 9/14 Coal Mixture

H	4.9
C	67.8
Total Sulfur	2.55
Organic Sulfur	1.63
FeS <sub>2</sub>	0.79
Sulfate Sulfur	0.13
Total Ash	7.16

Table 4. Description of Coal Minerals Or Catalytic Agents Studied

Species	Classification <sup>a</sup>	Description <sup>b,10,11</sup>
Ankerite (Ferriferrous Dolomite)*	Carbonate	An isomorphous mixture of CaMg (CO <sub>3</sub> ) <sub>2</sub> and Ca Fe (CO <sub>3</sub> ) <sub>2</sub> .
Calcite*	Carbonate	A crystalline form (hexagonal scalenohedral class of the hexagonal system) of CaCO <sub>3</sub> . Often, to a small extent, the Ca is replaced by iron, magnesium, and manganese. Clay, sand, bitumen, and other mechanical impurities may be present.
Oolomite*	Carbonate	A double salt with equal molecular quantities of CaCO <sub>3</sub> and MgCO <sub>3</sub> , and not an isomorphous mixture of these two compounds. Usually found in a curved rhombohedral form.
Kaolinite*	Kaolin	A common type of clay; often found in minute pseudo-hexagonal (monoclinic) crystals. Chemically, an acid aluminum silicate, H <sub>4</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>9</sub> or 2H <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> (H <sub>2</sub> O:14%). Iron is often present in small amounts.
Muscovite*	Shale	A lamina type silica substance, having a monoclinic crystal structure; and chemically classified as an acid potassium aluminum orthosilicate, H <sub>3</sub> KAl <sub>3</sub> (Si <sub>3</sub> O <sub>10</sub> ) <sub>3</sub> or 2H <sub>2</sub> O·K <sub>2</sub> O·3Al <sub>2</sub> O <sub>3</sub> ·6SiO <sub>2</sub> ·(H <sub>2</sub> O:4.3%). Often, the potassium is partially replaced by sodium, and some varieties contain an excess of silicon over that indicated above.
Pyrite	Sulfide	A cubic structure of FeS <sub>2</sub> , having, in its crystalline structure, a rock-salt-type of arrangement of Fe <sup>2+</sup> and S <sup>2-</sup> ions, with iron being octahedrally surrounded by 5 and each S atom having one S and three Fe atoms as neighbors. Uncommonly, Ni, Co, or sometimes both are found substituted for Fe. Obtained from Matheson, Coleman, and Bell (90-95% pure).
Quartz*	Accessory	A crystalline form of SiO <sub>2</sub> ; a member of the triangular trapezohedral class of the hexagonal system.
Siderite*	Carbonate	A crystalline form of FeCO <sub>3</sub> , with the brown to gray crystals usually being rhombohedral. Calcium, magnesium, and manganese are usually present in small amounts as replacing elements.
Co-Mo-Al	-	Commercial catalyst from Laporte Industries, Inc., (Comox 451, 1.5 mm Extrudate); surface area = 300 m <sup>2</sup> /g; pore volume = 0.66 ml/g. Chemical analysis: 3.7, 12.8, 0.06, 1.4, and 0.03% Co, MoO <sub>3</sub> , Na <sub>2</sub> O + K <sub>2</sub> O, SiO <sub>2</sub> , and SO <sub>3</sub> , respectively.
Iron	-	Reagent grade hydrogen reduced iron from Mallinckrodt, Inc.
Reduced Pyrite	-	Solid residue from hydrogenation-of-creosote oil in presence of 15% by weight of Fe <sub>2</sub> O <sub>3</sub> at 425°C, stirrer setting of 2000 rpm, and 3000 psig of initial hydrogen pressure.
SRC Residue	-	Obtained from filter cake from Wilsonville SRC pilot plant. Analysis: 55.2% ash content and 13.6% S for -325 mesh material; and, prior to screening, 30% filter aid, 53.6% ash, and 2.9% S.
Coal Ash	-	Obtained by burning Kentucky No. 9/14 mixture (7.2% ash) in a muffle furnace at ~ 1000°C; analysis: 13.7% iron.
Kaolin	-	Obtained from W. H. Curtis and Co.

\* Minerals obtained from David New, Minerals and Books, Providence, Utah.

Note: All agents were ground to -325 mesh prior to use, except muscovite which was ground only to -80 mesh because of its lamellar silica structure, and except as indicated.

Table 5. Final Gas Analysis and Conversion for Recycle of Mineral Residue Runs

Run	Total Pressure (PSIA)	Partial Pressure (PSIA)					Conversion Based on Cresol Solubles (MMF)		
		H <sub>2</sub>	H <sub>2</sub> S	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>3</sub> -C <sub>5</sub>	
Initial	1221	825	36.9	89.5	136.5	48.9	28.7		96.3
Duplicate of Initial	1218	832	36.2	83.4	133.0	47.0	26.5		-
1st Recycle	1089	648	45.3	116.7	173.6	60.5	38.1		100.0
2nd Recycle	1064	607	45.3	113.9	179.4	22.3	33.3		100.6

Table 6. Comparison of Hydrogenation and Hydrodesulfurization Activity of Coal in Prehydrogenated Solvent and That in Untreated Solvent

EFFECT OF PREHYDROGENATION OF OIL

Pretreatment of Solvent	Temperature (°C)	Atmosphere	Reaction Time (min.)	Solvent-to-Coal Ratio	Conversion (Based on Cresol Solubles)	Total Sulfur (%)	Organic Sulfur (%)
None	410	2000psi N <sub>2</sub>	15	3/1	42.13	.904 ± .023	0.34
70 Hydrogenation	410	2000psi N <sub>2</sub>	15	3/1	83.10	.487 ± .030	.39
None	410	2000psi H <sub>2</sub>	15	3/1	61.03	.912 ± .054	.35
Hydrogenation	410	2000psi H <sub>2</sub>	15	3/1	90.70	.506 ± .026	.41

Table 7. Ash and Total Sulfur Content of Kentucky No. 9/14 Coal and That After Slurrying  
 With Water and After Demineralization

	Ash Content (%) (ASTM D-271)	Total Sulfur Content (%)	Conversion* After Two Hours of Reaction
Original Coal	7.16	2.55	87.8
Coal From Slurry Feed Tank	6.28	2.43	77.38
Demineralized Coal	2.55	1.90	67.23

\*Refer to Figure 4

Reaction Conditions

Temperature: 425°C  
 H<sub>2</sub> Pressure: 3000 psig @ 425°C  
 Agitation Rate: 2000 rpm  
 Autoclave: 300 cc  
 Charge: 100 g Creosote Oil/15 g catalyst

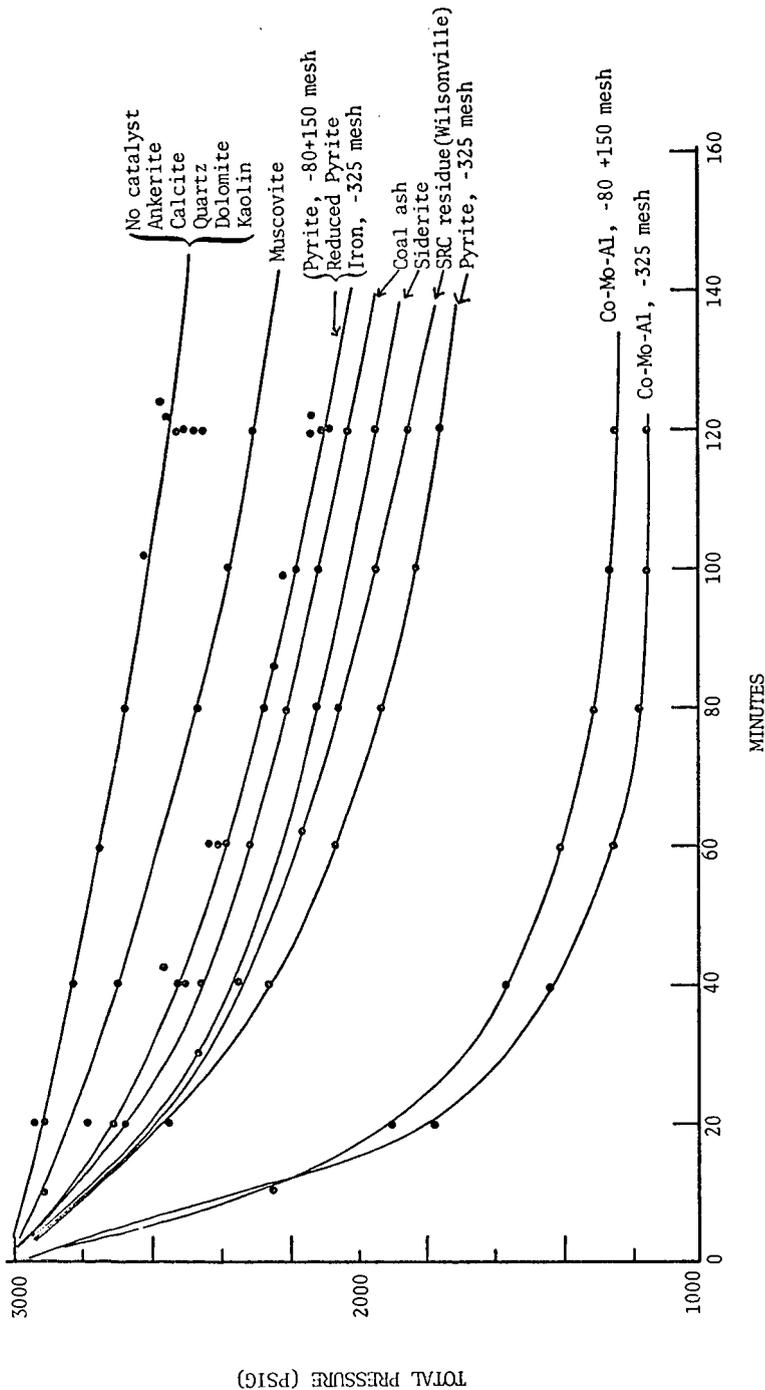


Figure 1. Catalytic effect of coal mineral matter as indicated by total pressure.

RUN

- Co-Mo-Al Catalysis
- ◇ First Blank
- Second Blank
- △ Third Blank
- X Fourth Blank

Reaction Conditions

Temperature: 425°C  
H<sub>2</sub> Pressure: 3000psig@ 425°C  
Agitation Rate: 2000 rpm  
Autoclave : 300cc

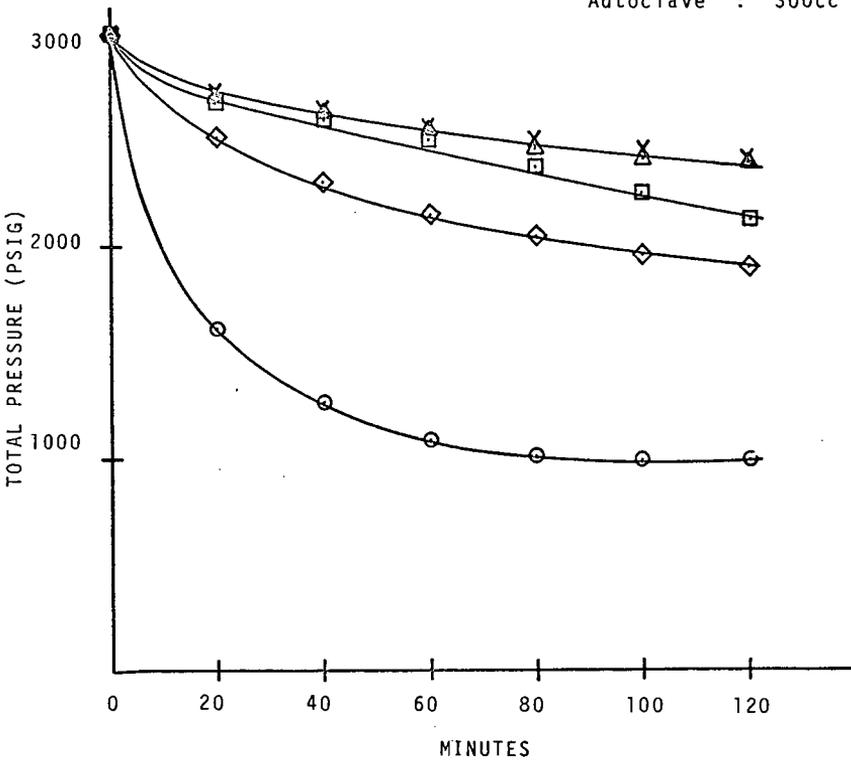


Figure 2. Determination of number of blank runs required to eliminate memory effect.

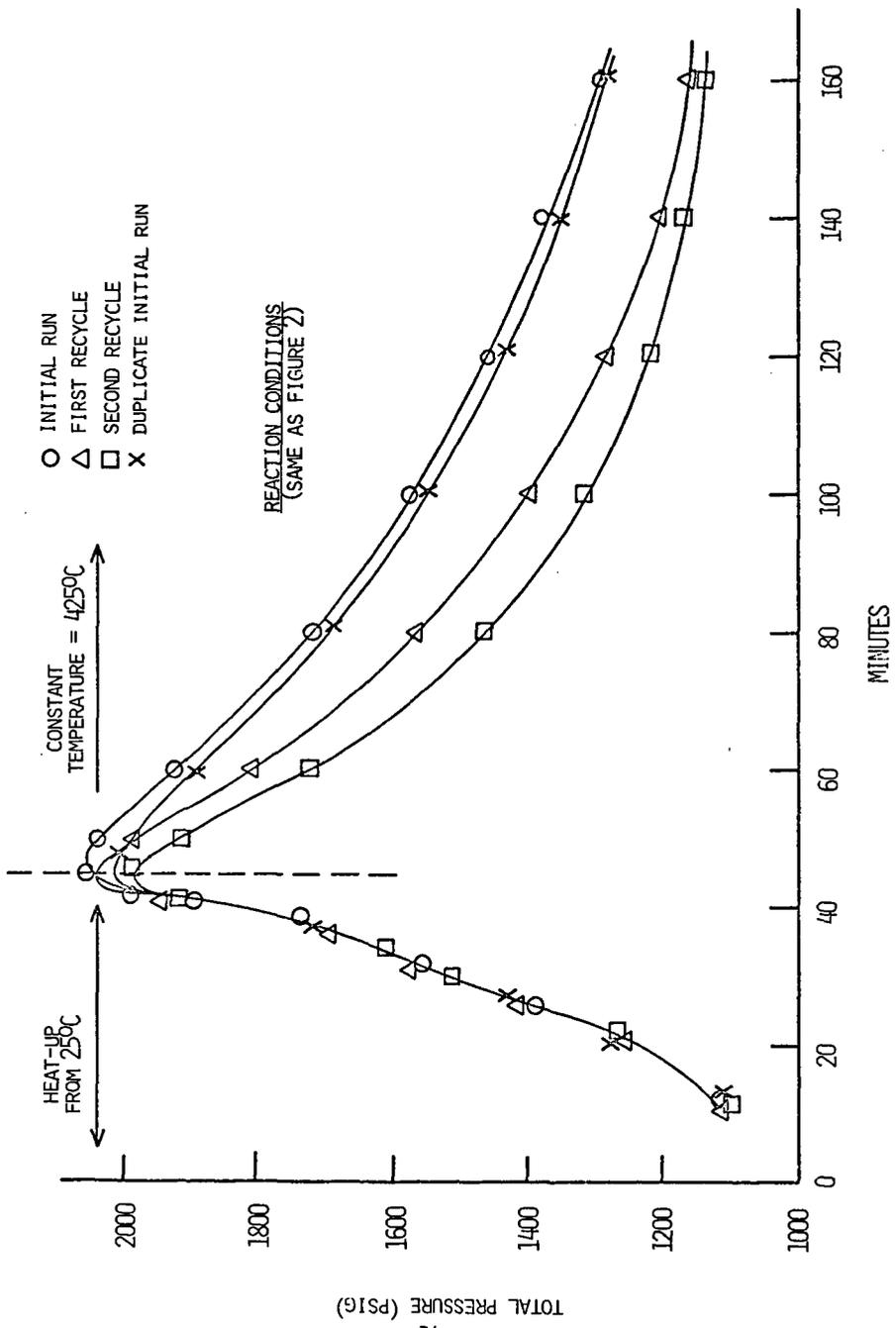
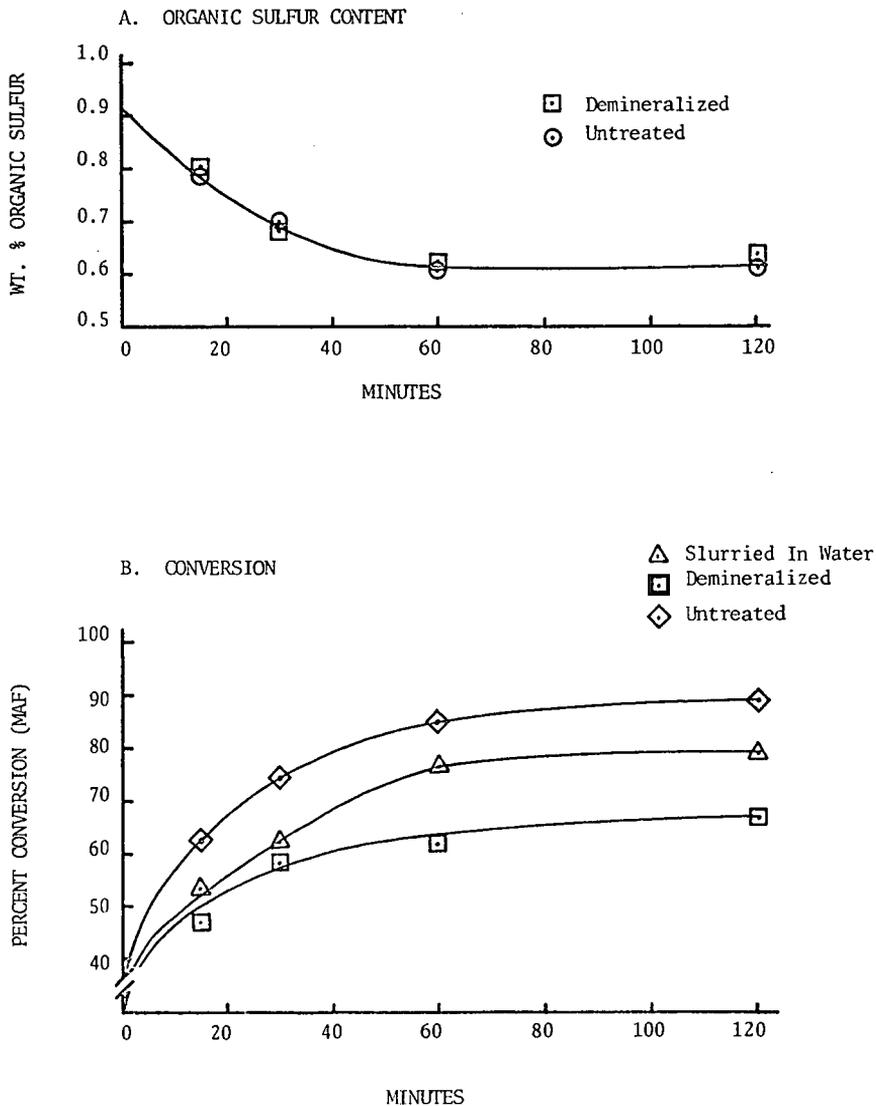
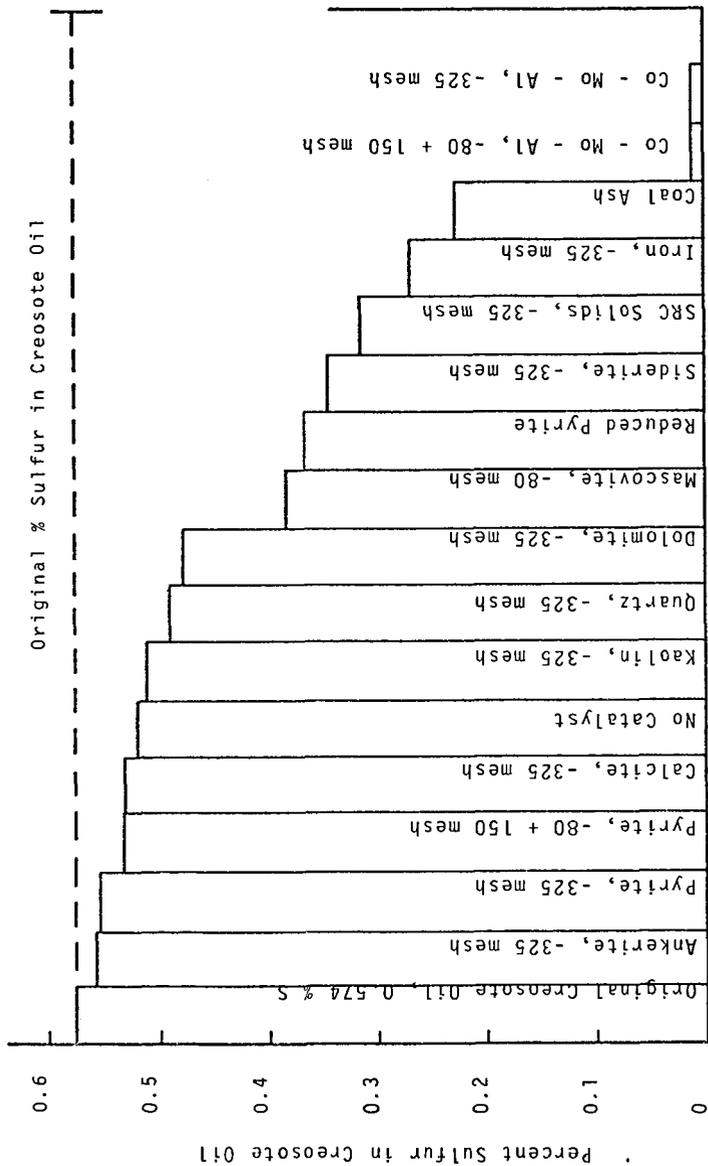


FIGURE 3. EFFECT OF RECYCLING MINERAL MATTER RESIDUE AS INDICATED BY TOTAL PRESSURE

FIGURE 4. EFFECT OF DEMINERALIZING COAL FEED AND SLURRYING COAL FEED WITH WATER ON CONVERSION

Temperature Reaction Conditions: 410°C  
 H<sub>2</sub> Pressure: 2000 psig @ 410°C  
 Agitation Rate: 1000 rpm  
 Autoclave: 300 cc





Species.  
 Figure 5. COMPARISON OF DESULFURIZATION ACTIVITY OF CATALYST

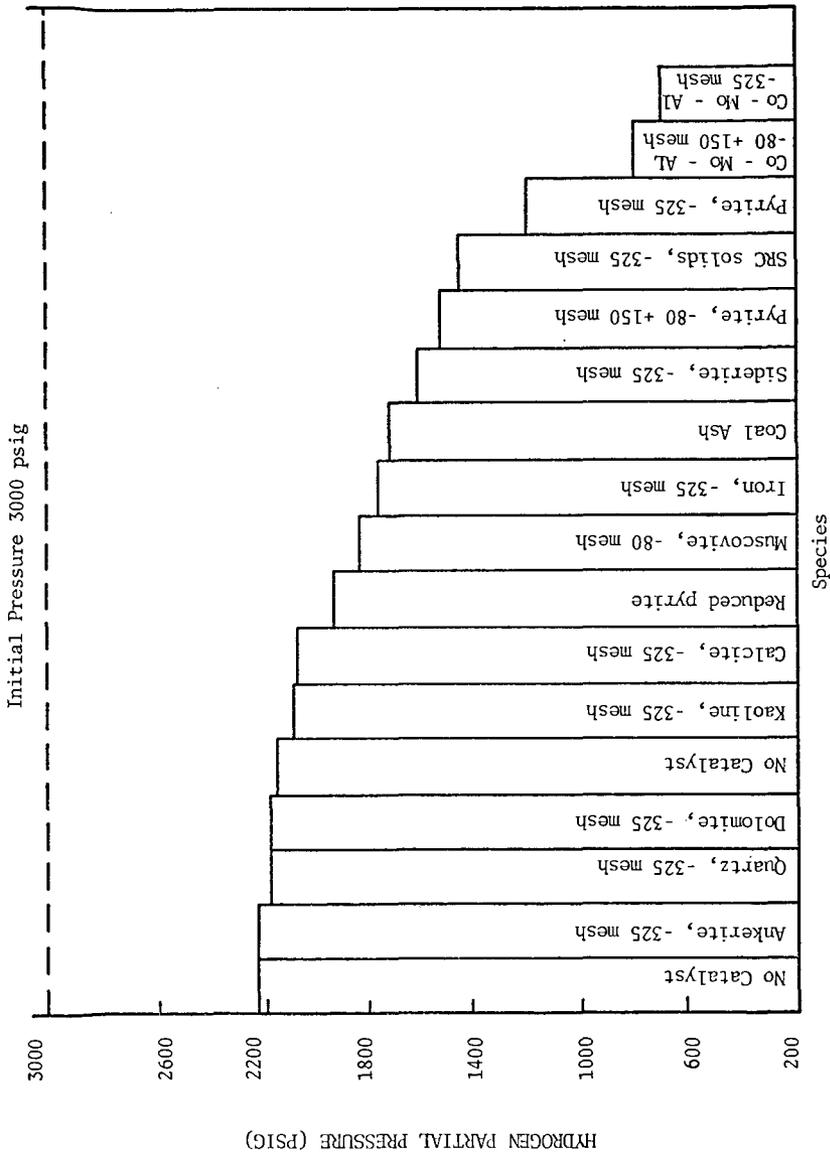


Figure 6. COMPARISON OF HYDROGENATION ACTIVITY OF CATALYST

## CATALYTIC LIQUEFACTION OF COAL

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### INTRODUCTION

Most catalytic liquefaction processes for producing low-sulfur liquid fuel from coal use large amounts of hydrogen which will have to be produced at high cost. In our previous work (1), we reported our attempt to use low-cost syngas to hydro-treat coal in the presence of added water, vehicle, and cobalt molybdate-sodium carbonate catalyst. Catalytic coal liquefaction using syngas reduces the capital and operating costs by eliminating shift converters and purifying systems needed for the liquefaction process using hydrogen. New catalysts have been prepared and tested with syngas to promote liquefaction and desulfurization as well as water-gas shift conversion. Cobalt molybdate catalyst impregnated with alkali metal compounds, such as potassium carbonate, sodium carbonate, and potassium acetate, exhibited good activities for these reactions.

The liquefaction of coal by syngas, like that by hydrogen, appears to proceed via production of asphaltene and conversion of the asphaltene to oil. Because of the important effect of asphaltenes on the viscosity of the product oil (2), the progress of asphaltene formation and asphaltene conversion during the coal liquefaction has been investigated, and some observations on the chemistry of asphaltenes are presented here.

### EXPERIMENTAL

The liquefaction of coal was studied in a magnetically-stirred autoclave. The experimental method is similar to that described earlier (1). The analyses of coal and vehicle used are shown in Table 1. Most coal liquefaction experiments used a liquid fraction (boiling point 270°-630°C) derived from the Solvent Refined Coal Process as the vehicle. For coal hydrotreating by hydrogen alone, the catalyst was a cobalt molybdate supported on alumina-silica (Harshaw CoMo 0402T, 3% CoO - 15% MoO<sub>3</sub>). For coal hydrotreating by syngas, the cobalt molybdate catalyst was impregnated with alkali metal compounds, such as potassium carbonate, sodium carbonate, and potassium acetate. The cobalt molybdate-alkali metal compound weight ratio was 2:1. Typically, 2.3 to 2.8 moles of reactant gas and 30 grams of coal as received were charged to the autoclave. The reaction was carried out in the temperature range of 400° to 450°C at about 3,000 psi in the presence of added water, vehicle, and catalyst. Total products were filtered at ambient or warmer temperature to obtain liquid oils. Asphaltenes, operationally defined as being soluble in benzene and insoluble in pentane, were isolated from the oil products according to procedures established by the Analytical Section of the Pittsburgh Energy Research Center. Gaseous products were analyzed by mass spectrometry. Data on conversion, oil yield, and asphaltene formed are given as weight percent based on moisture- and ash-free (maf) coal.

TABLE 1. Analyses of coal and vehicle, percent

	Coal				Vehicle	
	Kentucky	Bituminous	W. Virginia	Bituminous	Alkyl-naphthalene	SRC
	As used	maf	As used	maf		liquid
C	58.8	75.9	73.0	80.9	90.6	88.8
H	4.9	5.4	5.3	5.7	8.7	7.4
N	1.2	1.6	1.3	1.4	0.06	1.1
S	5.16	6.67	3.80	4.21	0.37	0.65
O	14.4	10.5	8.6	7.9	0.27	2.1
Ash	15.5		8.1			0.03
Moisture	7.1		1.7			
VM	35.7	46.1	43.3	48.0		
Btu/lb	11,500		12,900			
Asphaltene					0.8	7.1
H/C ratio		0.85		0.84	1.15	1.00

RESULTS AND DISCUSSION

Hydrotreating of Coal. New catalysts were prepared and tested with syngas for coal liquefaction. Catalysts were cobalt molybdate impregnated with alkali metal compounds such as potassium carbonate, sodium carbonate, and potassium acetate. Table 2 shows the results of hydrotreating West Virginia bituminous coal at 450°C by 2H<sub>2</sub>:1CO syngas. The amount of water added was 10 parts per hundred parts of coal plus vehicle, corresponding to 0.7 mole of steam per mole of CO in the reactor. The results obtained with various catalysts were quite satisfactory.

TABLE 2. Hydrotreating of West Virginia bituminous coal<sup>a</sup>

(Coal:SRC liquid = 1:2.3, 450°C, 15 min.)

Feed gas	Syngas (2H <sub>2</sub> :1CO)				H <sub>2</sub>
	K <sub>2</sub> CO <sub>3</sub> <sup>b</sup>	CoMo-K <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	CoMo-Na <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	CoMo-KOAc <sup>c</sup>	CoMo <sup>d</sup>
Water added, parts/100 parts coal + vehicle	10	10	10	10	
Operating pressure, psi	3,100	3,000	3,000	2,800	2,800
Conversion, %	93	95	94	96	94
Oil yield, %	59	68	64	70	71
Asphaltene formed, %	62.9	42.2	52.8	55.5	30.3
S in oil product, %	0.67	0.40	0.45	0.50	0.39
Kinematic viscosity, cst at 60°C	44	20	22	22	15
Syngas or H <sub>2</sub> consumed, scf/lb maf coal	5.4	8.6	10.5	11.5	10.7

a Data are given in weight percent of maf coal.

b One part per hundred parts coal plus vehicle.

c Three parts per hundred parts coal plus vehicle.

d Two parts per hundred parts coal plus vehicle.

Figure 1 shows the increase of syngas or H<sub>2</sub> consumption with increasing reaction temperature and time. CoMo impregnated with K<sub>2</sub>CO<sub>3</sub> was used as the catalyst in the syngas runs. Regardless of the reaction temperature and time, the asphaltene content of the oil product decreases with the increase of the syngas or H<sub>2</sub> consumption as shown in Figure 2. In general, the sulfur content and the oil viscosity also decrease with the increase of the syngas or H<sub>2</sub> consumption. Thus further improvements in the oil quality by reduction in asphaltene and sulfur contents could be attained at the expense of oil yield under more severe conditions at 450°C and increased reaction time as shown in Table 3. However, both syngas and H<sub>2</sub> usage would increase substantially. It would not be a major problem if low cost syngas were used in the liquefaction process, but it could be too costly if H<sub>2</sub> were used. It is noteworthy that one objective of the SYNTHOIL process (3) is to convert coal to a low-sulfur liquid fuel with minimum consumption of high cost H<sub>2</sub>.

TABLE 3. Effect of reaction time on hydrotreating of coal<sup>a</sup>

(Coal:SRC liquid = 1:2.3, 450°C)

Catalyst	Syngas (H <sub>2</sub> :CO = 2:1)		H <sub>2</sub>	
	CoMo-K <sub>2</sub> CO <sub>3</sub> <sup>b</sup>		CoMo <sup>c</sup>	
Reaction time, min.	30	60	30	60
Water added, parts/100 parts coal + vehicle	10	10		
Operating pressure, psi	3,000	3,000	2,700	2,800
Conversion, %	94	95	95	95
Oil yield, %	65	42	59	48
Asphaltene formed, %	38.2	32.2	14.8	14.7
S in oil product, %	0.43	0.32	0.31	0.26
Kinematic viscosity, cst at 60°C	16	9	10	7
Syngas or H <sub>2</sub> consumed, scf/lb maf coal	11.2	16.2	13.7	16.1
CO/H <sub>2</sub> consumption ratio	1.4	0.8		
H <sub>2</sub> /CO ratio of off-gas	4.3	3.2		

<sup>a</sup> Data are given in weight percent of maf coal.

<sup>b</sup> Three parts per hundred parts coal plus vehicle.

<sup>c</sup> Two parts per hundred parts coal plus vehicle.

Table 4 shows the hydrotreating of coal at various temperatures at which the consumption of syngas and H<sub>2</sub> would be 4,000 to 5,500 scf per barrel of oil, the normal range for a process. The asphaltene and the sulfur contents of the oil products obtained in the syngas and H<sub>2</sub> runs are comparable. Under these conditions, the syngas usage was in the range of 3,900 to 4,700 scf per barrel of oil as compared to the H<sub>2</sub> usage of 4,700 to 5,500 scf per barrel when pure H<sub>2</sub> was used. Use of 1H<sub>2</sub>:1CO syngas in place of 2H<sub>2</sub>:1CO syngas gave no significant difference in the results except that the H<sub>2</sub>/CO ratio of off-gas and CO/H<sub>2</sub> consumption ratio varied.

TABLE 4. Hydrotreating of coal at various temperatures<sup>a</sup>

Catalyst	Syngas (H <sub>2</sub> :CO = 1:1) CoMo-K <sub>2</sub> CO <sub>3</sub> <sup>b</sup>			Syngas (H <sub>2</sub> :CO = 2:1) CoMo-K <sub>2</sub> CO <sub>3</sub> <sup>b</sup>			H <sub>2</sub> CoMo-C		
	400	425	450	400	425	450	400	425	450
Temperature, °C	60	30	15	60	30	15	60	30	15
Time, Min.	10	10	10	10	10	10			
Water added, parts/100 parts coal + vehicle	3,100	3,100	3,100	3,000	3,100	3,000	2,900	2,900	2,800
Operating pressure, psi	89	95	93	89	94	95	89	95	94
Conversion, %	73	65	64	71	70	68	71	71	71
Oil yield, %	57.2	51.4	53.2	48.9	53.7	42.2	54.4	43.7	30.3
Asphaltene formed, %									
Oil analysis, %									
C	88.2			88.1			88.3		88.2
H	7.5			7.5			7.8		7.6
N	1.2			1.2			1.0		1.1
S	0.54	0.47	0.47	0.53	0.51	0.40	0.40	0.41	0.39
O	2.6			2.7			2.5		2.7
Kinematic viscosity, cst at 60°C	45	25	21	38	28	20	31	23	15
Syngas or H <sub>2</sub> consumed, scf/lb maf coal	7.8	9.9	10.3	7.5	9.2	8.6	9.1	10.3	10.7
CO/H <sub>2</sub> consumption ratio	15	23	6.1	3.2	2.2	2.1			
H <sub>2</sub> /CO ratio of off-gas	1.8	2.1	2.1	3.4	4.4	4.1			

<sup>a</sup> Data are given in weight percent of maf coal.

<sup>b</sup> Three parts per hundred parts coal plus vehicle.

<sup>c</sup> Two parts per hundred parts coal plus vehicle.

Formation of Asphaltene. The coal liquefaction by syngas, like that by H<sub>2</sub>, proceeds via production of asphaltene. The decrease in the asphaltene formation with the increase in the syngas consumption (Figure 2) indicates that the asphaltene formed is converted to oil under further hydrotreating. Sternberg et al. (2) reported a significant effect of asphaltenes on the viscosity of the SYNTHOIL product oil. We also found that the viscosity of the oil product correlates well with its asphaltene content, regardless of the reaction temperature and time (see Figure 3). A similar relationship is also observed when pure H<sub>2</sub> is used. The difference in the curves obtained from syngas and H<sub>2</sub> runs is probably attributable to the difference in the molecular structure and size of asphaltenes obtained (see below).

Because of the important effect of the amount and the type of asphaltene on the property of the liquefied product, studies were conducted on the formation of asphaltene and oil during the progress of coal liquefaction. Kentucky bituminous coal was liquefied in the presence of an asphaltene-free alkyl-naphthalene-based vehicle oil in both syngas and H<sub>2</sub> systems. Catalysts were CoMo - Na<sub>2</sub>CO<sub>3</sub> and CoMo for syngas and H<sub>2</sub> runs, respectively. An operating pressure of about 3,000 psi and reaction temperatures of 400° to 450°C were used. It required about 60 to 70 minutes for the autoclave to reach desired temperatures. The moment the desired temperature was reached was taken as zero time.

Figure 4 shows the results at 400°C. Nearly 30% of the conversion occurred before the autoclave reached the temperature in both syngas and H<sub>2</sub> runs. As viewed by earlier workers (4), the rate of coal conversion to asphaltene is far greater than the rate of asphaltene hydrogenation to oil, and the asphaltene formation goes through a maximum with respect to time. The hydrogenation of asphaltene to oil at 400°C is very slow and substantial parts of the conversion product — equivalent to about one-third of maf coal — still remained as asphaltene after 120 minutes. At 450°C, the asphaltene formation appears to reach a maximum rapidly but decreases relatively slowly by hydrotreating (see Table 5). The rates of asphaltene formation and asphaltene conversion are relatively greater in the coal liquefaction by H<sub>2</sub> than by syngas.

TABLE 5. Formation of asphaltene during coal liquefaction

(Kentucky bituminous coal:alkyl-naphthalene = 1:2.3, 2,900 psi, 450°C)

Reaction time, min.	Syngas (2H <sub>2</sub> :1CO)			H <sub>2</sub>		
	5	15	60	5	15	60
Asphaltene formed, % <sup>a</sup>	42.6	38.0	25.5	47.1	26.7	6.7
Asphaltene analysis, %						
C	84.1	85.8	87.0	85.4	87.1	86.9
H	6.3	6.3	5.0	6.5	6.3	5.7
N	1.6	2.1	2.0	1.5	2.0	2.1
S	1.3	0.15	0.4	0.64	0.23	0.36
O	7.0	5.7 <sup>b</sup>	4.0	6.0	4.3 <sup>b</sup>	5.1
Molecular weight of asphaltene	387	430	407	457	573	597

<sup>a</sup> Weight percent of maf coal.

<sup>b</sup> By difference.

It is interesting to note that, under similar liquefaction conditions, molecular weight (number average) of the asphaltene formed under syngas is lower than that of the asphaltene formed under H<sub>2</sub> (see Table 5). The molecular weight was determined by vapor pressure osmometry of the asphaltene in benzene. Table 6 shows molecular weights of asphaltene and total oil products obtained from the

liquefaction of West Virginia bituminous coal. Except where specified a cryoscopic method was used. Again, the molecular weight of asphaltene is lower when syngas is used. This suggests that the size of asphaltene molecules obtained in the syngas system is smaller, and this could, at a given asphaltene content, result in lower oil viscosity in the syngas system than in the H<sub>2</sub> system (see Figure 3).

TABLE 6. Molecular weights of oil products and asphaltenes

(West Virginia bituminous coal:SRC liquid = 1:2.3, 450°C, 3,000 psi)

Time, min.	Syngas (2H <sub>2</sub> :1CO)		H <sub>2</sub>	
	Molecular weight <sup>a</sup>		Molecular weight <sup>a</sup>	
	Asphaltene	Oil product	Asphaltene	Oil product
15	339 <sup>b</sup>	218	437 <sup>b</sup>	227
30	494	221	544	210
60	395	194	405	194

<sup>a</sup> By cryoscopic method.

<sup>b</sup> By osmometry.

Liquefaction Process Using Syngas. In evaluating a coal liquefaction process using syngas, a modification of the SYNTHOIL process was considered. A schematic flow diagram is shown in Figure 5, and the gas stream flows in scfh (on 100 lb/hr maf coal basis) and volume percent are shown in Table 7. It is assumed that the process is operated at 3,000 psi and 450°C and that the syngas flow rate is at a feed gas/coal-oil slurry volume ratio of 5.9. These operating conditions will result in turbulent flow in a packed-bed reactor. Since syngas has a higher density than H<sub>2</sub>, a lower volumetric flow is necessary than that of H<sub>2</sub> in the SYNTHOIL process. The syngas leaving a gasifier with the equilibrium composition at 1800°F (H<sub>2</sub>/CO = 0.53) is introduced to the recycle gas (H<sub>2</sub>/CO = 3.4) to make up the feed gas (H<sub>2</sub>/CO = 2). Steam is introduced to the feed gas to give an H<sub>2</sub>O/CO mole ratio of 0.7, corresponding to the autoclave conditions. The flow and composition of the off-gas (Stream 3) were estimated from vapor-liquid equilibria of various components with the liquid oil at the receivers. A small amount of the recycle gas can be removed, if necessary, to keep the methane level from building up. The syngas consumption is about 4,500 scf per barrel of oil when the oil yield is 3.5 barrels per ton of coal (as received). Since the syngas produced from the gasifier is used directly, shift converters and purifying systems required in the SYNTHOIL process can be eliminated.

TABLE 7. Gas stream flows

(Basis: 100 lb/hr maf coal feed to process)

Stream	Gas composition, mole percent				
	1	2	3	4	5
H <sub>2</sub>	46.4	47.6	15.8	61.7	30.6
CO	22.7	14.7	13.5	18.1	58.3
CH <sub>4</sub>	12.2	15.4	20.7	18.4	0
C <sub>2</sub> H <sub>6</sub>	1.2	1.9	6.9	1.8	0
H <sub>2</sub> S	0.2	0.5	1.8	0	1.3
CO <sub>2</sub>	1.6	12.9	41.3	0	8.7
H <sub>2</sub> O	15.7	7.0	0	0	1.1
Flow, scfh	4774.7	4206.4	336.7	3162.9	873.6

The thermal balance of the process is shown in Figure 6. The calculation was based on 100 Btu input of coal. Heating values are: coal as received = 12,900 Btu/lb, oil = 17,000 Btu/lb, recycle gas = 475 Btu/scf, and off-gas = 439 Btu/scf. The overall thermal efficiency was calculated to be 76.6%.

#### CONCLUSIONS

Liquefaction of high sulfur bituminous coal at 3,000 psi under syngas in the presence of steam, recycle vehicle, and cobalt molybdate catalyst impregnated with potassium carbonate gives high coal conversions and oil yields at 400° to 450°C. The asphaltene, the sulfur content, and the viscosity of the oil products decrease with increasing consumption of syngas, and the syngas consumption increases with increasing reaction temperature and residence time. When syngas is used in place of hydrogen in coal liquefaction, the rate of asphaltene conversion to oil is slower but asphaltenes formed have molecules of smaller sizes.

A catalytic coal liquefaction process using syngas gives high thermal efficiency and reduces the capital and operating costs by eliminating shift converters and purifying systems.

#### ACKNOWLEDGEMENT

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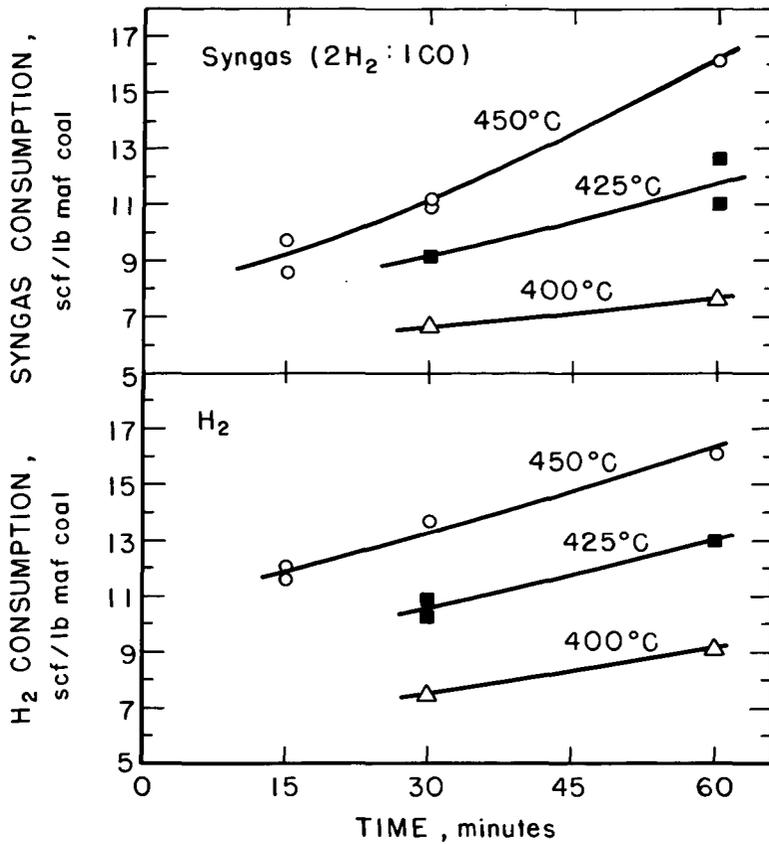


Figure 1 - Change of syngas or H<sub>2</sub> consumption with temperature and time.

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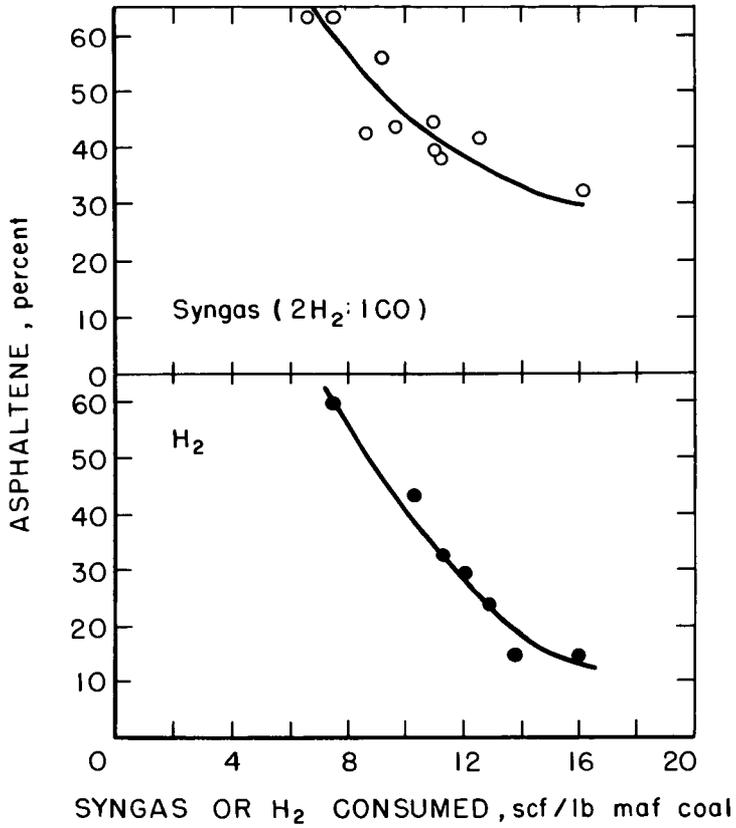


Figure 2 - Decrease of asphaltene with syngas or H<sub>2</sub> consumption.

4-26-76 L-14815

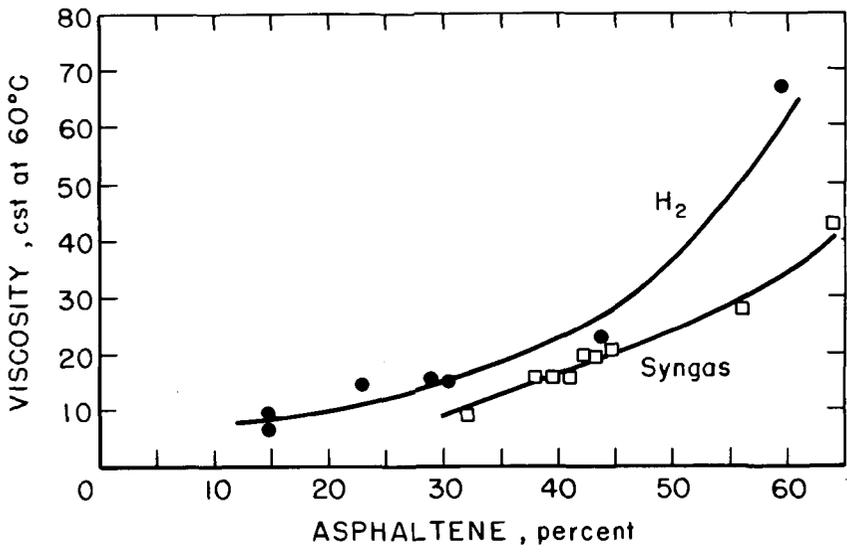


Figure 3- Oil viscosity vs asphaltene content .

4-26-76 L-14816

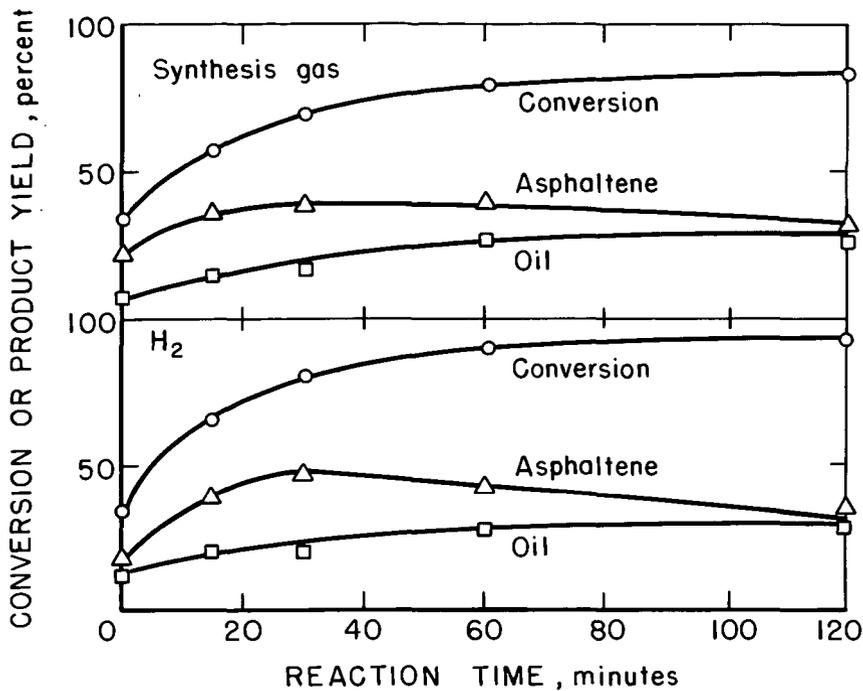


Figure 4 - Conversion and product yield vs reaction time at 400°C .

4-26-76 L-13769

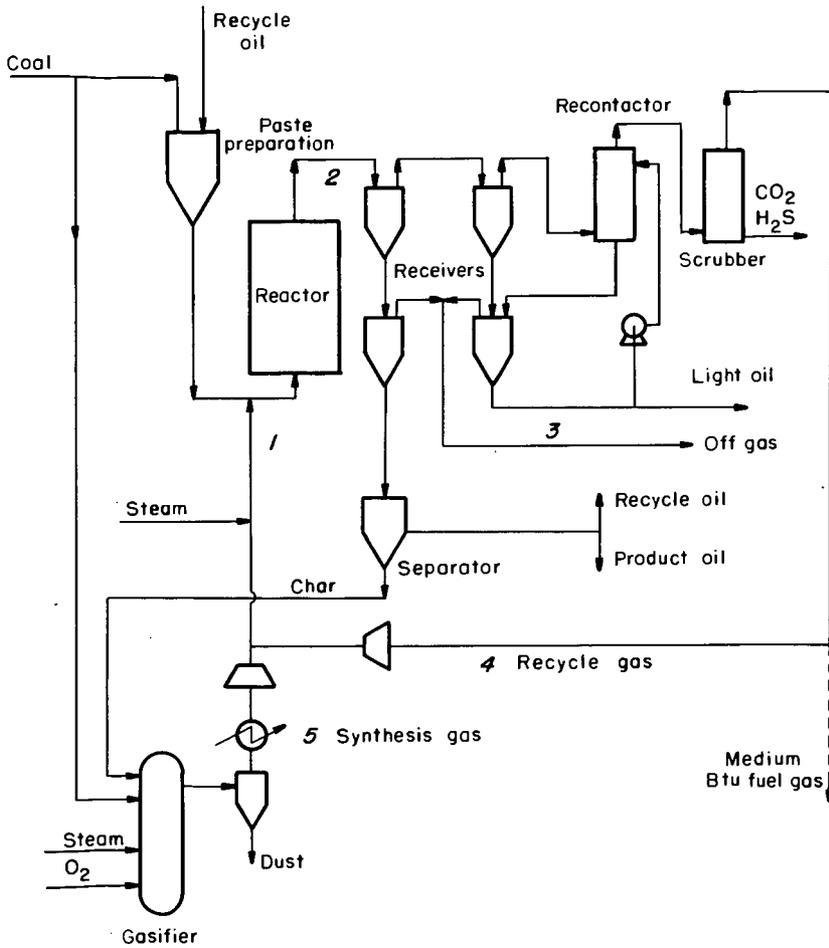
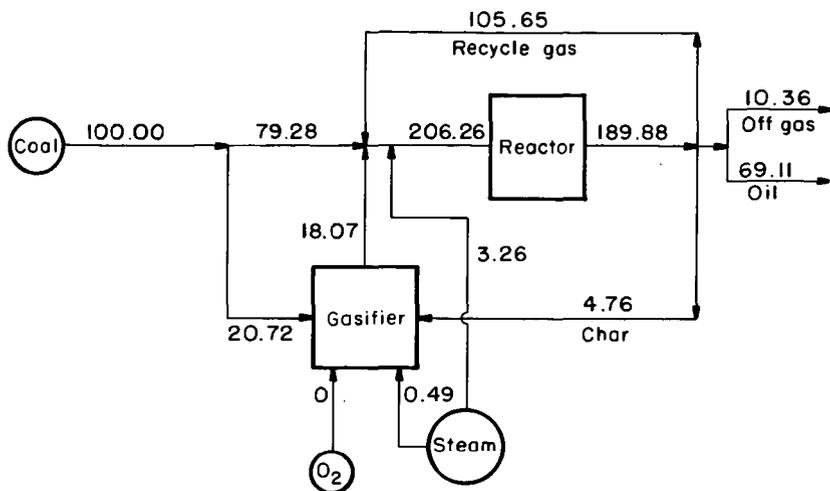


Figure 5 - Flow diagram of conceptual coal liquefaction process using syngas.

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$$\text{Thermal efficiency} = \frac{69.11 + 10.36}{100 + 0.49 + 3.26} = 76.6\%$$

Figure 6 - Thermal balance of liquefaction process (basis: 100 Btu input of coal).

4-28-76 L-14819

# LIQUEFACTION OF COAL WITHOUT CATALYST USING SELECTIVE HYDROGENATION

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## INTRODUCTION

Until recently refiners avoided the upgrading of residual fuels by catalytic hydrogenation. The difficulties experienced in the development of the catalytic desulfurization of residual fuels demonstrated the infeasibility of such a process. For example, heat sensitive asphaltenes (1) present in the residual fuels immediately deactivate the catalyst at the start of the process through excessive carbonization caused by the heats of hydrogenation and adsorption. Nevertheless, efforts are still made to upgrade coal extracts containing more asphaltenes than residual fuels, or even worse, components such as benzene insolubles or ash.

## EXPERIMENTAL CONSIDERATIONS

The most sensible approach is to selectively extract only the asphaltene free portion of the coal and use the remaining undissolved coal for the production of  $H_2$  and the energy necessary for processing. Approximately 40 to 50% of the coal will be needed to provide these essential services for the refining of coal. As an example, 100g moisture ashfree-maf-Illinois #6 coal contains: 81.0% C = 6.7 atoms; 5.2% H = 5.2 atoms; 9.5% O = 0.6 atoms; 2.9% S = 0.09 atoms; 1.4% N = 0.10 atoms. For every atom of C, approximately 0.8 atoms of H are present. This is less than 1H for 1C. In paraffins,  $H_2C-(CH_2)-CH_3$ , the ratio of  $H_2:C$  is 2:1 since the terminal  $CH_3$  groups do not affect this ratio very much. In reality, fuels which are saturated mixtures of paraffins and naphthenes like kerosene, do not achieve this ratio of 2:1 due to the presence of small amounts of benzene rings and condensed naphthenes. A more realistic ratio for a saturated fuel should be 1.8H:1C corresponding to 13.3% H.

If one wanted to upgrade 4 of the 6.7 carbons in the 100g maf coal by increasing the atomic H:C ratio from 0.8 to 1.8, this would require the addition of 2 moles of  $H_2$  to the 4C atoms, producing 55.2g of oil ( $4C = 48g$  and  $4 \times 1.8H = 7.2g$ ). Approximately 0.8 mole of  $H_2$  would also be necessary for the removal of the heteroatoms O, S, N. Therefore, 2.8 moles of  $H_2$  have to be produced from the 100g maf coal. Out of the 6.7 atoms of carbon, 4 are being hydrogenated to a hydrocarbon oil and 2.7 C are available to produce  $H_2$  via the water-gas and the subsequent shift reaction. The autothermic equation, coupling the maximum  $H_2$  production with a minimum C consumption,  $2.0C + 0.60 O_2 (+188 \text{ Kcal or } 2.0 \times 94) + 2.8 H_2O (-185 \text{ Kcal or } 2.8 \times 68) \longrightarrow 2.8 H_2 + 2.0 CO_2$  demonstrates that an absolute minimum of 2.0 carbon atoms of the remaining 2.7 C atoms is necessary for  $H_2$  production, 0.7 C, about 10% of the maf coal is available for the energy needed to run this reaction and the coal refinery.

This crude approximation demonstrates that it is only necessary to extract 55g oil from 100g maf coal, the remaining undissolved coal has to provide the  $H_2$  and the energy for the operation. If only 55% has to be dissolved it should be possible to extract selectively only heptane soluble oil, thereby avoiding all downstream refining difficulties caused by the presence of asphaltenes. Ideally, the solvent should do two things, dissolve 50-60% of the coal selectively, e.g., asphaltene free and thermo-hydrocrack using  $H_2$  from the  $H_2$  atmosphere to achieve a sufficiently low molecular weight to permit separation of the extract from the insoluble coal by distillation. The conditions under which the solvent must operate, i.e., the temperature and  $H_2$  pressure must also be established. Bituminous coal acts like a giant potential asphaltene. The coal is heat labile and begins to soften at about 380°C. At 400°C it starts coking, which produces gas, volatile liquids, tar, and coke. Increasing the temperature beyond 400°C produces additional coke from the tar. Coking can be repressed by the application of high  $H_2$  pressure. However, beyond 440°C the thermodynamic equilibrium favors complete aromatization. Obviously, it would be advanta-

geous to dissolve the coal below the coking temperature to keep coke and asphaltene production to a minimum. Yet the temperature should be sufficiently high for a reasonable rate of decomposition. It was found earlier that 400°C was a good compromise (2), and should probably not be exceeded. Increasing the temperature to 430°C yields undesirable extracts having a higher asphaltene content. High H<sub>2</sub> pressure is beneficial since it represses coking and stabilizes heat labile materials. However, for practical operating reasons, the pressure should not exceed 200 atm.

Organic material proposed as coal solvents have ranged from paraffins (3) to hydroaromatics, to aromatics; and from coal tar fractions, to coal tar itself to dissolve the coal. Pott and Broche (4), proposed a coal solvent consisting of 80% tetralin and 20% coal tar cresol which could dissolve as much as 90-95% of the coal. Tetralin, without the cresols, is a little more discriminating. It will dissolve only 80-85% coal. Such an extract will contain around 30% heptane insolubles, but only a relatively small amount of benzene insolubles. Many investigators have shown that part of tetralin's ability to liquefy coal consists of transferring its H<sub>2</sub> to coal, thus becoming naphthalene. To our knowledge, no one has proven that tetralin can also transfer H<sub>2</sub> from the atmosphere to coal, i.e., carry out a catalyst-like reaction. This type of claim would be very difficult to substantiate since even if the H<sub>2</sub> material balance did show an uptake of H<sub>2</sub>, this uptake could always be attributed to the catalytic activity of the walls of the reactor and/or the catalytic activity of coal constituents. Secondly, one would not expect a large effect and correlations drawn from very small differences in the analytical hydrogen data raise grave doubts as to their reliability. However, there is another means of proving hydrogenation activity, namely to demonstrate different degrees of hydrogenation with different solvents in the same reactor vessel with the same coal under identical H<sub>2</sub> pressure and temperatures. In addition, a solvent should be employed which leaves no doubt as to its direct role in the promotion of hydrogenation. Such a solvent was found in a partially hydrogenated refinery stream (5) used by A.W. Langer and co-workers for the thermal hydrocracking of petroleum residues (6).

#### EXPERIMENTAL RESULTS AND DISCUSSION

Vacuum bottoms were hydrocracked using a typical Ni-Mo on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> desulfurization catalyst under rather severe conditions, i.e., (760°F and 300 psi H<sub>2</sub>). The results are shown in Table I under Run 4. An oil was obtained which consisted of 50% hydroaromatics and 40% saturates. Unfortunately, the oil also contained 10% polycyclic aromatics. For comparison the following solvents were used:

- Run 1 - tetralin
- Run 2 - cocracker slurry oil which is practically all aromatic
- Run 3 - raw, non-hydrogenated vacuum bottoms
- Run 4 - hydrocracked vacuum bottoms. This solvent had the highest H<sub>2</sub> content (12%) while the slurry oil had the lowest H<sub>2</sub> content (7.2%)

TABLE I

Solvent	Run	1	2	3	4
	I, BP		545°F		475°F
API				8.2	18.8
C <sub>7</sub> insol.			1.3	4.7	1.1
%H		9.1	7.2	10.5	12
% P + N					40
% HAR		100			50
% cond. polycycl. Ar					10

As can be seen, even the hydrocracked vacuum bottoms still contain some C<sub>7</sub> insolubles. Whether or not these figures are reliable is questionable. Very often, C<sub>7</sub> insolubles in hydrocracked vacuum bottoms are not asphaltenes but microcrystalline waxes soluble in warm oil but insoluble in C<sub>7</sub> at ambient temperatures (?).

200 g Illinois #6 raw coal was extracted in autoclaves with 200 g solvent at 400°C under 200 atm. H<sub>2</sub>. The coal had the following composition (moisture and ashfree - maf): C 81.0%, H 5.2%, O 9.5%, S 2.9%, N 1.4%. The raw coal contains 7.8% ash and 7.2% water.

The results (Table II.) confirm that the extraction with the hydrogenated vacuum bottoms is a selective process (See Run 4-56%); while tetralin (Run 1) and slurry oil (Run 2) yielded the same extraction result, namely 83%. Run 3 using raw, unhydrogenated vacuum bottoms extracted only 10% so the products from this run were not investigated any further.

TABLE II.

Run	1	2	3	4
<u>Liquid Product</u>				
% Coal MAF (dissolved)	83	83	10	56
API			15.8	18.6
% C <sub>7</sub> insol. (of solution)	14	20	4	2
% C <sub>7</sub> insol. (of extract)	34	43		3.8
% Bz insol. (of solution)	2.5	5.7		
% Bz insol. (of extract)	6	14		
% H <sub>2</sub> (of solution)	8.4	7.1	10.6	11.4
% H <sub>2</sub> (of extract)	7.4	7.0		9.0
<u>Unconverted Solids</u>				
% H	2.8	1.7		3.8
mols H <sub>2</sub> added to 100 g MAF coal	0.8	0.5		1.35

The percentages in the extract (Table II.) were calculated from the percentages in the solvent and in the solution; % in extract = % in solution - % in solvent. In the case of % H<sub>2</sub>, the H<sub>2</sub> in the unconverted coal solids was used to arrive at the H<sub>2</sub> material balance.

In examining the extract figures, note that the C<sub>7</sub> insolubles of Run 4 are still too high, 3.8%, for easy refining, but remarkably low compared to the asphaltenes in the tetralin extract, 34%, Run 1. This is most likely due to the 10% polycyclic aromatics in the solvent of Run 4. That effect is especially apparent in Run 2, where the whole solvent, slurry oil, is polycyclic aromatic. The extract contained 43% C<sub>7</sub> insolubles and an additional 14% benzene insolubles, which leaves 43% of the extract soluble in C<sub>7</sub>. Such a product could not be refined economically since it would have to be de-asphalted first, a very expensive process yielding only 43% C<sub>7</sub> solubles. The tetralin extract (Run 1) does not look much better; 34% C<sub>7</sub> insolubles and 6% benzene insolubles. The last horizontal line in Table II indicates the values of H<sub>2</sub> consumption for 100 g of maf coal. According to this table, the hydrogenated vacuum bottoms (Run 4) are not only more selective solvents, but much better H<sub>2</sub> transfer agents or if you wish, catalysts. The absolute accuracy of these figures is questionable due to the increasing error in arriving at the smaller absolute H<sub>2</sub> values. However, even though the values are not very accurate, they still show real differences (i.e. 1/2 or 1/3 as much, etc.). The figures also establish that organic compounds cannot only transfer H<sub>2</sub> from themselves to another organic compound, but also molecular H<sub>2</sub> from the surrounding atmosphere.

A repeat of these experiments with another hydrocracked vacuum bottom containing only 4% polycyclic aromatics showed a much greater selectivity (Table III.). Notice that the tetralin contains 1% C<sub>7</sub> insolubles and the resulting coal solution

had the same percentage. Thus, the extract itself also contained 1% C<sub>7</sub> insolubles. The total coal solution can be distilled by vacuum distillation and thereby facilitate the separation of the undissolved coal. In addition, these solvents actually upgrade the undissolved solids also.

TABLE III.

W.K.T. Gleim and M. J. O'Hara	U. S. 3,867,275	February 18, 1975
Hydrocracked VB's	Solvent	Coal Solution
I. BP	475°F	
API	18.8	20.5
C <sub>7</sub> insol.	1.1	1.2
% P + N	46	
% HAR	49	
% cond. polycycl. Ar	4	
% H in solids		5.9
% extract of MAF coal		58.1
% Bz extract		18.6

Furthermore, the upgrading of this residue was demonstrated by the fact that additional material was extracted from the residue by boiling benzene at atmospheric pressure. This second extract yielded 18.6% and consisted of 50% C<sub>7</sub> insolubles and 50% solubles.

In reference to the first extract, by reusing it over and over again without removing the dissolved coal, it is possible to slowly increase the dissolved coal content of the solvent thereby increasing its hydroaromaticity. Thus, the solvent would dissolve more coal, thereby losing its selectivity, meaning that the % C<sub>7</sub> insolubles would increase with the number of extractions. Rehydrogenating the coal solution between extractions will not totally reconstitute the selectivity of the original coal solvent. The paraffins in the original solvent derived from petroleum, contribute to its selectivity. These paraffins would be diluted by the additional of dissolved coal. In order to maintain this selectivity, a continuous fresh stream of solvent from a petroleum refinery would be necessary. This is a good argument for combining coal liquefaction with petroleum refining.

As shown in Table III., 58% of the maf coal can be dissolved, which means 50% of the raw coal. Assuming that all of the refined crude boiling above 500°F, can be used as coal solvent means that 70% of the total crude can serve as solvent in a coal-to-solvent ratio of 1:1.

#### CONCLUSIONS

How much additional distillate could such a scheme provide for the United States? Right now the U. S. produces  $8.5 \times 10^6$  bbls/day crude; in 5-6 years with Prudhoe Bay, the U. S. will be producing about  $10 \times 10^6$  tons/day. With  $6.5 \times 10^6$  bbls/day ( $\sim 1 \times 10^6$  tons/day),  $1 \times 10^6$  tons/day of raw coal can be extracted yielding 500,000 tons/day of coal extract, i.e.,  $3.25 \times 10^6$  bbls/day. At present, the U. S. uses approximately  $11 \times 10^6$  bbls/day of distillate. In ten years it will probably be at least  $13 \times 10^6$  bbls/day. This deficit could be balanced by  $3.25 \times 10^6$  bbls/day oil taken from coal in addition to the  $10 \times 10^6$  bbls/day from petroleum production. This means the yearly requirement will be  $365 \times 10^6$  tons of coal. Substituting coal for the  $3.3 \times 10^6$  bbls of residual oils that the U.S. uses daily would require another  $0.5 \times 10^6$  tons of coal/day, or  $182 \times 10^6$  tons/year. Therefore, a total of  $550 \times 10^6$  tons of coal per year will be needed to substitute for imported oil.

The present U. S. coal production is about  $600 \times 10^6$  tons per year. That means

that the U. S. coal industry would have to double their output in ten years. I do not believe that this can be achieved in the current political climate. The ideal conditions for these concepts I have expressed, exist in the Midwest. Oil, coal, and refineries are situated close together, with sufficient H<sub>2</sub>O available. One would begin with the total conversion of oil, including asphaltenes, to distillate. For this, coal would serve as the refinery fuel and H<sub>2</sub> source. When this is achieved, the second step, namely the selective extraction of coal is undertaken, leaving the undissolved coal to serve as a source of energy to power the refining of crude and coal.

To summarize, the better part of coal, that is the heptane soluble fraction, can be extracted selectively and thermohydrocracked to distillate with a petroleum derived solvent in an high pressure H<sub>2</sub> atmosphere without the help of an external hydrogenation catalyst.

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## KINETICS OF COAL HYDRODESULFURIZATION IN A BATCH REACTOR

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### Background

In recent years there has been a renewed interest in developing this nation's coal reserves because of our growing reliance on foreign oil sources. Due to the stringent air quality standards set by the Environmental Protection Agency, however, the burning of coals with sulfur contents of greater than one percent has been essentially prohibited.

An alternative to the production of low-sulfur coal reserves exists in the desulfurization of high-sulfur coal reserves by the techniques of solvent refining and hydrogenation. It is generally accepted (1) that sulfur occurs in coal in three forms: organic, pyritic, and sulfate. These forms vary in concentration and ease of removal from one coal to another. The purpose of this paper is to develop a kinetic model that will represent the rate of removal of sulfur for all three forms simultaneously. Since several different sulfur reactions occur at the same time it is feasible to consider a model in which the reaction rate appears to vary as a function of conversion. Such models were successfully applied by Hill, et al. (2) to the dissolution of coal in tetralin and by Lessley, et al. (3) to thermal cracking of shale gas oil under a hydrogen atmosphere.

Much of the earlier work done on coal desulfurization took the form of carbonization studies in which coal or coal char was heated in the presence of various gas streams and the percent removal of total sulfur from the coal was determined. A good review of the work done on this subject prior to 1932 is given by Snow (4).

In 1960 Batchelor, et al. (5) published an article describing a method in which a bed of char was fluidized with a known mixture of hydrogen and hydrogen sulfide to establish the equilibrium distribution of sulfur between gas and char. He also developed an equation for calculating the maximum amount of desulfurization that could be achieved.

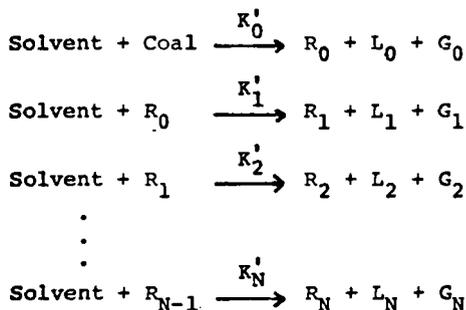
In more recent years a non-isothermal method for determining the kinetics of coal desulfurization has been developed in which the sample is subjected to a constant rate of heat. Vestal, et al. (6) suggests that this method is superior to isothermal methods since it avoids the uncontrolled occurrence of chemical reactions during the time that the sample is being heated to reaction temperature. A good review of this method, complete with theory, experimental procedure and apparatus, results, and discussion, is given by Yergey, et al. (1). The study reveals that in most cases the kinetics of hydrogen sulfide removal can be described by five processes. These processes are directly related to the five forms of sulfur present in the coal which are designated as Organic I,

Organic II, Pyrite, Sulfide, and Organic III. With each of the processes there is an associated activation energy, reaction order, and rate constant.

Another kinetic model for desulfurization is given by Qader, et al. (7). This article discusses the hydroremoval of sulfur from coal tars and concludes that the reaction is first order with respect to heterocyclic molecules. The experimental results also show that sulfur removal follows a true Arrhenius temperature dependence.

To date no articles dealing with the kinetics of hydrodesulfurization of coal in liquid phase have appeared, but several articles have been published on coal dissolution kinetics.

Hill (8) proposed a model for coal dissolution in which a series of reactions take place between the solvent and the coal residue. The model is given as follows:



where

- $R_i$  is the solid coal residue
- $L_i$  is the extract in solution
- $G_i$  is the gaseous products.

In another article Hill, et al. (2) develops a model in which the first-order reaction velocity constant varies with the fraction of coal extracted. This model fits the kinetic data in the range of 350° to 450°C quite well. Plots of the Arrhenius energy of activation and the Eyring enthalpy of activation are included in the article and both plots exhibit straight line relationships.

Wen, et al. (9) have proposed a rate equation for the dissolution of coal under hydrogen pressure which describes fairly closely the experimental data reported from two independent sources. Wen's equation describes the rate of dissolution as a function of the fraction of undissolved solid organics and the coal-solvent ratio. It also incorporates an Arrhenius temperature dependence and an exponential dependence on the hydrogen partial pressure.

Another semi-empirical correlation which adequately represents coal dissolution data is discussed by Curran, et al. (10). This

correlation deals more specifically with the mechanism of hydrogen transfer and does not lend itself to the application of conventional kinetic data analysis techniques.

### Experimental Design

The purpose of this study was to determine the effects of temperature and time on the desulfurization of coal and to develop a kinetic model that can satisfactorily represent the rate of total sulfur removal.

The coal used in this study was a bituminous coal from the Madisonville No. 9 seam, Fies Mine, in Kentucky. The proximate and ultimate analyses for the coal are given in Table 1. This coal was selected because it is currently being used in the start up of the Fort Lewis ERDA solvent refining plant. Coal of minus 200 mesh size fraction was used for this study.

The solvent used was straight run anthracene oil purchased from the Reilley Tar and Chemical Company. The raw solvent was vacuum distilled at an absolute pressure of 2-3 mm of mercury and the cut between 125°-250°C was saved. This cut is similar to the cut used in the Pittsburgh and Midway Solvent Refined Coal Process (11). Hydrogen gas for this study was 3500 psig grade with a purity of 99.95%. The gas was manufactured by the Linde division of the Union Carbide Corporation.

The temperatures chosen for this study were 360°, 390°, and 420°C. The lower temperature was selected since literature (12) indicates that at temperatures below 350°C the dissolution of coal in the solvent is incomplete. The upper temperature was selected because at temperatures of greater than 450°C coking occurs.

Studies on the kinetics of dissolution of coal (2) indicate that at times of greater than 4 hours the percent dissolution does not significantly increase. For this reason reaction times of 1/2, 1, 2, and 4 hours were selected. The lower limit was selected because the 10 minutes required for heating up the injected slurry would interfere with runs of less than 30 minutes.

Initial pressures of 750, 785, and 820 psig were used for runs at 420°, 390°, and 360° respectively. These initial pressures resulted in a reaction pressure of approximately 1900 psig.

The solvent-to-coal weight ratio was set at 10 to 1. This ratio was chosen because it kept the amount of slurry injected into the reactor at a minimum.

The determination of the percent of sulfur remaining in the solvent refined coal was done by an ASTM total sulfur method. This number was then corrected to give the amount of sulfur remaining in the coal on a solvent free basis. Sulfur analyses were also made on the reclaimed solvent and the reaction off gas. Based on these analyses and the analysis of the original coal and solvent a sulfur balance was completed for each run.

## Experimental Equipment

All experimental runs in this study were carried out in a 300 cc Magnedrive batch autoclave, manufactured by Autoclave Engineers of Erie, Pennsylvania. A manual Ruska piston pump (250 ml capacity) was used for injection of slurry into the autoclave. An equipment flow sheet is presented in Figure 1.

## Experimental Procedure

One hundred eighty milliliters of vacuum distilled solvent were added to the reactor and the head sealed. The reactor was then purged with helium and pressurized with hydrogen to the desired initial (cold) pressure, and the jacket heater turned on. One hundred grams of a thick paste (1:1 ratio by weight) of 200 mesh coal and solvent was then charged to the Ruska pump and all air bled from the system. The reactor was allowed to heat (with constant stirring) to reaction temperature, at which time exactly 40 ml of slurry were charged to the hot reactor via the Ruska pump. At the conclusion of the reaction, the reactor was quenched by dropping the heating jacket and cooling the autoclave vessel with a high speed fan. Product gas was analyzed on a gas chromatograph and solvent recovered by vacuum distillation of the resulting liquid product.

## Run Conditions

Table 2 shows the run numbers and the corresponding reaction conditions. Runs 1-11 were all performed using the same coal. Different samples of coal were used for runs 12-14 and 15-17 because an insufficient quantity was prepared initially.

## Percent Desulfurization of the Coal

A plot of sulfur conversion for each temperature level as a function of time is given in Figure 2. The data points for 360°C were fit by the method of least squares for a straight line. The data points for 390° and 420° were fit with a flexible curve. Attempts to fit these data points with second and higher order polynomials proved unsuccessful and there was no theoretical basis for trying to fit the data with other mathematical models.

## Correlation of the Data

Initial attempts to plot the data according to a rate equation of nth-order proved unsuccessful. Although the data at 360°C fit a first-order model quite well the data at the higher temperatures would not yield straight lines for any simple rate expression. The fact that a constant value could not be obtained for the rate constant suggested that the rate constant might be a function of some other variable such as the fractional conversion of the sulfur compounds to hydrogen sulfide and desulfurized products. This would seem feasible since several sulfur reactions are occurring simultaneously (1) with different rate constants and activation energies for each reaction. The idea of the reaction rate varying as a

function of conversion is not a new one and has found application in several areas. Hill, et al. (2) developed a model which successfully described the rate of dissolution of coal in tetralin and Lessley, et al. (3) developed a similar model for the thermal cracking of shale gas oil under a hydrogen atmosphere. Other applications are described by Fabuss, et al. (15) to the thermal decomposition rates of saturated cyclic hydrocarbons and Buekens, et al. (16) to the thermal cracking of propane.

The model of Hill, et al. (2) proved successful in representing the data taken in this study and is developed below.

Rearranging the rate expression for a simple first-order irreversible reaction yields the equation

$$\frac{dx/dt}{1-x} = k.$$

For each temperature level the value of  $dx/dt$  was evaluated at several different times by using the method of "Equal Area Graphical Differentiation" as described by Fogler (17). A plot of  $(dx/dt)/(1-x)$  vs.  $x$  was then made (see Figure 3), and the data exhibited a linear relationship. The best fit straight line through each data set was determined by a least squares fit.

The linear change of the rate constant,  $k$ , with  $x$ , the fraction converted can be expressed as

$$k = C_1 - C_2 x$$

$$k = C_1 \left( 1 - \frac{C_2}{C_1} x \right)$$

If  $C_1 = k_0$  and  $C_2/C_1 = a$

then  $k = k_0 (1-ax)$  (1)

The values of  $k_0$  and  $a$  were found by rearranging the coefficients of the best fit straight line to the form of equation (1).

Substituting equation (1) into the first-order rate expression gives:

$$\frac{dx}{dt} = k_0 (1-ax) (1-x)$$

where  $k_0$  is a pseudo second-order rate constant.

Separating the variables and integrating gives:

$$\frac{dx}{(1-ax)(1-x)} = k_0 dt \quad \text{and}$$

$$\ln \left( \frac{1-x}{1-ax} \right) = (k_0 t + C) (a-1)$$

Using the boundary condition:  $t = 0, x = 0$ , the value of  $C$  is found to equal 0. Therefore, the final equation becomes

$$\ln\left(\frac{1-x}{1-ax}\right) = k_0 t(a-1)$$

The values of  $k_0$  and  $a$  for this equation are listed in Table 3 as a function of temperature.

#### Arrhenius Activation Energy

Based on the values of  $k_0$  given in Table 3 a plot of  $\ln k_0$  vs.  $1/T$  was made to determine the Arrhenius energy of activation. This plot is shown in Figure 4. The linear relationship indicates that the desulfurization reactions follow a true Arrhenius temperature dependence at low conversions. The value of the activation energy obtained from this graph is 33.04 Kcal/mol. This value is within the range of reported values for hydrodesulfurization reactions (1).

#### Reproducibility

Runs 15, 16, and 17 were carried out under the same set of conditions to serve as a check on the reproducibility of the data. The conditions chosen were a temperature of 360°C and a reaction time of 1/2 hour. This set of conditions represents an extreme that should give the maximum variance in the results. At the other extreme the large reaction time would tend to minimize the effect of the temperature drop after injecting the slurry. The percentage of desulfurization for these three runs are shown in Table 4 along with the mean and standard deviation.

#### Sulfur Balances

A sulfur balance was completed for each run based on the weights and sulfur contents of the reactants and products. In no case was the weight of the sulfur in the products more than 0.4 grams less than the weight of the sulfur in the reactants. It is quite probable that these sulfur losses can be attributed to the volatilization of sulfur-containing compounds during the vacuum distillation. The results of the sulfur balances, expressed as percent recovery are shown in Table 5.

#### Conclusions

The following conclusions can be made from this study.

(1) The percent desulfurization of coal is a function of both time and temperature. Increasing either of these variables within the range of conditions for this study will cause the conversion to increase.

(2) The reaction rate constant appears to be a variable of conversion as well as temperature. The relationship between these variables can be adequately described by an equation of the form

$$k = k_0(1-ax)$$

where  $k_0$  and  $a$  are constants.

The general expression showing conversion as a function of time is then given by

$$\ln\left(\frac{1-x}{1-ax}\right) = k_0 t(a-1).$$

This expression represents the kinetic data taken in this study quite well.

(3) At low values of conversion the reaction rate constant shows a true Arrhenius temperature dependence. The value of the activation energy as calculated from the Arrhenius plot is 33.04 Kcal/mole.

(4) The desulfurization of coal is affected to a large extent by the nature of the coal. Even coal taken from the same sample will give large variations in the percent of desulfurization if it is not carefully mixed.

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Table 1

Proximate and Ultimate Analyses of Coal Used

Coal: Fics Mine  
Source: Kentucky  
Rank: Bituminous

(A) Runs 1-11

<u>Proximate Analysis</u>	<u>As Received</u>	<u>Dry Basis</u>
% Moisture	6.00	-
% Ash	16.20	17.20
% Volatile	32.80	34.90
% Fixed Carbon	45.00	47.90
	100.00	100.00
<u>Ultimate Analysis</u>		
% Carbon	62.90	66.90
% Hydrogen	4.60	4.89
% Nitrogen	1.10	1.17
% Sulfur	2.86	3.04
% Oxygen	11.34	6.80
% Ash	17.20	17.20
	100.00	100.00

(B) Runs 12-14

<u>Ultimate Analysis</u>		
% Carbon	64.50	65.70
% Hydrogen	4.41	4.49
% Nitrogen	1.33	1.35
% Sulfur	3.40	3.46
% Oxygen	9.56	7.90
% Ash	16.80	17.10
	100.00	100.00

(C) Runs 15-17

<u>Ultimate Analysis</u>		
% Carbon	61.00	63.50
% Hydrogen	3.88	4.04
% Nitrogen	1.34	1.39
% Sulfur	3.66	3.81
% Oxygen	11.60	7.96
% Ash	18.50	19.30
	99.98	100.00

Table 2

Run Conditions

<u>Run No.</u>	<u>Reaction Temperature (°C)</u>	<u>Reaction Time (min)</u>
1	420	120
2	420	30
3	420	60
4	360	60
5	390	240
6	360	30
7	390	120
8	360	240
9	390	30
10	390	60
11	420	240
12	360	120
13	390	60
14	420	120
15	360	30
16	360	30
17	360	30

Table 3  
 Values for the Parameters  $k_0$  and  $a$

<u>Temperature (°C)</u>	<u><math>k_0</math></u>	<u><math>a</math></u>
360	0.03544	-1.165
390	0.1166	3.373
420	0.3454	2.787

Table 4  
 Reproducibility Results

<u>Run Number</u>	<u>Percent Desulfurization</u>
15	19.42
16	21.26
17	20.21
Mean	20.30
Standard Deviation	0.92

Table 5  
 Sulfur Balance Results

<u>Run No.</u>	<u>Percent Recovery</u>
1	91
2	91
3	95
4	97
5	91
6	97
7	93
8	97
9	99
10	93
11	79
12	83
13	83
14	77
15	95
16	93
17	91

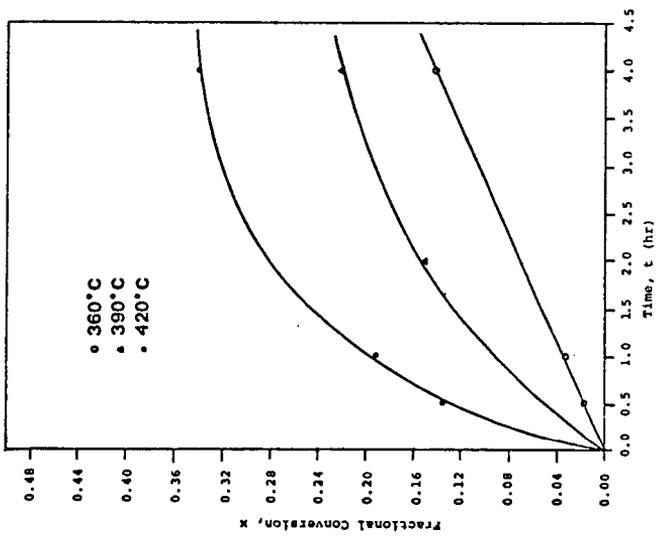


Figure 2: Fractional Conversion

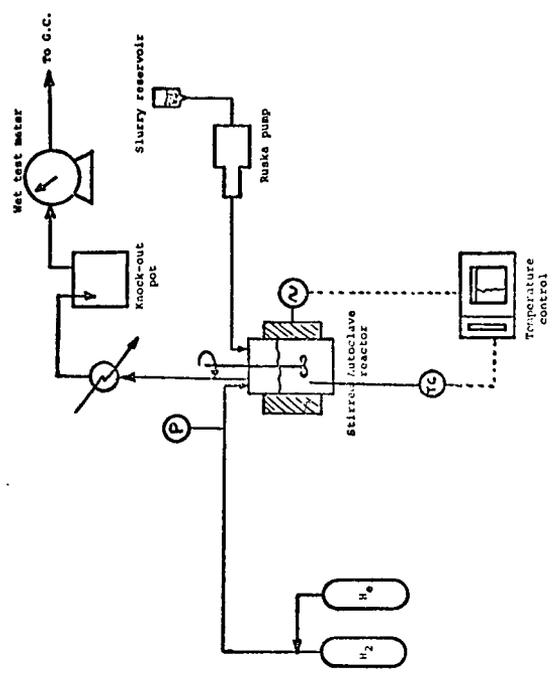


Figure 1: Experimental Apparatus

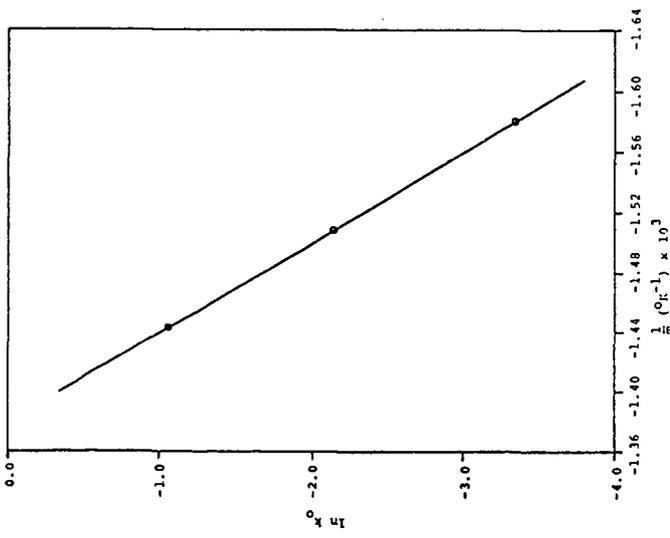


Figure 4: Arrhenius Plot

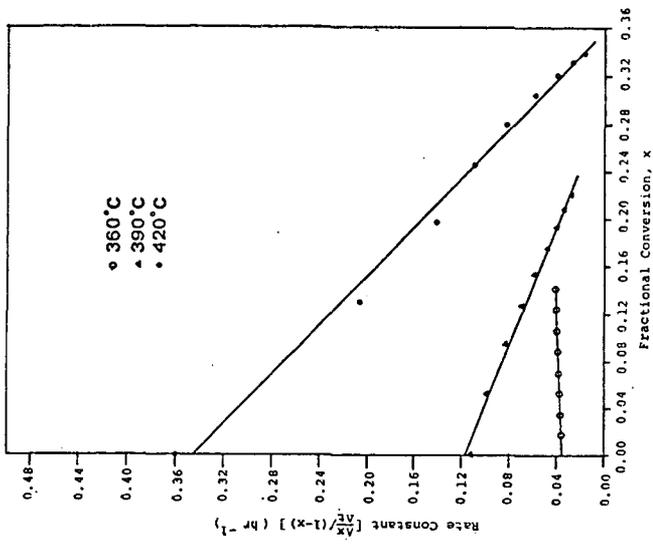


Figure 3: Rate constant vs. Fractional Conversion

## COAGULATION AND FILTRATION OF SOLIDS FROM

### LIQUEFIED COAL OF SYNTHOIL PROCESS

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#### Introduction

The idea of improving the separation of solids from coal liquefaction product by dilution with a solvent or coagulation with an antisolvent is not new. The literature on the subject is reviewed in a recent report (1)<sup>4</sup>. A patent dated 1970 suggested using a solvent such as acetone, or aromatic or aliphatic hydrocarbons (2). An earlier patent suggested adding a paraffinic liquid (anti-solvent) to precipitate benzene insolubles and asphaltenes (3). A 1972 patent described the agglomeration of solids by recycling a fraction of the coal liquefaction product (4). A 1974 patent, assigned to The Lummus Company, emphasized the use of an antisolvent with paraffinic characteristics (5). Additional information on the agglomeration and separation of solids by the Lummus process was presented in 1975 (6). Separation of the agglomerated solids is conducted by gravity settling. Deasphalting of coal extract with saturated hydrocarbons is described in (7).

The purpose of the present investigation was to coagulate the solids in liquefied coal from the SYNTHOIL process with a process-generated antisolvent and to remove the agglomerated solids by filtration rather than settling. In the SYNTHOIL process for converting coal to a nonpolluting utility fuel oil, coal is liquefied and hydrodesulfurized catalytically by reaction with hydrogen in a turbulent-flow, packed-bed reactor (8). The gross liquid product is then centrifuged, or filtered, to remove the minor amounts of residual unreacted coal and mineral matter. If a method for agglomerating the finely divided solids in the gross liquid product could be developed, the subsequent separation of solids will be easier and more complete. Such a method and the experimental data in support of it are described below. It is not yet possible to comment on the economics of the method.

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<sup>4</sup> The numbers in parentheses refer to the numbered references at the end of the text.

### Method

The method for agglomerating and separating the solids present in the gross liquid product consists of the following steps:

- (1) Prepare a blend of the gross liquid product with an accumulation of light oil derived from the SYNTHOIL process (9). The blend may contain 40 to 50 weight per cent of the gross liquid product.
- (2) Hold the blend at 105° - 115°C for 10 minutes in a vessel fitted with a reflux condenser.
- (3) Filter.
- (4) Wash the filter cake with the same light oil as used for preparing the blend.
- (5) Recover light oil from the filtrate by distillation.

In the experiments described below, product oils containing less than 0.1 per cent ash were obtained by the method and the residual oil in the solids appeared to be negligible.

### Materials and Experimental Procedure

Analyses of the gross liquid product and the light oil used in this work are given in tables 1 and 2, respectively. Although not evident from the analysis, the light oil had an ammonia odor. Using a Waring blender, mixtures of the gross liquid product and the light oil were prepared by the following techniques:

1. The components were blended for 5 minutes during which time the frictional heat raised the temperature of the mixture to 60°C.
2. The components were blended for 15 minutes during which time the mixture boiled due to the frictional heat.
3. A mixture of 80 parts by weight of the gross liquid product and 20 parts by weight of the light oil was blended for 5 minutes and then diluted to mixtures containing 10 to 50 per cent by weight of gross liquid product by shaking with calculated quantities of the light oil.
4. The diluted mixtures prepared in 3 were refluxed for 10 minutes, at 105° - 115°C.

The mixtures prepared in 1 to 4 were cooled to room temperature for filtration tests and viscosity and density determinations.

The filtration equipment, shown in figure 1, consisted of an 8 inch length of 1-3/8 inch ID steel pipe fitted with a screwed top gas and thermocouple adapter and a bottom filter assembly. The latter comprised a paper disc clamped between a 1.3 inch ID Teflon ring and a disc of 62 x 62 per inch square weave gauze on a perforated brass disc. The filter assembly was tightened with a wrench but the top assembly was only hand-tightened, enabling it to be rapidly opened, refilled, and screwed tight. The filter was clamped above a beaker mounted on a triple beam scale. For filtration rate determinations, mixtures were poured into the tube, the top assembly fitted, a constant nitrogen pressure of 25 psig applied, and the time intervals for collecting known quantities of the filtrate noted. With dilute mixtures, it was necessary to build-up filter cake to reduce the filtration rate before rate measurements could be made. Specific resistances of filter cakes were calculated by the method described by McCabe and Smith (10).

The viscosities of the mixtures and filtrates were measured on 8 ml samples with a Brookfield Synchro-Lectric model LVT viscometer in a Thermosel constant temperature unit. The spindle model was SC4 -18. The measurements were conducted at room temperature and at a high shear rate of  $79.2 \text{ sec}^{-1}$  at 60 rpm. A series of viscosity determinations on the gross liquid product over a range of shear rates at three different temperatures had shown that the apparent viscosity is very sensitive to shear rate at low values of the latter (figure 2).

### Results

The filtration rates are given as plots of reciprocal filtration rate,  $\Delta t/\Delta v$ , against average filtrate volume,  $\bar{v}$ , in figures 3, 4, and 5. Specific cake resistances calculated from the slopes of the graphs in figure 5 are given in table 3. The filtrates obtained from the experiments shown in figure 5 were analyzed for ash, organic benzene insolubles, asphaltene, and pentane-soluble oil and the concentrations of these components in light oil-free SYNTHOIL product were calculated by allowing for the known quantity of light oil in the filtrate. The calculated analysis of the recovered SYNTHOIL product is given in table 4. The viscosities of mixtures of gross liquid product and light oil, refluxed for 10 minutes, and of the filtrates obtained from them are given in table 5 and plotted logarithmically against log light oil fraction in figure 6.

### Discussion

Generally, the results suggest that the gross liquid product contains fine solids that block the capillaries of filter cakes and prevent rapid filtration. The solids are agglomerated by thermal treatment with light oil and cooling to room temperature. High concentrations of light oil give very open filter cakes capable of extremely rapid filtration rates. Addition of light oil also reduces the viscosities of the gross liquid products and filtrates.

Figure 3 shows that a 50 per cent mixture of gross liquid product in light oil prepared without sufficient heating was slow to filter. A marked improvement in filtration rate was obtained by refluxing the slurry for 10 minutes, where a specific cake resistance of  $3 \times 10^{11}$  ft/lb (2 technical units) was found. Figure

4 shows similar effects with a 20 per cent mixture of gross liquid product in light oil. Blending for 5 minutes gave a cake resistance little different from that of the shaken mixture. Blending for 15 minutes showed a marked improvement but not as great as that obtained by refluxing the mixture for 10 minutes, where a specific cake resistance of  $0.1 \times 10^{11}$  ft/lb (0.06 technical units) was attained.

Comparison of the reciprocal filtration rates of 50 per cent to 20 per cent mixtures of gross liquid product in light oil, as seen in figure 5, highlights the marked dependence of the filtration rate of refluxed mixtures on concentration. The filtration rate of the 10 per cent mixture was too rapid to measure and that of the 60 per cent mixtures was very slow. The specific cake resistances found in these tests and given in table 3 tend to a lower limit of  $0.1 \times 10^{11}$  ft/lb (0.06 technical units) at 30 per cent gross liquid product and less. The curvature of the plots for the 50 per cent and 40 per cent gross liquid product concentrations shows that, inspite of agglomeration by thermal treatment, capillary blockage did occur. Once capillaries blocked, they could not be opened by washing.

The results in table 4 show that the concentration of organic benzene insolubles in the recovered SYNTHOIL product is also markedly reduced by thermal treatment with light oil followed by filtration. The odd breakpoint in the plots of log viscosity versus log concentration of gross liquid product in mixtures shown in figure 6 could be due to precipitation of the organic benzene insolubles and larger asphaltene molecules (macromolecules) normally soluble in the products of coal liquefaction. The breakpoint occurs at about 30 per cent to 40 per cent gross liquid product concentration where there is a sharp decrease in organic benzene insolubles in the recovered SYNTHOIL product.

It should be noted that no solid filter-aids were added in these tests, the agglomerated solids acting as their own filter medium. From the electron micrographs in plates 1 and 2, the agglomerates appear to be chain-like. Many fine particles are also clearly visible.

The agglomerating action, or the antisolvent characteristics, of the light oil may be due to the saturates in it. As given in table 2, mass spectrometric analysis of the light oil showed it contained 44 per cent of  $C_5$  to  $C_{16}$  saturates.

#### Conclusions

- (1) The finely divided solids in the gross liquid product from the SYNTHOIL process are coagulated by heating a mixture of the gross liquid product and a process-derived light oil at  $105^\circ - 115^\circ C$  for 10 minutes.
- (2) The coagulated solids are amenable to rapid separation by filtration after the mixture is cooled.
- (3) The concentration of ash in the product oil is not sensitive to the concentration of the gross liquid product in the mixture (see table 4).
- (4) The filtration rate of a mixture is sensitive to the concentration of the gross liquid product in it (see table 3). The filtration rate of a mixture containing 60 per cent gross liquid product was too slow for practical purposes. The mixture must contain a minimum of 50 per cent light oil for adequate rate of filtration.

#### Acknowledgments

This work was in part supported by the British Coal Utilization Research Association Ltd. through the award of the Jack Carrington Memorial Fellowship to Mr. John O. H. Newman. The work was conducted at the facilities of the Pittsburgh Energy Research Center. The encouragement of the Center's Director, Dr. Irving Wender, is gratefully acknowledged.

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Table 1

Solvent Analysis of the Gross Liquid Product

	<u>Weight per cent</u>
Organic benzene insolubles	8.1
Asphaltene <sup>1</sup>	26.3
Oil <sup>2</sup>	61.0
Ash	4.6

<sup>1</sup> Asphaltene is soluble in benzene but insoluble in pentane.

<sup>2</sup> Oil is soluble both in benzene and pentane.

Table 2  
Analysis of Light Oil

ASTM distillation D-158

Volume per cent distilled	Temperature, °C	Volume per cent distilled	Temperature, °C
F.D. -----	78.0	60 -----	169.0
5 -----	104.5	70 -----	179.5
10 -----	113.5	80 -----	193.0
20 -----	124.0	90 -----	213.0
30 -----	134.5	95 -----	229.0
40 -----	146.5	End point -----	232.0
50 -----	158.0		
		Recovery: 96 per cent	
		Residue: 3 per cent	
		Loss: 1 per cent	

Mass spectrometric analysis

<u>Component</u>	<u>Weight per cent</u>
Saturates, C <sub>5</sub> - C <sub>16</sub> -----	44.0
Benzenes -----	21.3
Indanols and benzothiophenes -----	0.2
Phenols -----	7.9
Dihydrophenols, resorcinols, and thiophenols -----	7.1
Acenaphthenes and biphenyls -----	0.5
Naphthalenes -----	4.5
Indenes -----	1.6
Indans and tetralins -----	12.7
	99.8
Total:	

Table 3

Specific Resistances of Filter Cakes from Mixtures of Gross  
Liquid Products and Light Oil Refluxed for 10 Minutes

Gross liquid product in mixture, weight per cent	Specific cake resistance	
	ft/lb x 10 <sup>11</sup>	Technical units
10	<u>1</u> / <sub>1</sub>	<u>1</u> / <sub>1</sub>
20	0.1	0.06
30	0.1	0.07
40	0.5	0.3
50	3.2	2.0
60	<u>2</u> / <sub>2</sub>	<u>2</u> / <sub>2</sub>

1/<sub>1</sub> Filtration rate was too rapid for rate measurement.

2/<sub>2</sub> Filtration rate was too slow for rate measurement.

Table 4

Analysis of Light Oil-Free SYNTHOIL Product Recovered  
from Filtrate

(Calculated from analyses of the filtrates and  
the known quantities of light oil in them).

*Gross liquid product in mixture, weight per cent	<u>Analysis of Recovered Synthoil Product</u>			
	Ash	Organic Benzene insolubles	Asphaltene	Oil
10	0.03	0.2	27.0	72.8
20	<0.02	0.4	24.3	75.3
30	0.04	0.4	26.8	72.8
40	0.05	1.4	29.5	69.1
50	0.01	2.5	31.3	66.2

\* The mixtures were refluxed for 10 minutes.

Table 5

Viscosity of Mixtures and Filtrates  
(Mixtures refluxed for 10 minutes)

Gross liquid product in mixtures, weight per cent	Viscosity of mixture, cp	Viscosity of filtrate, cp
0 (neat light oil)	-	1.6
10	2.5	1.8
20	3.4	2.2
30	4.6	3.0
40	8.6	5.1
50	27	13
60	129	65
70	800	N. D.*
80	4,090	N. D.*

\* N. D. = Not determined

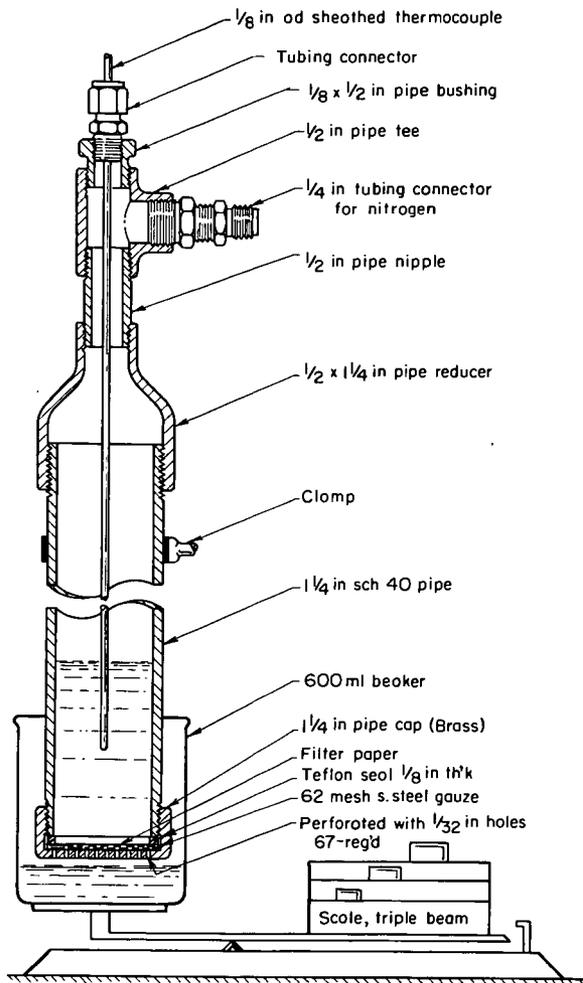


Figure 1.- Apparatus to measure filtration rates.

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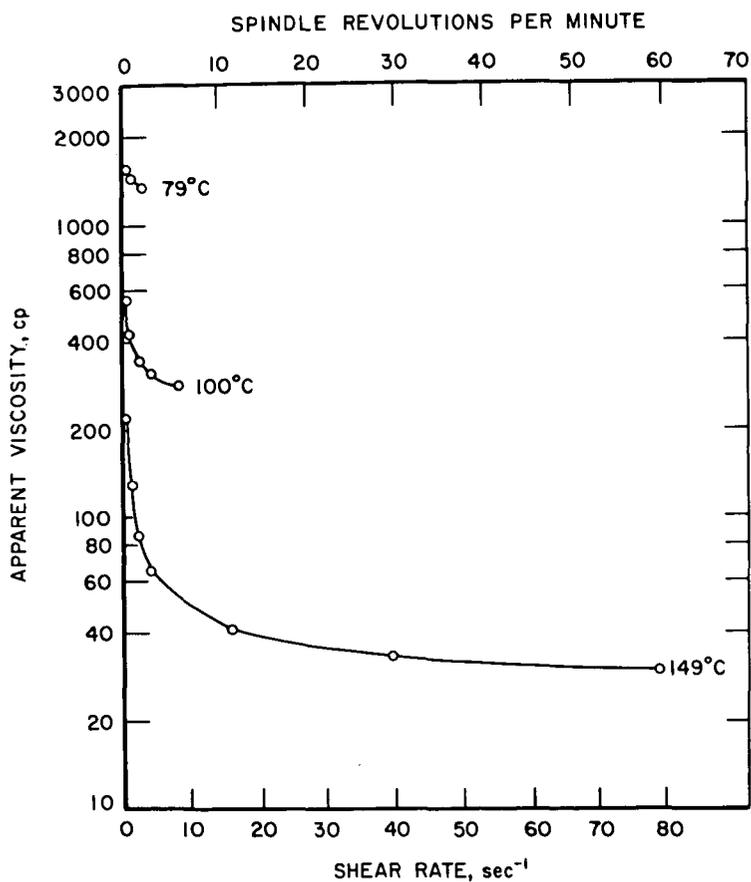


Figure 2-The effect of shear rate on apparent viscosity of gross liquid product.

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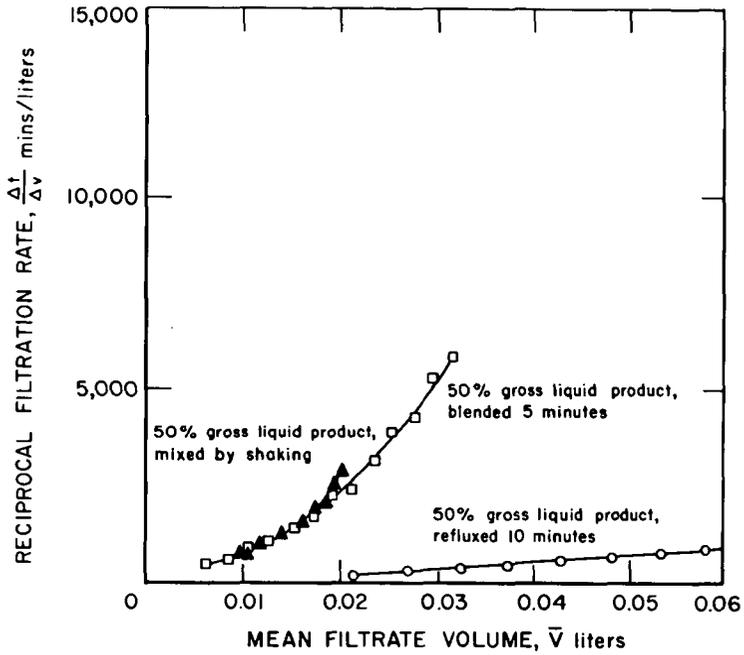


Figure 3—Dependence of reciprocal filtration rate on mixture treatment, (50% gross liquid product, 50% light oil).

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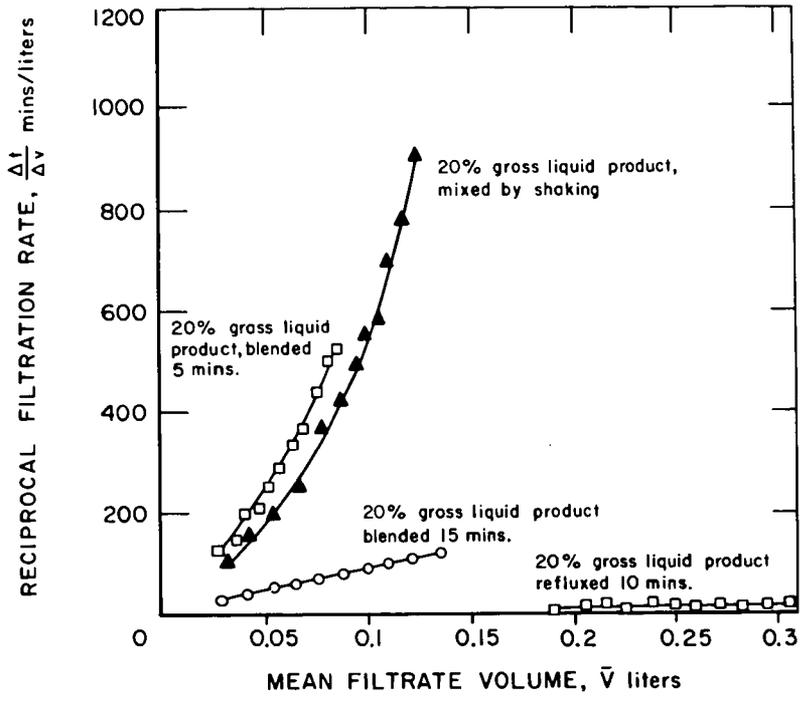


Figure 4—Dependence of reciprocal filtration rate on mixture treatment, (20% gross liquid product, 80% light oil).

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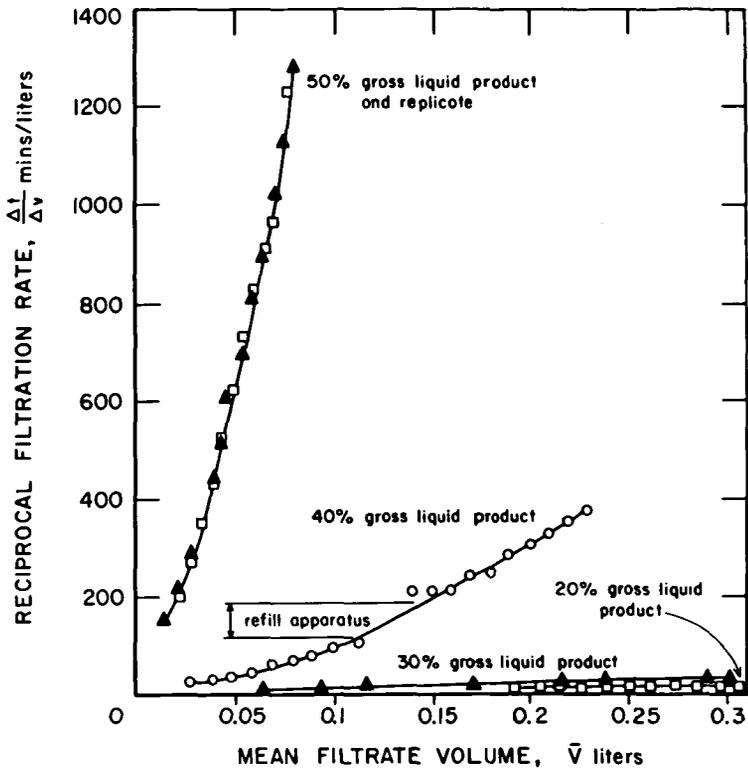


Figure 5-Dependence of reciprocal filtration rate on gross liquid product concentration in light oil (refluxed).

4/16/76 L-14805

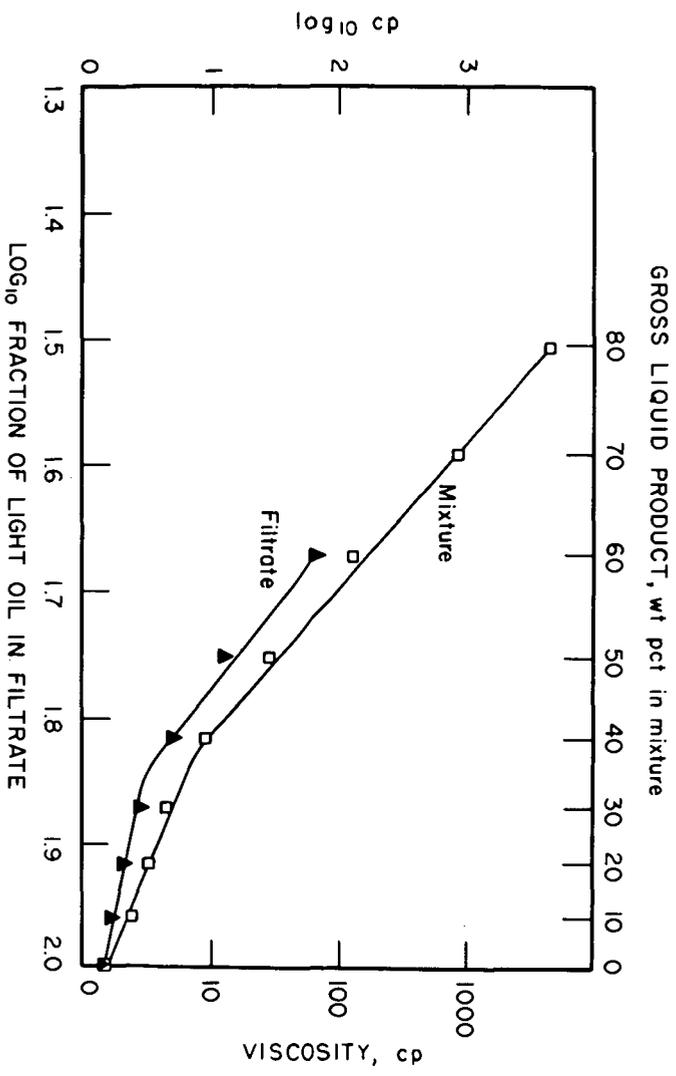


Figure 6—The effect of light oil concentration on viscosity of mixture and filtrate.

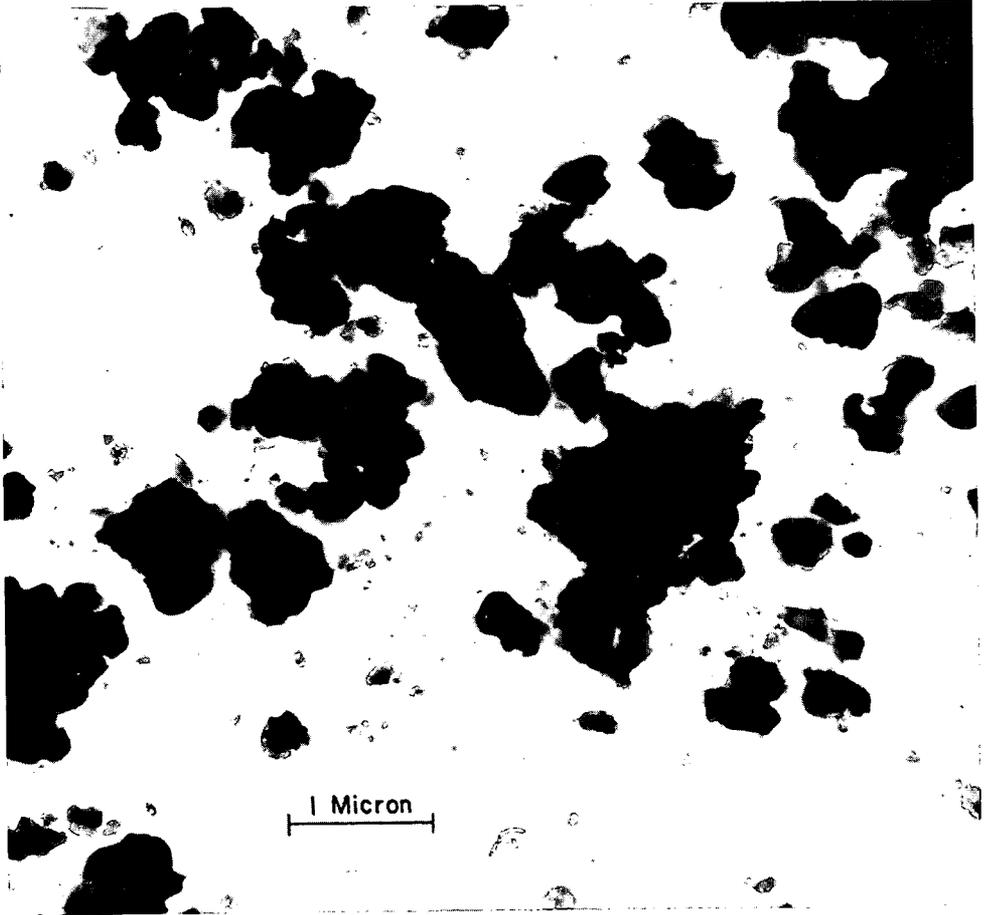


Plate I

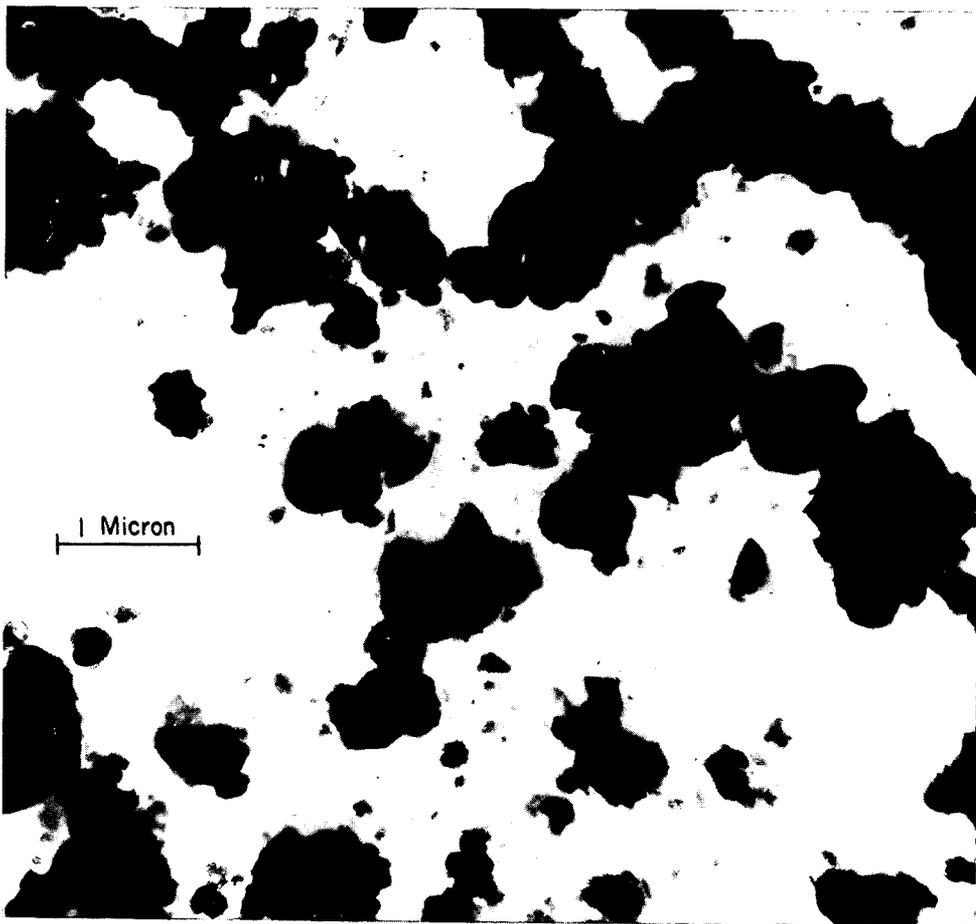


Plate 2

SHORT CONTACT TIME COAL LIQUEFACTION  
1. Techniques & Product Distributions\*

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INTRODUCTION

In our investigation of the nature and origin of asphaltenes in processed coals we have concentrated on the chemistry and kinetics of reactions accompanying the dissolution of coals. These investigations have been facilitated by the development of two new techniques for the study of coal liquefaction reactions and their products. First, we have designed and operated a 300-ml batch autoclave system capable of such rapid injection, sampling, and quenching, that contact times as short as 15 seconds can be achieved. Second, we have developed a rapid but detailed high pressure liquid chromatographic procedure for classifying coal liquid products into ten fractions of known chemical functionality.

In this report we will describe the design and operation of the short contact time reactor and show its capabilities, and the types of information we have obtained, by giving the details of several runs. We will then present some of our early key findings on the chemistry and kinetics of the solvent-refined coal process. The development and use of the fractionation procedure will be presented elsewhere (1).

The type of coal liquefaction method being studied is exemplified by the solvent-refined coal process in which a slurry of coal in a solvent derived from the coal in the process is passed through a reactor in which it is heated in the presence of  $H_2$  under conditions sufficient to liquefy the coal and partially desulfurize the products. The unreacted residue is removed and the remainder distilled to produce a variety of products, including the solvent which is recycled.

Coal Conversions: Techniques

Coal Preparations - Coals obtained for study in this project have been stored in wet lump form in an inert atmosphere. All coal preparations were conducted under a subcontract with the Department of Aerospace and Mechanical Sciences, Princeton University, project titled "Mechanisms of Coal Dissolution and Asphaltene Formation," M. Summerfield, principal investigator. Prior to grinding each sample was placed in an oven at 125°C for 1 hour in a  $CO_2$  atmosphere and allowed to cool as the oven cooled. Fragments over 0.5 cm diameter (for which it was assumed no prior oxidation had occurred) were transferred to a water-cooled rotary cutter and ground in a  $CO_2$  atmosphere for from 0.25 to 2 min. All subsequent operations (including screening and slurry formulation) were performed in an inert atmosphere.

\* This work was carried out under a jointly-sponsored contract between Mobil Research and Development Corporation and the Electric Power Research Institute, Contract #RP-410-1/2.

Portions in various size ranges were obtained by passing the coal through a series of standard screens shaken by an electric screen vibrator for 3 hours. Agglomeration was prevented by placing rubber stoppers on each screen. Size distributions were determined from the yield of coal on each screen.

The coals used in the runs described in this paper were West Kentucky 9,14 (a high volatile B bituminous coal) and Wyodak (a sub-bituminous coal). Proximate and ultimate analyses are given in Table 1. Particles ranged in size from  $\sim 1 \mu\text{m}$  to  $625 \mu\text{m}$  (the majority being  $45\text{--}150 \mu\text{m}$ ).

Conversion Apparatus and Procedure - A schematic diagram of the high pressure autoclave system is given in Figure 1. The autoclave was a conventional 300-ml stainless steel autoclave manufactured by Autoclave Engineering, Erie, Pennsylvania (#MAWP-5400) with fixed head, removable lower unit, and magnedrive stirrer; all external connections were through the head. Connections included 1/4" sample injection line, a 1/8" liquid sample withdrawal line fitted with a metal filter, and a 1/16" stainless steel shielded dual thermocouple for reading and controlling temperatures, all below the liquid level. Also attached were gas inlet and gas sampling lines above the liquid level. The stirrer drive was a Cole Palmer Constant Speed and Torque Control unit which allowed recording of motor torque during a run. The stirring blade was spiral shaped and as large as possible to produce maximum agitation; viscosity was monitored by measuring the stirrer torque. A cooling coil was mounted inside the vessel in direct contact with the contents. We have incorporated a cooling water reservoir pressured to 200 psi with  $\text{N}_2$  to give a high coolant flow rate. The injection system consisted of a barrel with a floating piston insert having "O" ring seals.

To initiate a run a small amount of solvent was pumped up into this barrel from below, then slurry was forced in from below by means of a large metal syringe, followed by a little more solvent so that no slurry remained in the valve. With this sequence solvent was injected after the slurry to flush all the coal into the vessel. Above the piston was a reservoir of squalane (easily detected by our analytical system in case leaks occurred) which was pressured with  $\text{N}_2$  just before the injection. All lines throughout the system were fitted with appropriate vents, rupture discs, drop-out pots, check valves, filters, pressure gauges, etc.

In a typical run, 60 g solvent was placed in the vessel, the unit was sealed, flushed twice with  $\text{H}_2$ , pressure-tested with  $\text{H}_2$  at the intended reaction pressure, and vented to 200 psi. Heating with an electric heater and stirring (1200 rpm) were then initiated. As the desired operating temperature was approached (typically after about 1 hr.) the injection system was sequentially loaded with 15 g solvent, 40 g 1:1 solvent coal slurry, and 5 g solvent. The time between injector loading and injection was kept as short as possible to minimize slurry settling. If the run was to be very short, the  $\text{H}_2$  pressure was increased so that the desired pressure was reached after injection, otherwise it was adjusted after injection.

When the temperature lined out  $10^\circ\text{C}$  above the desired temperature, a solvent sample was taken from the vessel to establish the pre-injection solvent composition. The injector was pressured to  $\sim 100$  psi

above the vessel and the contents forced into the vessel in about 1 sec. The temperature drop under these conditions, depending upon the temperature and the exact amounts of material in the vessel and injector, was generally 50-115°C. Recovery to the desired temperature required about .5-1 min; reaction time was assumed to start when the temperature had recovered to 10°C below the desired reaction temperature. A typical time-temperature profile is shown in Figure 2. Liquid and gas samples were occasionally taken during a run; pressure was adjusted if significant drops occurred during sampling.

To end a run, the heater was removed and simultaneously cooling water flow was started. The temperature typically dropped about 100°C within 10 sec. The temperature was adjusted to 125°C and H<sub>2</sub> was added to raise the pressure to ~1200 psi. The stirring speed was then reduced to ~10 RPM and the gas vented over a period of 5 min. through a dry ice trap into an 18 l evacuated reservoir. The trap then contained water, some solvent, and some light coal products. Water was determined volumetrically. The light components were distinguished from solvent by gas chromatography. The gas reservoir pressure was noted and a sample taken for mass spectroscopy.

The autoclave vessel was then cooled to room temperature and opened. The contents were removed and solids washed out with pyridine; solids adhering to surfaces were loosened with a brush. The mixture of solids and liquid was passed through a Soxhlet thimble; the thimble contents were washed with pyridine which was then combined with the liquid portion. The solids were then extracted with pyridine for 16 hrs. and that pyridine added to the other liquids. The residue was dried at 125°C in a vacuum oven and stored under Ar until further characterization was carried out.

The pyridine was removed from the combined liquids with a rotary evaporator. The resulting mixture of solvent, SRC, and light organic coal products was subjected to a vacuum distillation at 12 mm pressure. A first cut was taken at 130°C (true boiling point 260°C). If the solvent was our synthetic solvent, this was in the first cut; the boiling point of 2-methylnaphthalene is 240°C. A second cut was taken at 200°C (true boiling point 343°C, 650°F). The residue was the SRC. Within each distillate, product was distinguished from solvent by gas chromatography. The second cut was usually so small that it had to be removed from the condenser with THF.

The injector system was then flushed with THF to remove uninjected coal which was dried and weighed to complete the mass balance.

Temperature and pressure were recorded throughout the autoclave run on a strip chart.

All slurries for conversions were about 1:1 coal-to-solvent by weight and were made up at least 24 hrs. in advance of a run to insure equilibration.

We have recently converted to a new injection system using the same barrel but no piston. Instead, the slurry was driven directly into the autoclave with H<sub>2</sub>. Injections were found to be easier and more complete with this method. The slurry was simply poured into the injector, a solvent layer was added, pressure was applied, and the injection made. Washing was as described above.

The products of a run were separated by the work-up into the following fractions:  $H_2S$ ,  $H_2O$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $C_2-C_5$  (fully-identified by mass spec),  $C_6-257^\circ F$  (the contents of the trap, corrected for  $H_2O$  and solvent),  $6-257-650^\circ F$  (the overhead from the distillation, corrected for solvent), SRC (pyridine-soluble,  $650^\circ F^+$ ), and residue (pyridine-insoluble). Elemental analyses of the SRC and residue were determined by Galbraith Laboratories, Knoxville, Tennessee.

Synthetic Recycle Solvent - In the choice of a reaction solvent, three factors were considered. First, the coal products must be distinguishable from the solvent. Second, the solvent must have, as nearly as possible, properties similar to true recycle solvents in terms of chemical functionality, H-transfer properties, and ability to solubilize products. Third, the solvent must provide a means by which the extent of H-transfer and the occurrence of thermal or catalyzed side reactions (such as cracking and isomerization) could be evaluated.

The following synthetic solvent composition was chosen: ~2% 4-picoline; ~17% p-cresol; ~43% tetralin; ~38% 2-methylnaphthalene. This mixture has the proper amounts of basic nitrogen, phenol, and hydroaromatics. It is more aromatic and lower boiling than a real recycle solvent.

A paper is in preparation describing in detail the reactions of this solvent mixture under coal liquefaction conditions, with and without coal or coal products present. Much has been learned about the chemistry of the SRC process from this system. A brief discussion will be presented here to explain the hydrogen consumption data given in the next section.

By following the solvent composition, we can measure the thermal background reactions by observing the isomerization of tetralin to methylindane. This is not affected by the presence of coal. The hydrogen-transfer rates are affected by coal, possibly by catalysis by coal minerals. This is measured by observing the formation of methyltetralin from methylnaphthalene (by transfer from tetralin to form naphthalene). Correction can be made for the reaction in the absence of coal, either by calculations based on methylindane formation or by comparison to blank runs with solvent alone. Hydrogen consumption from the solvent by coal or its products is determined by observing the formation of naphthalene and correcting for the hydrogen only transferred to make methyltetralin, and the naphthalene produced through thermal reactions. The solvent: coal ratios are high, and temperatures and H-consumption low. Our results are therefore not affected by solvent hydrogen depletion or an approach to thermodynamic equilibria.

#### Coal Conversions: Product Distributions

Three key factors in coal liquefaction processes for which data and understanding are particularly important are: 1. the rate of conversion to soluble products and the maximum yield obtainable, 2. sulfur removal, and 3. the hydrogen consumption required to achieve a high yield of low sulfur product. [Our results on the chemical nature of the SRC's will be presented elsewhere (1).]

In order to derive the kinetics of the conversion of coal to soluble

form it is necessary to develop understanding of reactions which occur very rapidly during the initial transformations of the coal. Most commercial operations or pilot studies now being operated can provide data only of products that result from extended reactions of coal and some process optimizations may not be observable under these conditions. It has been reported (2) that coal can be dissolved rather rapidly at temperatures  $\geq 800^\circ\text{F}$ . The shortest times that were defined were 2-5 min. It was also noted that the yield of soluble product could actually decline on extended reaction at high temperature due to char formation.

The emphasis of the work described in this report was on developing understanding of the chemical nature of the initially-soluble coal products and mechanisms by which they are formed and interconverted. Our initial efforts have focused on conversion of coal under mild conditions ( $\sim 800^\circ\text{F}$ ), where the rate of formation of char is rather low. This will provide the background information needed to study coal conversion at higher temperatures (charring conditions) which is one of the objectives of future work.

A series of conversions of West Kentucky and Wyodak coals was carried out at  $800^\circ\text{F}$ , 1000-1300 psig  $\text{H}_2$  in our synthetic solvent. The balances of these runs are shown in Table 2. Product composition for these runs is summarized below.

<u>Kentucky Coal</u>					
Run No.	Ext	10.00	9.00	7.00	12.00
Time (mins.)	.00	.50	1.30	40.00	417.00
% Sol.	28.00	50.00	78.20	92.52	96.10
SRC Yield	28.00	46.80	76.10	80.11	61.05
% O SRC	9.47	6.68	7.25	5.15	2.93
% S SRC	2.17	1.51	1.40	1.31	.63
$\text{H}_2$ Consp.	.00	.13	.34	.89	1.59
<u>Wyodak Coal</u>					
Run No.	Ext	19.00	31.00		
Time (mins.)	.00	1.30	137.50		
% Sol.	11.50	45.97	91.52		
SRC Yield	11.50	38.53	70.03		
% O SRC	12.20	11.75	5.08		
% S SRC	.70	.53	.37		
$\text{H}_2$ Consp.	.00	.41	2.46		

It can be seen from the above data that conversion of the coal to  $>90\%$  soluble form occurs very rapidly (we estimate  $\sim 3$  min for West Kentucky and  $\sim 20$  min for Wyodak).

In order to achieve  $>90\%$  solubility, the oxygen content of the West Kentucky SRC had only to be reduced to about 6 wt. %. The oxygen content systematically became lower with increasing contact time and there appear to be two forms of oxygen which are kinetically distinct. One form ( $\sim 40\%$  of all the oxygen) is very readily lost. The other form requires more vigorous treatment to eliminate it. This is shown in Figure 3, where the log of the % oxygen remaining in West Kentucky coal products is plotted against time (this assumes first-order dependence).

The organic sulfur content of SRC appears to be linearly related to the oxygen content of SRC. This is shown in Figure 4. Again, 40% of the organic sulfur is easily removed, but the rest is more difficult. Thus, merely dissolving the coal is not sufficient to lower the sulfur content to acceptable levels, at least not for West Kentucky 9,14.

The nitrogen content of all SRC's was not substantially affected by solvent refining of the coal. Thus, catalytic processing may be needed to lower nitrogen content, if this is required for end use.

The time-yield behavior for Wyodak and West Kentucky coals appears to be different. There may, however, be a common feature in that the maximum yield of SRC appears to be co-incident with the minimum time required for >90% conversion to soluble form. This is illustrated in Figures 5 and 6. It can be seen that the yield of SRC from West Kentucky 9,14 coal continually drops after 5-10 min. of reaction. This loss in yield is not due to char formation, however, but is the result of converting SRC to solvent and lighter products.

As can be seen in Figure 6, one significant kinetic parameter that can be used as an alternative to time is the percent O converted to CO<sub>2</sub> and H<sub>2</sub>O. This parameter is not meaningful when comparing two different coals, however, as the amount and chemical type of oxygen can vary widely.

The hydrogen consumption observed for a given coal generally increases with increasing degree of solubilization. However, the yield of SRC vs. hydrogen consumption goes through a maximum. This is shown in Figure 7. Solvent yields become appreciable only with high hydrogen consumption and methane formation appears to be a major factor in high hydrogen consumption at high conversion levels.

Only limited data are presently available on the effect of temperature on the reaction kinetics or selectivity. This aspect of the work is presently being pursued. One comparison was made of the conversion of West Kentucky 9,14 coal at 800°F and 850°F at 30 sec contact time. The product balances are shown in Table 3.

It can be seen that even at this short contact time, major changes in the product are observed on increasing the temperature by ~50°F. The over-all conversion increased by 20% and the yield of SRC was increased by about 10%. Increased solvent range material yields were also observed. Because the oxygen conversion was still below 40%, no additional hydrogen consumption was noted.

A brief series of runs was made to examine the relative importance of H<sub>2</sub> and of solvent H-donor capacity in the early stages of liquefaction. The results are presented in Table 4. It is apparent that in the absence of H<sub>2</sub> gas, and H-donor solvent, heating the coal in pyridine to 800°F under N<sub>2</sub> pressure for either 1.3 or 60 min did not increase the pyridine solubility (Soxhlet extraction) above that observed for untreated coal. From run 18 it can be seen that the use of H<sub>2</sub> without a H-transfer agent resulted in a small increase in solubility. In Run 16 the use of a H-donor solvent without H<sub>2</sub> gave a substantial increase, approximately doubling the conversion over

extraction alone. For comparison, use of H<sub>2</sub> and H-donor gave 2.6 times the conversion.

These results suggest that in the early stages of liquefaction the availability of a H-transfer agent is the most important factor, although H<sub>2</sub> gas does have an effect. The possible importance of mass transfer of liquid solvent and product molecules to and from the reactive surface is clearly indicated. Complete liquefaction of Kentucky 9,14 coal in the absence of H<sub>2</sub> appears feasible in the presence of a good H-donor.

#### Initial Products in Solution

Information has been obtained on two additional facets of coal liquefaction: 1. the nature of the first solubilized species, and 2. the possibility of mass transport limitations on escape of the initial products from the particles.

To investigate these areas, we needed a procedure for distinguishing between coal that has been dissolved and is reacting but still remains within particles, and species that have escaped to the bulk solvent. Accordingly, we have attached a filter, below the liquid level inside the autoclave, to the liquid sampling line. We can, therefore, withdraw solution samples during a run, and these samples can contain only that portion of SRC product that is outside the coal particles. (This is also useful in scoping conversion vs. time to establish appropriate quench times for other runs.) The SRC content of these samples was determined by high pressure liquid chromatography. We used purified SRC's from previous high and low conversion runs to calibrate the system. A highly-polar solvent, pyridine, and a non-activated, trimethylsilylated silica, were used to ensure complete elution of SRC. Corrections were made for the synthetic solvent, which gives a very low response to our moving hot wire detector.

The results of run AC-31 (Wyodak coal, 800°F) are reported in Table 5. (The observations of molecular weight distribution changes as determined on these samples by gel permeation chromatography will be discussed below.)

We find that at least in the first four minutes of run AC-31 there is less SRC observed in solution than we know had been produced. In run AC-19, 1.3 min long, 38.5% of the coal was converted to SRC; after ~3 min in AC-31 only 2/3rds of this amount was observed in solution. It appears therefore that in the initial stages of the reaction a significant portion of the product remains within the coal particles. It must be pointed out that the SRC in run AC-19 was obtained after exhaustive pyridine extraction. The above conclusion is valid unless we make the unexpected finding that the synthetic solvent at 800°C is a poorer solvent for SRC than pyridine at typical extraction conditions (<100°C).

There is therefore a strong indication that even in a fast-stirred reactor with a good H-transfer solvent, there may be reactions occurring inside coal particles that could be different from those occurring outside. The results of initial studies indicate that SRC contains a bimodal molecular weight distribution. There is a high

molecular weight component (>2000 MW), or very strongly associated complexes of smaller very functional molecules, which in the early stages represent up to 40% of the product appearing in solution. The relative concentration of this material then rapidly declines, producing material in the 300-900 molecular weight range. This is shown in Figure 8. For the conversion of Wyodak coal in which the contents of the autoclave were sampled with time and analyzed by GPC, the results are shown in Table 5. These show that the absolute yield of this high molecular weight material (weight % of the coal fed) decreases throughout the run. Liquid chromatographic study of the high molecular weight material shows that it is very polar and highly functional. Furthermore, we find that the THF soluble portion of the pyridine extract of West Kentucky coal shows none of this high molecular weight material; the THF insoluble portion of the extract contains a significant amount of high molecular weight material. In addition, GPC examination of SRC's from our autoclave runs with Kentucky coal show high molecular weight material in low conversion runs, but very little in high conversion runs. The key point is that on pyridine extraction or at very low conversion, the coals show significant amounts of high molecular weight materials which are consumed rapidly on further conversion (times greater than ~3 min).

#### CONCLUSIONS AND WORK IN PROGRESS

From the data presented here we conclude that coal dissolution is very fast and requires very little hydrogen consumption. The presence of H<sub>2</sub> gas in the early stages of conversion is not critical, but a good H-donor solvent must be present. Sulfur and oxygen are removed in a kinetically-parallel fashion. About 40% of each may be removed readily and rapidly with little or no H-consumption; thereafter, considerably more hydrogen is consumed than the stoichiometry requires for the production of H<sub>2</sub>S and H<sub>2</sub>O. The initial products of coal dissolution contain significant amounts of high molecular weight material which is rapidly converted to low molecular weight products. The highest SRC yield is obtained early in the reaction process; improvement of SRC quality is accompanied by a decrease in yield and a large increase in hydrogen consumption.

Our present work includes more detailed chemical analysis of the SRC, extension of our studies to more coals and a wider range of conditions, and an investigation of possible mass transport limitations.

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#### ACKNOWLEDGEMENTS

We wish to acknowledge helpful discussions with M. Farcasiu and the experimental assistance of B. O. Heady.

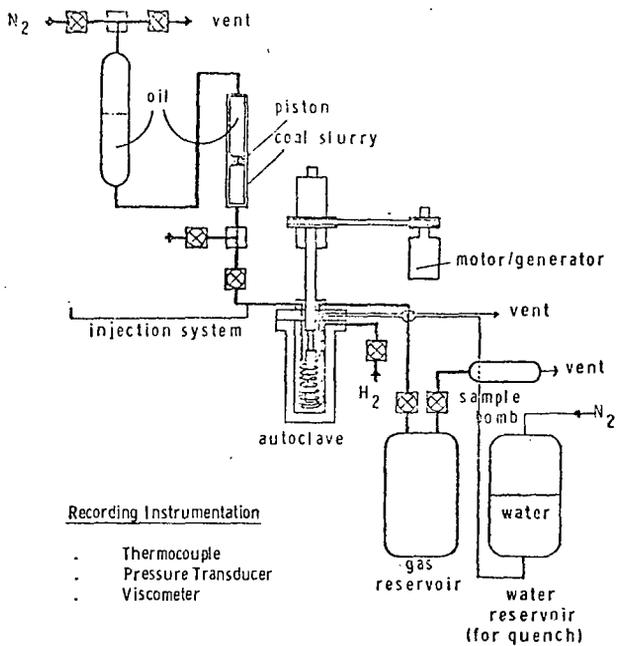


Figure 1

Figure 2

TYPICAL TIME-TEMPERATURE PROFILE

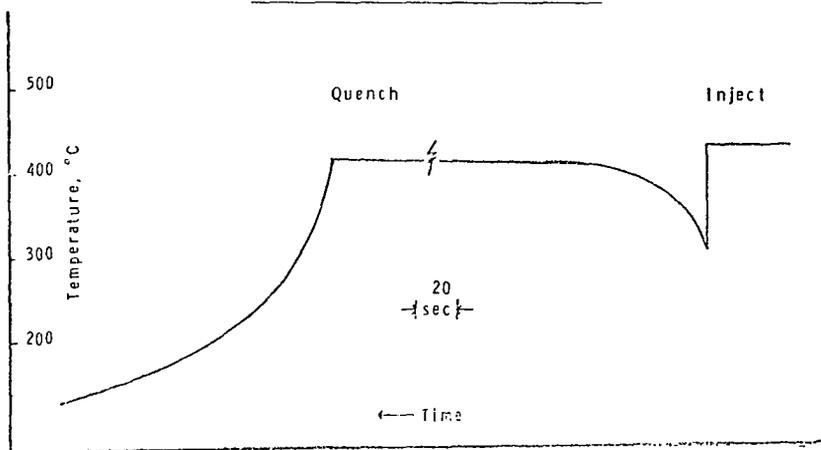


FIGURE 3

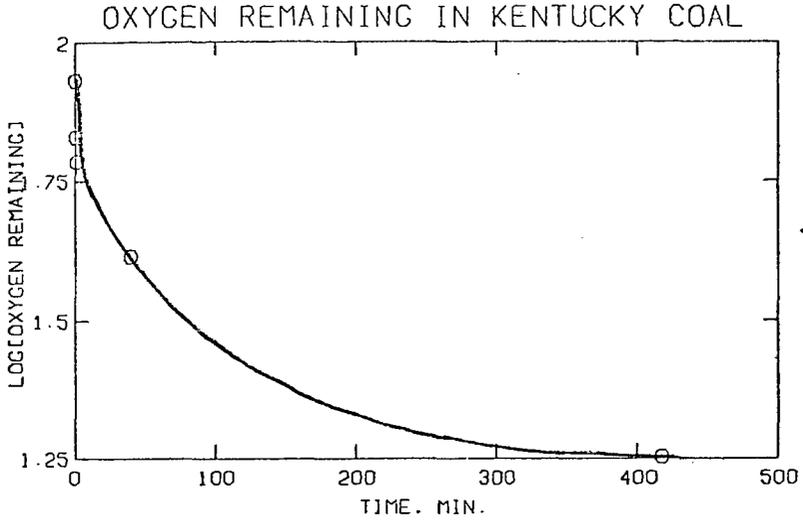


FIGURE 4

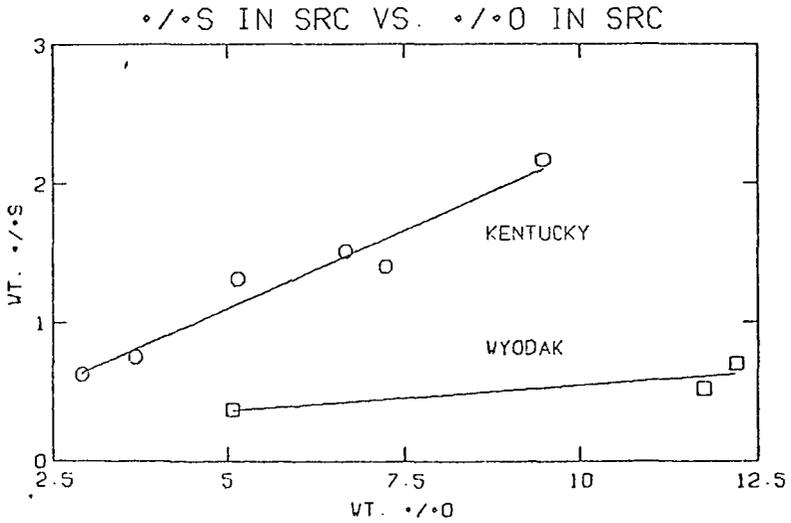


FIGURE 5

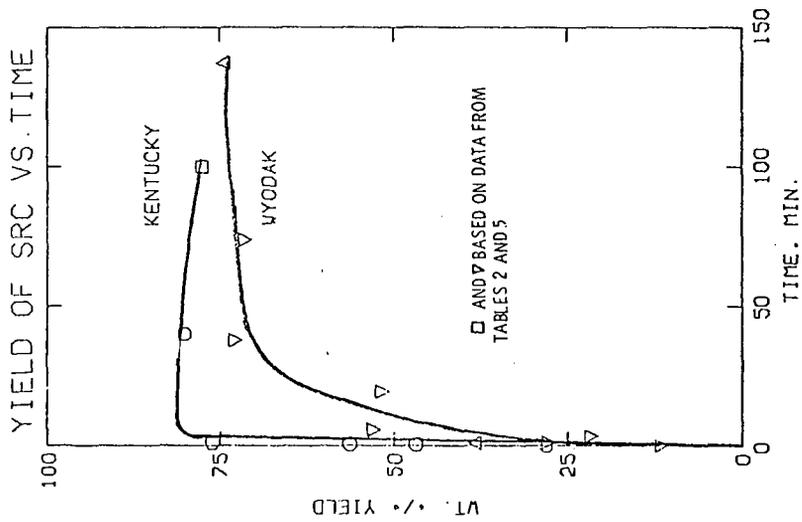


FIGURE 8

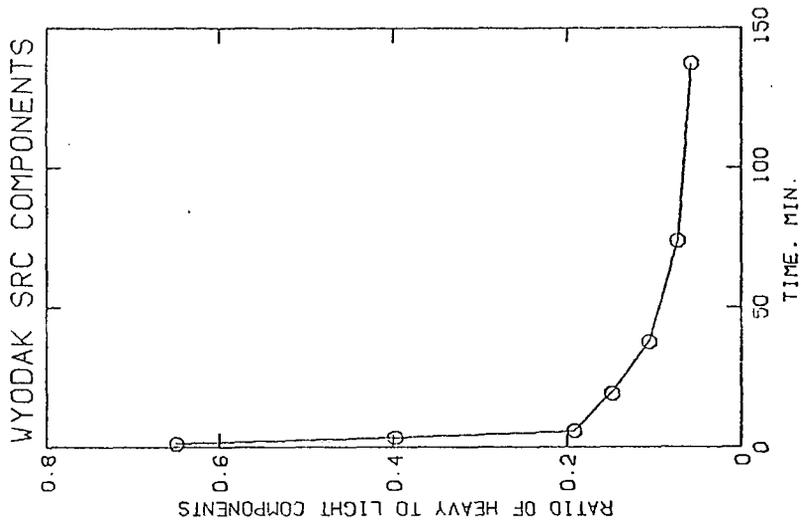


FIGURE 6

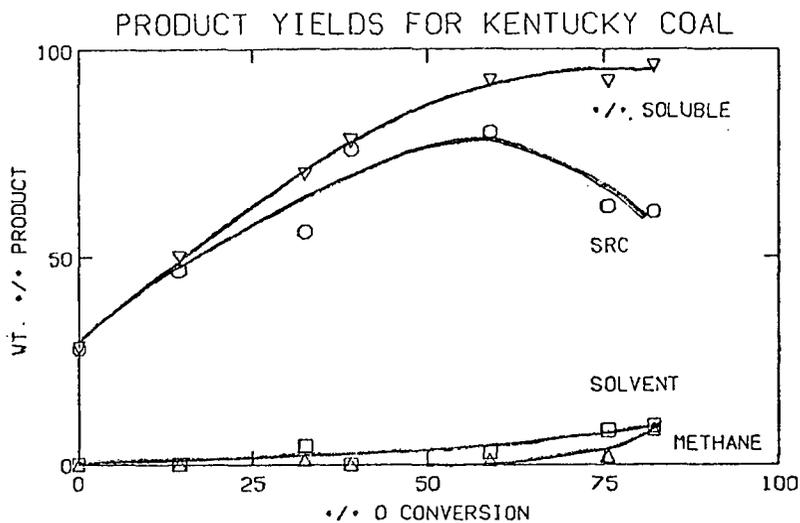


FIGURE 7

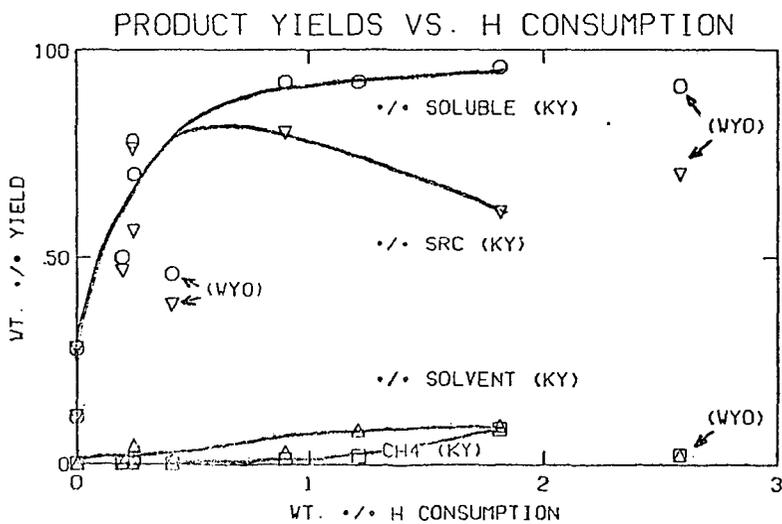


Table 1

Analyses of Coals of the Project

Name of Coal		Wyodak	W. Kentucky
State		Wyoming	Kentucky
County		Campbell	Hopkins
Seam		Anderson	9,14
Name of Mine		Bell Ayre	Colonial
% Moisture (as rec.)		22.03	6.05
% Ash (as rec.)		3.63	7.83
% Volatile Matter		47.44	36.61
% Fixed Carbon		47.90	55.06
BTU (as rec.)		9599.	12291.
BTU		12311.	13082.
Free Swelling Index		.5	4
% C		71.82	73.06
% H <sub>2</sub>		5.20	5.00
% O <sub>2</sub>		17.12	9.17
% N		.90	1.47
% S (total)		.30	2.97
% S (pyritic)		.06	1.19
% S (organic)		.23	1.36
% S (sulfate)		.01	.42
% Cl		0.0	.00
% Ash		4.66	8.33

\* All analyses, are given on a dry weight basis unless otherwise stated.

† by difference

Table 2

Run Balances for Coal Conversions at 800°F

Run Number	10.00	9.00	7.00	12.00	19.00	31.00
Solvent	Synth	Synth	Synth	Synth	Synth	Synth
Coal	WKy 14	WKy 14	WKy 14	WKy 14	Wyodak	Wyodak
Temperature, °F	800.00	800.00	798.00	800.00	806.00	800.00
Pressure, psig H <sub>2</sub>	1348.00	1300.00	1160.00	1030.00	1415.00	1072.00
Duration (feed), min.	.50	1.30	40.00	417.00	1.30	137.50
MAF Conversion, wt. %	50.00	78.20	92.52	96.10	45.97	91.52
Solvent/Coal	4.65	6.66	4.56	9.06	8.48	6.17
H <sub>2</sub> S	.24	.20	.67	.00	.01	.00
Water	4.39	3.46	4.87	5.16	4.21	4.59
CO	.10	.00	.16	.31	.28	1.28
CO <sub>2</sub>	.49	.54	.83	1.65	1.61	6.04
C <sub>1</sub>	.17	.18	1.18	8.57	.17	2.50
C <sub>2</sub> -C <sub>5</sub>	2.51	.36	1.60	8.47	.21	4.53
(C <sub>6</sub> -257°F)	.34	.14	.22	1.14	.14	.14
(257-650°F)	.00	.00	2.89	9.40	.77	2.38
SRC	46.78	76.12	80.11	61.05	38.53	70.03
MAF Residue	49.76	21.80	7.46	3.93	54.03	8.48
Balance	104.78	102.80	100.00	100.00	99.96	100.00
Ash in Residue	19.30	31.20	53.08	52.50	8.20	37.21
Duration (Solv), Min.	17.00	15.00	42.00	429.00	32.00	149.50
4-Picoline	1.90	1.90	1.87	3.20	2.01	1.28
p-Cresol	16.10	16.10	16.11	15.80	16.21	13.07
Methyl Indane	.97	.92	1.88	6.50	1.37	2.59
Tetralin	41.00	41.22	33.41	25.30	40.02	25.22
Naphthalene	2.24	2.10	8.64	14.50	2.32	18.13
Methyl Tetralin	.09	.28	1.44	4.70	.30	2.37
2-Methyl Naphthalene	37.67	37.48	36.62	29.60	37.76	37.36
H <sub>2</sub> Consumption	.13	.34	.89	1.59	.41	2.46
FOOTNOTE:	5.00		11.00	8.00		10.00

- 5) Gas analysis questionable
- 8) Piston pressure resisted syringe; balance forced to total recovered products.
- 10) Balance forced; samples removed during run.
- 11) Water content based on oxygen balance.

Table 3

The Effect of Temperature on Liquefaction of W. Kentucky Coal

Run Number	10.00	14.00
Solvent	Synth	Synth
Coal	WKy 14	WKy 14
Temperature, °F	800.00	847.00
Pressure, psig, H <sub>2</sub>	1348.00	1012.00
Duration (feed), min.	.50	.50
MAF Conversion, wt. %	50.00	70.07
H <sub>2</sub> S	.24	.10
Water	4.39	3.65
CO	.10	.21
CO <sub>2</sub>	.49	.83
C <sub>1</sub>	.17	1.25
C <sub>2</sub> -C <sub>5</sub>	2.51	2.71
(C <sub>6</sub> -257°F)	.34	.63
(257-650°F)	.00	4.38
SRC	46.78	56.31
Residue	49.76	28.93
Balance	104.78	100.00
Ash in Residue	19.30	16.93
Duration (Solv), Min.	17.00	15.00
4-Picoline	1.90	2.14
p-Cresol	16.10	16.98
Methyl Indane	.97	1.93
Tetralin	41.00	39.55
Naphthalene	2.24	1.82
Methyl Tetralin	.09	.26
2-Methyl Naphthalene	37.67	37.31
FOOTNOTE:	5.00	7.00

- 5) Gas analysis questionable  
 7) Mat bal. low; bal forced to total recovered prods; gas analysis poor

Table 5

Wyodak SRC in Solution During Run AC-31

<u>Time, Min.</u>	<u>Wt. Percent of Original Coal</u>		<u>Total</u>
	<u>Low Molecular Weight</u>	<u>High Molecular Weight</u>	
1.20	16.86	10.97	27.80
3.60	15.41	6.13	21.53
6.00	44.32	8.48	52.80
19.50	44.99	6.70	51.69
38.00	65.77	6.87	72.64
74.00	66.45	4.79	71.24
137.50	70.54	4.03	74.57

Table 4

Criticality of Solvent and Hydrogen

Run Number	16.00	9.00	17.00	12.00	7.00	3.00
Solvent	Synth	Synth	Pyrd	Pyrd	Synth	Pyrd
Coal	WKy 14	WKy 14	WKy 14	WKy 14	WKy 14	WKy 14
Temperature, °F	800.00	800.00	800.00	800.00	798.00	796.00
Pressure, psig H <sub>2</sub>	.00	1300.00	.00	809.00	1160.00	.00
Duration (feed), min.	1.28	1.30	1.28	1.18	40.00	60.00
MAF Conversion, wt. %	65.36	78.20	30.95	40.13	92.52	29.78
Solvent/Coal	5.04	6.66	5.17	5.10	4.56	5.00
H <sub>2</sub> S	1.00	.20	.00	.00	.67	.00
Water	5.28	3.46	4.75	4.59	4.87	.00
CO	.00	.00	.00	.05	.16	.00
CO <sub>2</sub>	1.90	.54	.00	.05	.83	1.40
C <sub>1</sub>	.53	.18	.00	.00	1.18	1.32
C <sub>2</sub> -C <sub>5</sub>	2.43	.36	.00	.05	1.60	2.01
(C <sub>6</sub> -257°F)	.16	.14	.11	.00	.22	.00
(257-650°F)	.58	.00	.05	.48	2.89	12.11
SRC	58.58	76.12	26.00	28.56	80.11	19.67
MAF Residue	37.35	21.80	69.05	59.87	7.46	63.49
Balance	107.81	102.80	100.00	93.65	100.00	100.00
Ash in Residue	20.63	31.20	10.97	12.30	53.08	12.02
Duration (Solv), Min.	21.00	15.00	18.00	22.00	42.00	60.00
4-Picoline	1.78	1.90	.00	.00	1.87	.00
p-Cresol	15.43	16.10	.13	.02	16.11	.00
Methyl Indane	1.79	.92	.00	.00	1.88	.00
Tetralin	38.95	41.22	.37	.25	33.41	.00
Naphthalene	2.86	2.10	.02	.00	8.64	.00
Methyl Tetralin	.12	.28	.00	.00	1.44	.00
2-Methyl Naphthalene	39.08	37.48	.27	.18	36.62	.00
H <sub>2</sub> Consumption	.29	.34	.00	.00	.89	.00
FOOTNOTE:			9.00	9.00	11.00	2.00

- 2) Balance forced; feed not injected but present during heat-up.  
 9) H<sub>2</sub>O assumed to force balance 17; same H<sub>2</sub>O amount assumed for 18.  
 11) H<sub>2</sub> content based on oxygen balance.

HIGH PRESSURE LIQUID CHROMATOGRAPHIC  
STUDIES OF COAL LIQUEFACTION KINETICS

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Introduction

A major obstacle to the advancement of coal conversion technology has been the lack of effective means for analyzing the highly complex mixtures occurring in coal conversion processes. High pressure liquid chromatography (HPLC) is a recently developed analytical tool that typically provides rapid, reproducible analysis of complex systems (1,2). Using HPLC, preparatory experiments can be performed to separate 50-100 mg samples of relatively pure compounds from a complex mixture - allowing subsequent positive identification of the compounds by other means such as infrared or ultraviolet spectroscopy, and melting point. This asset of HPLC (ie., preparatory scale chromatography) is one of the main advantages that it offers over comparable analytical methods. Because HPLC does offer positive identification of individual species, it is a very effective tool for characterizing and quantifying process streams in coal liquefaction processes, and provides a means for developing a more fundamental understanding of such processes.

The present work demonstrates the feasibility of employing HPLC to characterize creosote oil, a coal-derived liquid used as a start up solvent in coal liquefaction processes such as the Solvent Refined Coal (SRC) process. Characterization of the creosote oil is done by HPLC during hydrogenation/hydrodesulfurization of the oil; and is then used to follow the catalytic effects of a commercial Co-Mo-Al catalyst; a coal mineral, iron pyrite; coal ash; and actual SRC mineral residue from the Wilsonville pilot plant. Each of these agents has a significant effect on the hydrogenation and, except for pyrite, on the hydrodesulfurization of creosote oil under conditions similar to those in the SRC process. Evidence that coal minerals have a catalytic effect on hydrogenation of coal has been reported (3,4). However, specifically which compounds in recycle or process solvent are most

affected by hydrogenation in the presence of coal minerals has not been previously studied. Also the effect of coal mineral catalysis on rate of removal of various heteroatom compounds - particularly sulfur bearing compounds such as dibenzothiophene - has not been studied. HPLC provides a tool for monitoring changes in major constituents of coal-derived liquids during hydrogenation/hydrodesulfurization, and can be used to study the selectivity of catalytic agents for accelerating reactions involving specific species of coal-derived liquids - as is demonstrated here.

### Experimental

Apparatus. A Model ALC/GPC-201 high speed liquid chromatograph (Waters Associates, Milford, Mass.) was used throughout this study. The following accessory hardware was used: a Model 6000 solvent delivery system, a Model 660 solvent programmer, and a Model U6K injection system. In addition, a Model GM77 UV/VIS detector (Schoeffel Instrument Corporation, Westwood, N.J.) was used; this detector was chosen because it has a continuously variable UV source. After thorough exploratory studies, a wavelength setting for the detector of 232 nm was found to provide the best overall sensitivity and stability for detection; this setting was used throughout the study.

Reagents. The acetonitrile used in this study was of spectroquality. The creosote oil was obtained from Southern Services, Inc., at the SRC pilot plant located at Wilsonville, Alabama. Southern Services, Inc., obtained the oil, creosote oil 24-CB, from the Allied Chemical Company. The oil has a boiling point range of 175° to 400°C and a specific gravity of 1.096 at 20°C. Hydrogen was obtained from Linde Hydrogen in 6000 psi grade, with a purity of 99.995%.

A commercial Co-Mo-Al catalyst (Comox-451) was obtained from W. R. Grace and Company, Davidson Chemical Division, Baltimore, Maryland. This catalyst is commercially produced by Laporte Industries of England. Our analysis of the catalyst showed that it consists of 3.7% CoO and 12.8% MoO<sub>3</sub>, and the catalyst was specified by the manufacturer to have a surface area of 300 m<sup>2</sup>/g and a total pore volume of 0.66 ml/g. The pyrite used in these experiments was obtained from Matheson Coleman and Bell Chemical Company, Norwood, Ohio. Our analysis of the pyrite showed that it was 90-95% pure, the difference being primarily silica. Coal ash was obtained by burning a mixture of Kentucky No. 9/14 coal mixture (7.2% ash) in a muffle furnace at 1000°C. Analysis of the ash gave an iron content of 13.7%. SRC solids were obtained from the filter cake from the Wilsonville, Alabama SRC Pilot Plant. Analysis of the material gave an ash content of 55.2% and a sulfur content of 13.6%. The reported analysis of this material showed that it was 30% filter aid (diatomaceous earth) (5). All materials were ground and screened; and only -325 mesh (45 micron) size material was used.

High Pressure Liquid Chromatography. Two 4mm (ID) X 30 cm microbondapak/C<sub>18</sub> columns (Waters Associates, Milford, Mass.) were used in series for separation of the creosote oil components. The mobile phase was a 45:55 volume-to-volume acetonitrile-water mixture. The

flow rate was nonlinearly (curve 8 on the 660 solvent programmer) programmed to increase from 0.6 to 0.8 ml/min in 1.5 hours in such a way that the major portion of the increase takes place in the last 45 minutes of the program. This allows for the most efficient use of the time necessary for elution by minimizing dead-time and axial diffusion - while keeping resolution at a maximum during the initial portion of the separation. System pressure was kept below a maximum of 2200 psi.

The sample was dissolved in pure acetonitrile (4mg/ml) prior to injection, and normally about 10  $\mu$ l of the resulting solution was injected for analysis. Retention times ranged from as short as a few minutes for the more polar compounds to as much as several hours for the more nonpolar compounds, which are typically the higher molecular weight constituents.

Procedure. Creosote oil was treated for two hours at 425°C under an initial pressure of 3000 psig of hydrogen, in the presence of 13% by weight of either Co-Mo-Al catalyst, iron pyrite, coal ash, or SRC solids. Treatment was also made without any catalytic agents present. The reaction mixtures were stirred continuously at 2000 rpm in a batch autoclave (Autoclave Engineers, Erie, PA.). After two hours of reaction, samples of the partially hydrogenated and hydrodesulfurized oil were taken. Then, aliquot amounts of these samples were dissolved in acetonitrile (4mg/ml), filtered through 0.5 $\mu$  filters (Millipore Inter-tech, Inc., Bradford, MA.) to remove any solids; and after filtration, 10 $\mu$ l portions of the filtrate were analyzed by HPLC. To eliminate unavoidable variations due to differences in the amount of sample injected, benzofuran was used as an internal standard.

Computer Deconvolution. As is seen in Figure 1 the chromatograms obtained in this work gave peaks that seldom had base-line resolution - a common problem in chromatography - and, to be accurate, it was necessary to deconvolute the chromatograms. To this end, a specialized computer program was developed (6) based on the method of Marquardt (7).

### Results and Discussion.

Typical chromatograms of the product from the various treatments of the creosote oil are shown in Figure 1. Good separation of the multicomponent system was obtained by varying the acetonitrile/water ratio in the eluting solvent: the best resolution resulted with a 45:55 volume-to-volume acetonitrile-water mixture. Preparatory scale columns were used to obtain sufficient amounts of twelve major constituents to permit their positive identification by infrared spectroscopy. These major constituents, which compose 50.3% by weight of the original creosote oil, were of interest in this preliminary work (Table 1).

The components fall into basically two categories: polynuclear aromatics and heteroatom compounds. Compounds of the first type -

namely, naphthalene, acenaphthene, phenanthrene, and anthracene - are angular polycyclic aromatics. These compounds, and compounds like them, are considered to play an important role in hydrogen transfer reactions occurring during coal liquefaction, e.g. as in the SRC process (8,9,10). Compounds of the second type - namely, dibenzothiophene, carbazole and naphthonitrile - are of interest because these constituents, during combustion of coal, form pollutants, SO<sub>2</sub> and NO<sub>x</sub>. Determination of the degree to which these constituents are removed with processing is therefore most important for process analysis.

The results from this work and those from previous analysis using gas chromatography are compared in Table 2. In evaluating this comparison, it should be noted that the creosote oil is somewhat unstable: after standing for long periods of time (several months) some constituents do indeed precipitate from solution. For this reason some discrepancies exist between our gas chromatographic analysis, that performed by Allied Chemical Company, and that performed by Southern Services.

Table 1 lists the analysis of the creosote oil after the various treatments. Obviously, hydrogenation and hydrodesulfurization of the creosote oil at 425°C in the presence of an initial hydrogen partial pressure of 3000 psig causes a significant decrease (20%) in percent by weight of the analyzed components. Currently, preparatory scale work is in progress to determine what compounds are produced by this treatment. In the presence of the various catalytic agents, even more reduction (34%, when pyrite is present, to 49%, when actual SRC mineral residue is present, as compared to 20%, when no catalyst is present) in the weight percent of the analyzed components results during hydrogenation of the oil. Apparently then, these agents (Co-Mo-Al, pyrite, coal ash, and SRC mineral residue) do indeed catalyze hydrogenation of the oil, and the increase in hydrogen consumption observed when they are present is, in fact, due to greater hydrogenation of the oil, rather than reduction of the agent, itself, with hydrogen to produce a reduced form of the agent, water, hydrogen sulfide, etc.

As shown in Table 1, HPLC offers sufficient specificity to detect differences in the final concentration of major constituents of the oil when hydrogenated in the presence of the different catalytic agents. For example: Assuming that the disappearance of the major constituents is due to hydrogenation, then Co-Mo-Al, coal ash, and SRC mineral residue show a decisive preference for accelerating hydrogenation of naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene; whereas pyrite favors hydrogenation of acenaphthene and, to a lesser extent, anthracene. Also, in the presence of commercial Co-Mo-Al catalyst, the concentration of dibenzothiophene, a major organic sulfur component, is reduced to a much greater extent than when the other catalysts were present. In fact, the concentration of dibenzothiophene was reduced essentially to zero when Co-Mo-Al was present. Since Co-Mo-Al is an excellent catalyst for hydrodesulfurization reactions, these results are not surprising. Most interestingly, however, the trend in dibenzothiophene removal is

exactly the same as that found by analysis of total sulfur (4): namely, Co-Mo-Al >> coal ash > SRC mineral residue > pyrite > H<sub>2</sub> only. Carbazole, on the other hand, has essentially the same concentration as that in the original oil, despite the catalyst used; whereas the naphthonitriles are completely removed when either Co-Mo-Al, coal ash, or SRC mineral residue is present.

### Conclusions

The HPLC procedure described here permits analysis of major constituents of creosote oil in about two hours. No extensive sample preparation is required; and the method is quantitative - the results comparing well with those obtained using gas chromatography. Using preparatory chromatography, samples of essentially pure compounds can be separated from creosote oil and positively identified by subsequent analysis. As a result, with HPLC neither tentative identification as, for example, by "spiking" - i.e. addition of known compounds to the mixture so as to determine the peaks in the chromatogram of the mixture caused by different constituents - nor an expensive, sophisticated gas-chromatograph/mass-spectrometer system are required. Hence HPLC offers a simple and powerful technique for analysis of complex mixtures like creosote oil.

### Acknowledgments

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TABLE 1  
HPLC Analysis of Treated Creosote Oil

Compound	Wt. %					
	A	B	C	D	E	F
1 and 2-naphthanitrile	0.611	0.458	0.243	trace	0.046	trace
carbazole	0.423	0.386	0.418	0.386	0.443	0.526
naphthalene	8.92	7.49	6.55	4.16	4.01	4.17
2-methylcarbazole	0.106	0.084	0.059	0.067	0.102	trace
1-methylnaphthalene	5.23	4.56	3.14	3.13	2.33	2.08
2-methylnaphthalene	8.00	6.21	7.63	5.42	4.61	4.37
acenaphthene	6.28	4.15	1.56	2.38	2.24	2.08
fluorene	5.22	5.02	3.78	3.62	3.64	4.55
dibenzothiophene	1.27	0.888	0.720	trace	0.576	0.622
phenanthrene	12.4	9.10	7.95	8.05	7.11	5.96
anthracene	1.86	1.88	1.31	2.17	1.50	1.53
Total	50.32	40.23	33.36	29.39	26.61	25.89

- A - original oil
- B - oil heated with hydrogen, no catalyst
- C - oil heated with hydrogen and pyrite
- D - oil heated with hydrogen and cobalt molybdate
- E - oil heated with hydrogen and coal ash
- F - oil heated with hydrogen and SRC solids

Three runs were made for each treatment with a relative standard deviation between runs of 8% of the determined mean weight per cent.

TABLE 2

## Comparison of Creosote Oil Analyses

Compound	Wt. %			
	A	B	C	D
1 and 2-naphthonitrile	0.32	-	0.61	-
carbazole	2.2	-	0.42	-
naphthalene	5.1	9.08	8.92	10.0
2-methylcarbazole	1.7	-	0.11	-
1-methylnaphthalene	0.38	3.55	5.23	3.0
2-methylnaphthalene	1.3	10.2	8.00	8.0
acenaphthene	6.0	9.73	6.28	5.0
fluorene	10.3	5.54	5.22	5.0
dibenzothiophene	0.52	0.94	1.01	-
phenanthrene	18.6	17.92 <sup>a</sup>	12.45	17.0 <sup>a</sup>
anthracene	4.3		1.86	

A - Allied Chemical Company by gas chromatography  
 B - Southern Services by gas chromatography (ASTM D2887)  
 C - Auburn University by HPLC  
 D - Auburn University by gas chromatography

a - includes both phenanthrene and anthracene

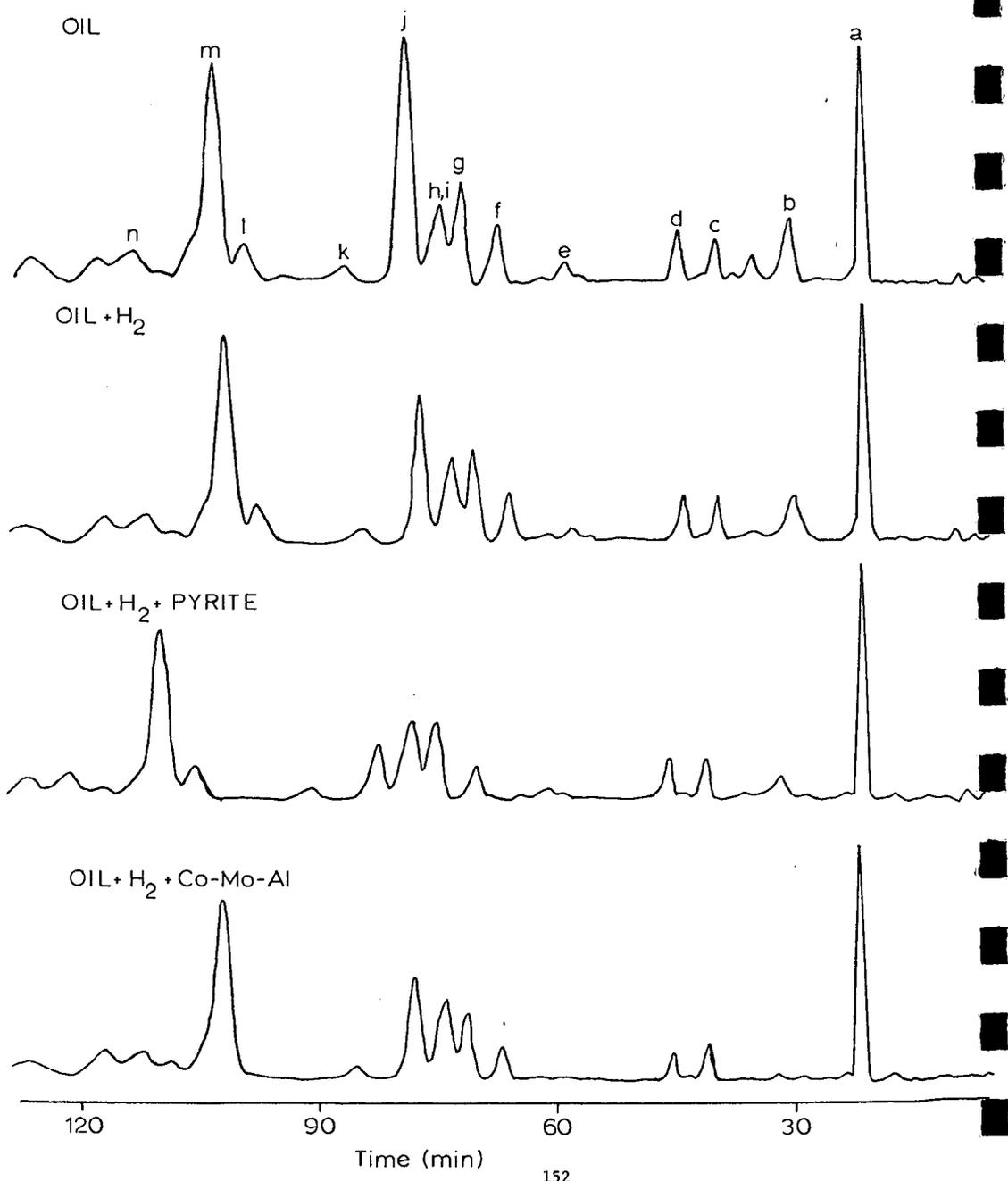


Figure 1

Chromatograms of creosote oil which show the effect of the various treatments. Positively identified components in order of elution are:

- a. internal standard (benzofuran)
- b. 1 and 2-naphthonitrile
- c. carbazole
- d. naphthalene
- e. 2-methylcarbazole
- f. 1-methylnaphthalene
- g. 2-methylnaphthalene
- h. dibenzofuran
- i. biphenyl
- j. acenaphthene
- k. fluorene
- l. dibenzothiophene
- m. phenanthrene
- n. anthracene

## SHORT RESIDENCE TIME (SRT) COAL HYDROLYSIS

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### INTRODUCTION:

For the last two years, Cities Service R & D has been investigating the Short Residence Time (SRT) Hydrolysis Process which noncatalytically hydrogenates dry coal to produce directly, in a one-step process, light aromatic liquids (essentially benzene), and high Btu gas ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ )<sup>(1)</sup>. In addition, heteroatoms in the coal are removed as  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_x$ . The product char can be used to produce make-up hydrogen or hydrogasified further in another reactor to make additional high Btu gas.

A continuous, bench-scale unit to process 1 to 2 lb/hr. coal has been constructed at the CSR&D laboratories in Cranbury, N.J., and has been in operation since the summer of 1975. Coal conversions of the order of 50-80 wt.% MAF coal have been routinely attained with a light aromatics yield of the order of 12-16 wt.% MAF coal and a gas yield ( $\text{C}_1 + \text{C}_2$  and  $\text{CO}$ ) of the order of 34-68 wt.% MAF Coal.

### EXPERIMENTAL PROGRAM:

The Cities Service program was as follows:

1. Design, construct and operate a 2 lb/hr. experimental unit.
2. Perform cold flow model studies to determine optimum nozzle designs.
3. Derive mathematical models to predict experimental results.
4. Identify scaleable coal feeder designs.
5. Define metallurgical requirements.

A relatively simple free-fall, dilute phase reactor system was designed to utilize as simple an apparatus as possible to prove or disprove the intrinsic chemistry for producing light aromatics directly from coal. Operation of the unit has demonstrated that coal can be converted directly to light aromatic liquids without the intermediate production of high boiling tars.

The bench-scale unit, as designed, is also being utilized to carry out the following objectives:

1. Determination of the role of major process variables on conversion and selectivity.
2. Development of commercially scaleable equipment necessary for the successful operation of an SRT Hydropyrolysis unit.
3. Development of a simple, working kinetic model of SRT Hydropyrolysis experimental data.
4. Determination of the critical scaleup parameters and their effect on product yields and selectivities.

The unit is performing essentially trouble-free and is giving the necessary smooth operation required to perform process variable studies. About three dozen runs each of four to five hours duration have been completed.

#### DESCRIPTION:

Figure 1 is a schematic of the bench scale unit. Hydrogen is supplied from a tube trailer to a diaphragm compressor capable of recompressing the hydrogen to 3000 psi. The hydrogen is then metered to the controller valves which control the flow of hydrogen to the preheater and to the quench cooler. These hydrogen streams then enter the reactor assembly as indicated in the schematic. Dried, pulverized coal is fed batchwise to a hopper which is then pressurized to reactor pressure with hydrogen. A star-wheel feeder then delivers the coal through a standpipe into the reactor. The coal then mixes with the hydrogen, which has been heated to the approximate reaction temperatures desired. The mixing occurs in a manner formulated to achieve very high heating rates of the coal which is necessary for a high degree of coal conversion. The coal then falls in free-fall through the four-foot reactor pipe into the char pot devolatilizing as it traverses the reactor. The temperature-time history of the coal is controlled by the introduction of a cold quenching medium (cryogenically cooled hydrogen) through a variable length probe within the reactor. The variable length probe allows for the change in reactor length easily thus providing the mechanism for varying residence time without changing the reactor. The entire reactor is immersed in an adiabatic enclosure (electrical furnace). The resultant quenched hydrogen-product gas mixture exits the char pot at a temperature between 440-880°F which is below the reaction temperature of the product stream. The residual char remains in the char pot until removal at the completion of a run. The hydrogen-product gas stream then passes through three stages of indirect heat exchange where the liquid products are sequentially condensed from the hydrogen stream. Condensation temperature can be controlled between -200°F and +200°F by the use of suitable coolants. The non-condensable hydrogen stream is then depressured, metered, analyzed by gas chromatography and then vented to the atmosphere.

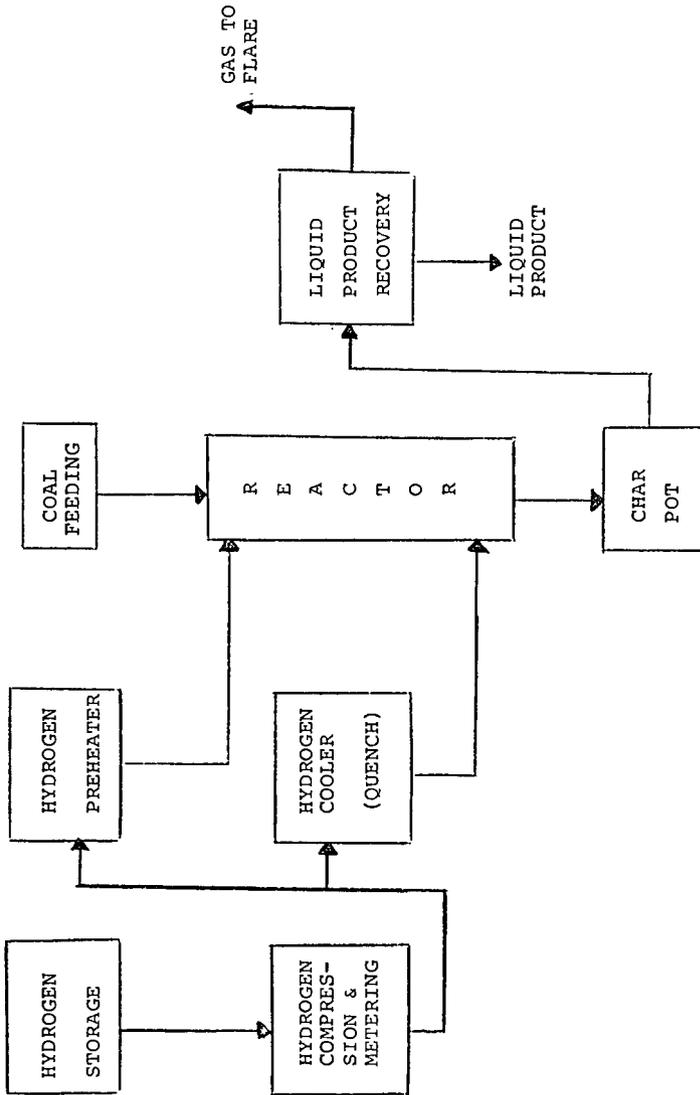


FIGURE 1: SCHEMATIC OF CITIES' COAL LIQUEFACTION 2 LB/HR. UNIT

Figure 2 is a schematic of the reaction section. It shows the coal hopper delivering coal to a star-wheel feeder similar in design to one that has been used for a number of years by the Pittsburgh Energy Research Center. The coal flows from the star-feeder into the reactor in which hot hydrogen is made to intimately mix with the cold coal. The coal then free-falls through the reactor into the char pot where the products are separated from the char by the use of a simple filter. The reactor contains a variable length quench probe which has been perfected by Cities Service and allows for the residence time to be explicitly defined by moving the probe to varying lengths within the reactor. For the initial studies, hydrogen was used as a quench medium because it did not complicate the analysis of the products.

Table 1 shows the range of operating conditions studied using North Dakota lignite. Although Western Kentucky bituminous coal has been run, this paper will be confined to discussions on lignite. The Table shows coal has been run continuously from 1.25-8.0 hours. Most of the runs, however, have been in the 4-5 hour range. The reactor temperatures were varied from 1150° to 1575°F average hydrogen-coal temperatures. This reactor temperature was indirectly measured from the skin temperature of the reactor by using a mathematical model generated by Cities Service. The residence time has been varied from 100-3000 milliseconds by the use of this variable length quench probe. One of the more critical parameters on this Table is heatup rate; this parameter has been varied from 50,000-150,000F°/sec.

Table 2 is the analysis of the lignite that was used. The coal was dried to 3% moisture before it was used in the experiment. Table 3 shows the range of conversion and yields obtained using North Dakota lignite. Carbon conversion of 80% have been achieved and the liquid yields have been as high as 16 wt.% based on moisture and ash free coal. This liquid is essentially 94% pure benzene with smaller amounts of naphthalene and anthracene. Above about a 1200°F reactor temperature, only light aromatic liquids are produced. The gas produced is essentially composed of methane and ethane. These products are identified by using a gas chromatographic system designed so that a thermal conductivity detector is in series with the flame detector. Using this system, carbon balances are calculated.

The following are the pilot plant achievements to date:

1. Continuous, steady-state operation with coal feeding for 8.0 hours.
2. No pressure drop buildup in nozzles, reactors or recovery system.
3. Preheating, reacting and quenching of coal--hydrogen mixtures at total residence times of less than one second.
4. Coal heatup rates of the order of 50,000-100,000F°/sec.
5. Quenching of reaction products within reactor vessel.
6. No tar formation with principal hydrocarbon products being benzene, methane, ethane.
7. Exceeded Fisher assay coal and carbon conversions at all three operating severities.

REACTION SECTION

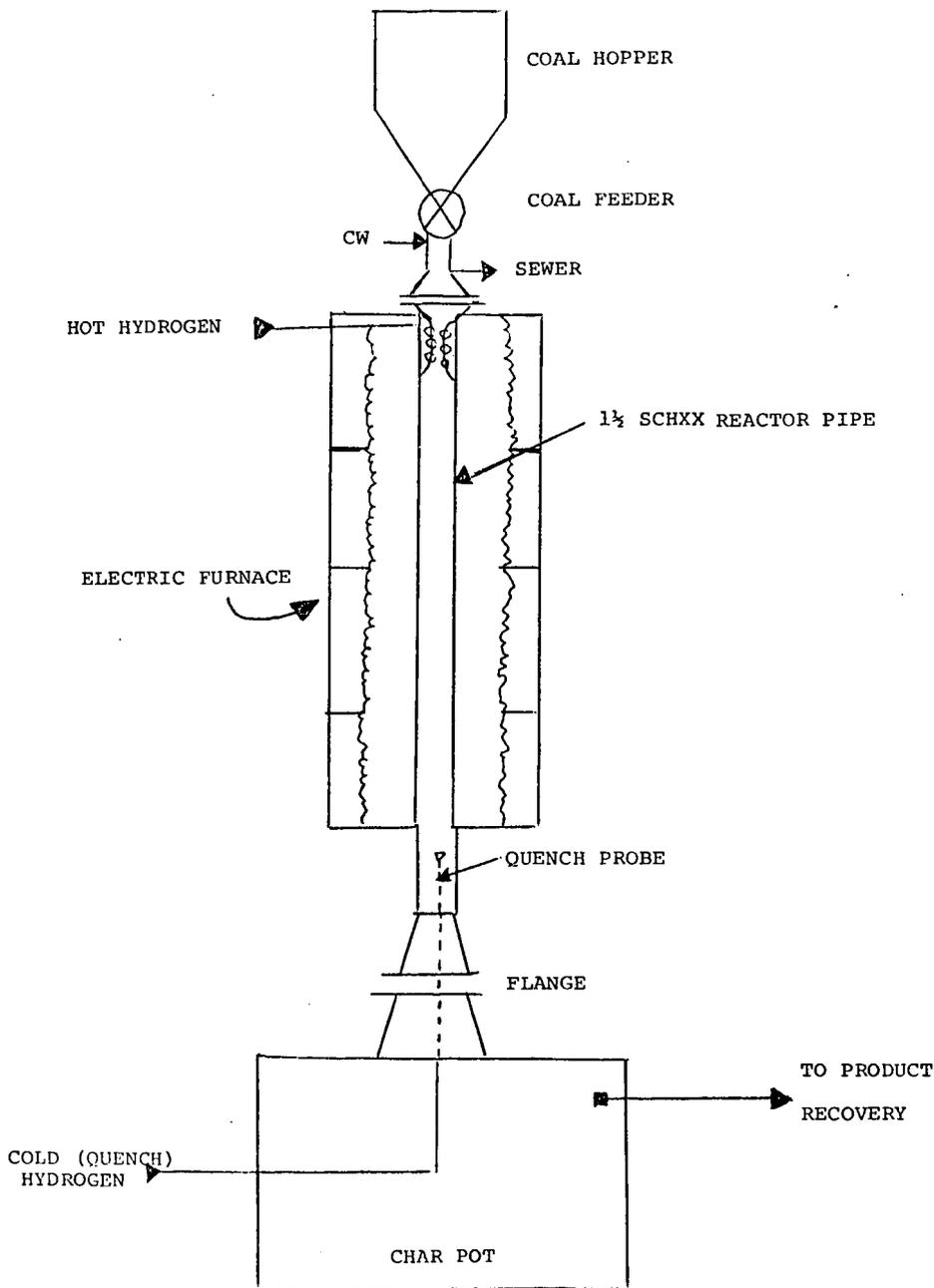


FIGURE 2 158

TABLE 1

RANGE OF OPERATING CONDITIONS STUDIED

NORTH DAKOTA LIGNITE

RUN TIME (COAL)	1.25 - 8.0 HOUR
REACTOR TYPE	FREE-FALL
HYDROGEN/COAL RATIO	0.18 - 2.0 LB/LB.
AVERAGE PARTICLE SIZE	50 - 450 MICRONS
COAL HEATUP RATE	50,000 - 150,000F <sup>o</sup> /SEC.
AVERAGE REACTOR TEMPERATURE	1150 - 1575 <sup>o</sup> F
REACTOR PRESSURE	500 - 3000 PSI
AVERAGE PARTICLE RESIDENCE TIME	100 - 3000 MSEC.
MAXIMUM VAPOR RESIDENCE TIME	0.8 - 14 SECONDS
QUENCH TEMPERATURE	450 - 1000 <sup>o</sup> F

TABLE 2  
NORTH DAKOTE LIGNITE COAL ANALYSIS

I.	<u>ULTIMATE WT. % MAF</u>	
	CARBON	68.1%
	HYDROGEN	4.6
	NITROGEN	1.3
	SULFUR	1.6
	OXYGEN	24.4
II.	<u>PROXIMATE (AS RECEIVED) WT. %</u>	
	MOISTURE	38.8%
	ASH	6.1
	VOLATILE MATTER	25.7
	FIXED CARBON	29.4

TABLE 3  
RANGE OF CONVERSION AND YIELDS OBTAINED  
NORTH DAKOTE LIGNITE

CONVERSION

COAL	40 - 85 WT.% MAF BASIS
CARBON	25 - 80 WT.%
DEVOLATILIZATION	60 - 99 WT.%
DEOXYGENATION	30 - 99 WT.%

YIELDS

GAS (C <sub>6</sub> <sup>-</sup> , CO <sub>x</sub> )	14 - 65 WT.%
LIQUIDS (C <sub>6</sub> <sup>+</sup> )	4 - 16 WT.%
LIQUOR	1.1 - 1.4 BBL/TON

HYDROGEN CONSUMPTION

12,000 - 40,000 SCF/TON

SELECTIVITY TO PRODUCTS

LIQUIDS (C <sub>6</sub> <sup>+</sup> )	15 - 50 WT.%
GAS (C <sub>6</sub> <sup>-</sup> , CO <sub>x</sub> )	85 - 50 WT.%

PRINCIPAL PRODUCTS

GAS

METHANE  
 ETHANE  
 CO (CO<sub>2</sub>)  
 C<sub>3</sub>H<sub>8</sub>

LIQUIDS

BENZENE  
 NAPHTHALENE  
 TOLUENE  
 ANTHRACENE/PHENANTHRENE

## RESULTS:

A approximately three dozen runs have been made with the experimental system. Figure 3 shows the carbon selectivity to gas and liquid as a function of carbon conversion. At a carbon conversion of approximately 45%, carbon selectivity to liquids of 43% is attained. As carbon conversion increases, the lignite is hydrogasified with the principal product being methane. These results were obtained with short residence times in the order of 500 milliseconds. As the residence time is increased, the BTX is cracked to coke and hydrogen rather than converted directly to methane. As a result, if the liquid product is not removed, there is a decided decrease in carbon conversion because the liquid ends up as coke which is deposited onto the remaining char. Kinetic calculations verify these assumptions.

Figure 4 shows the effect of reaction temperature on carbon conversions at residence time in the order of 500 milliseconds. At these medium pressures, the carbon conversion is asymptotic at about 46 wt. %.

Figure 5 depicts a family of curves for the hydrogasification of lignite. It shows how the heatup rates effect carbon conversion. The Cities Service. data fall above IGT<sup>(2)</sup> data because the heatup rates are higher.

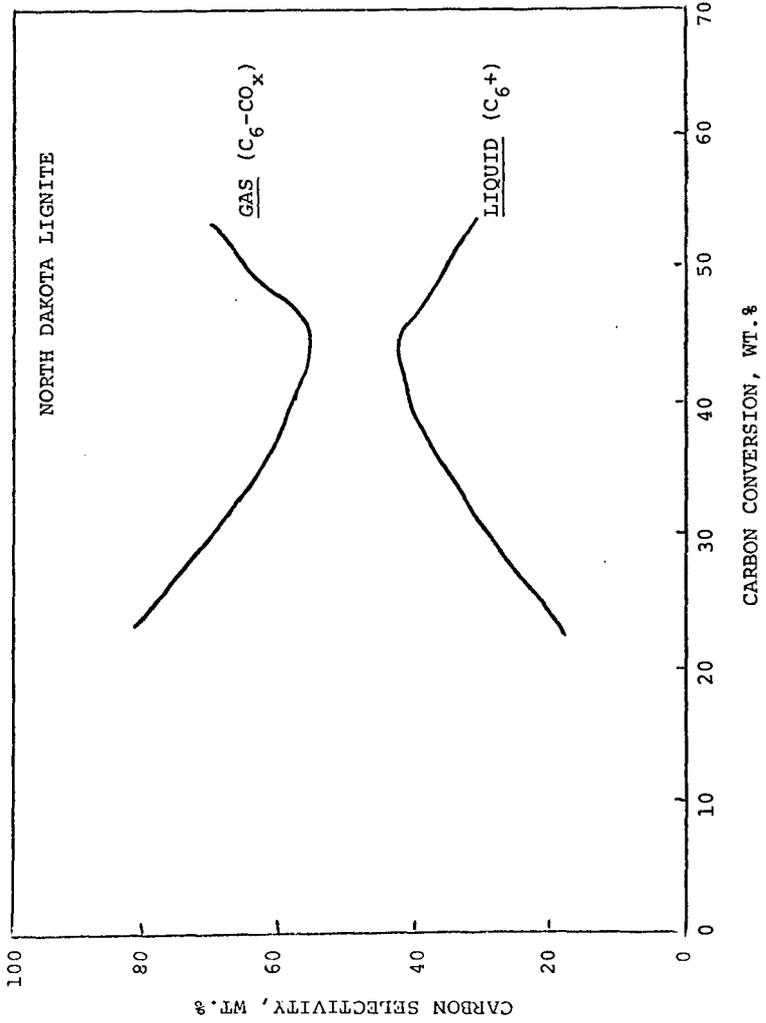
Figure 6 contains the same data as Figure 5, but depicted differently. It shows that as you increase the reaction temperature and also increase the heating rate, carbon conversion increases.

## DISCUSSION:

The experimental results achieved to date suggest that non-catalytic hydroxyprolysis of coal to methane and BTX is technically feasible. Sufficient data has been accumulated to explicitly define the operating conditions necessary to design a commercial unit that will react lignite to methane and BTX. In the commercial design, it is anticipated that an entrained flow reactor would be used. The advantage of this process is that no further hydrotreating of liquid products is necessary and that the products can be sold "as is" from the plant. Several cases have been developed to determine an optimum flow diagram for this process. Two schemes will be shown.

Figures 7 and 8 are process flow diagrams of possible routes. Figure 7 shows a scheme whereby the char is gasified with steam and oxygen. In both schemes, 16,800 T/D of MAF lignite are delivered to the SRT reactor, 324 MM SCFD of CH<sub>4</sub>; 10,600 B/D BTX, 235 T/D NH<sub>3</sub> and 126 T/D S are produced. The overall thermal efficiency for Figure 7, i.e., BTU's out over BTU's in on a nitrogen and sulfur-free basis is 68%. Approximately 10,000 SCF of CH<sub>4</sub> are produced per ton of coal. In this scheme coal is required to supplement the char so that hydrogen and oxygen can be produced.

FIGURE 3  
CARBON SELECTIVITY DURING SRT HYDROLYSIS



HYDROGASIFICATION OF LIGNITE

EFFECT OF REACTOR TEMPERATURE ON CARBON  
CONVERSION AT  
LOW COAL RESIDENCE TIMES

P: 500 - 1500 psi

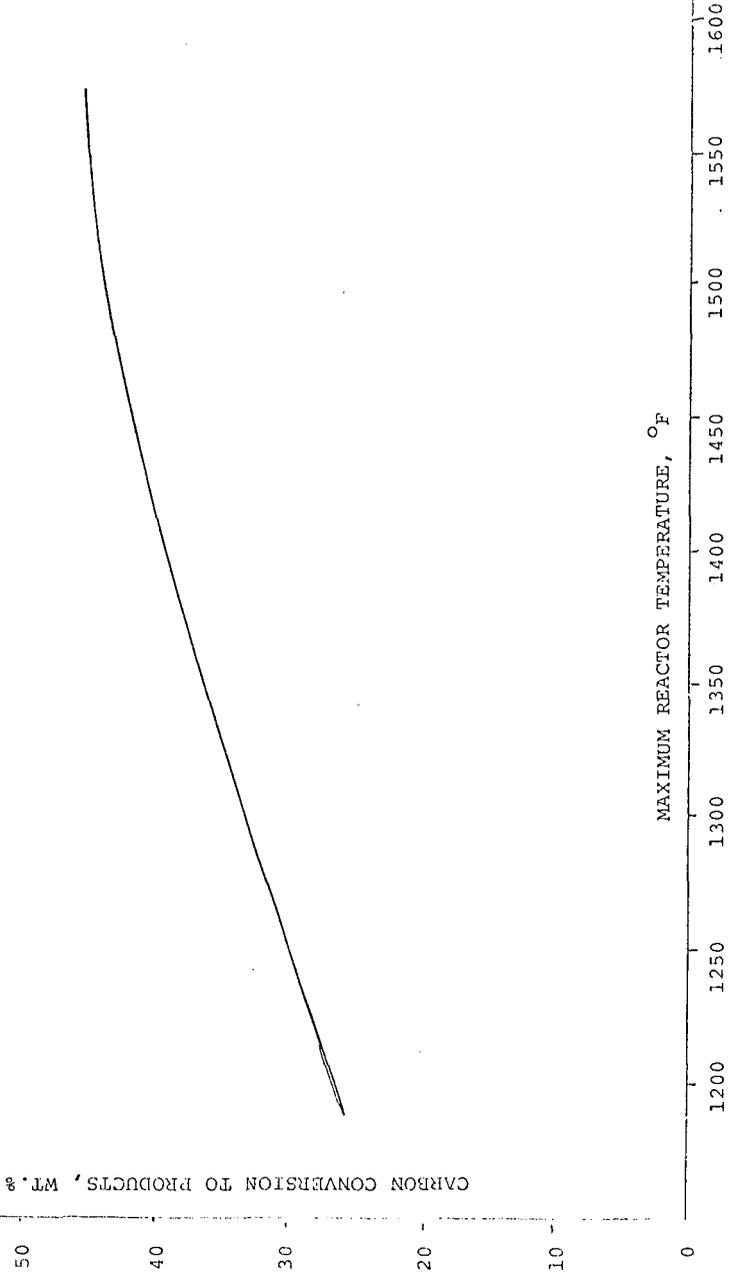


FIGURE 4

HYDROGASIFICATION OF LIGNITE

EFFECT OF PARTICLE HEATING RATE ON CARBON CONVERSION  
AT SHORT SOLIDS RESIDENCE TIME

P: 500 - 1500 psi

CARBON CONVERSION TO PRODUCTS, WT. %

60

50

40

30

20

10

0

50,000 - 150,000 °F/SEC.

2000 - 5000 °F/SEC.

50 °F/SEC.

CSR

IGT

MAXIMUM REACTOR TEMPERATURE, °F

1200

1250

1300

1350

1400

1450

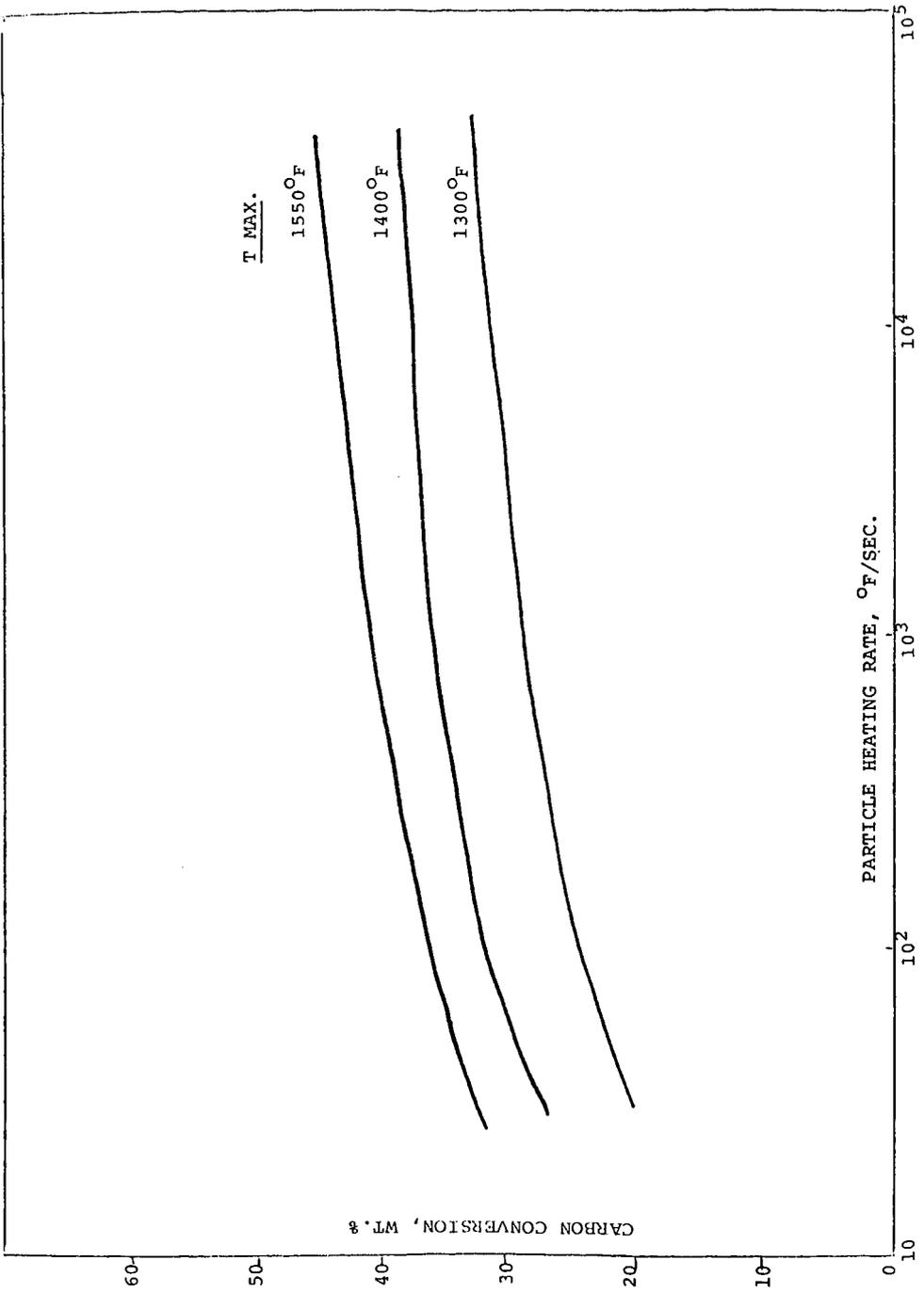
1500

1550

1600

FIGURE 5

FIGURE 6: HYDROGASIFICATION OF LIGNITE



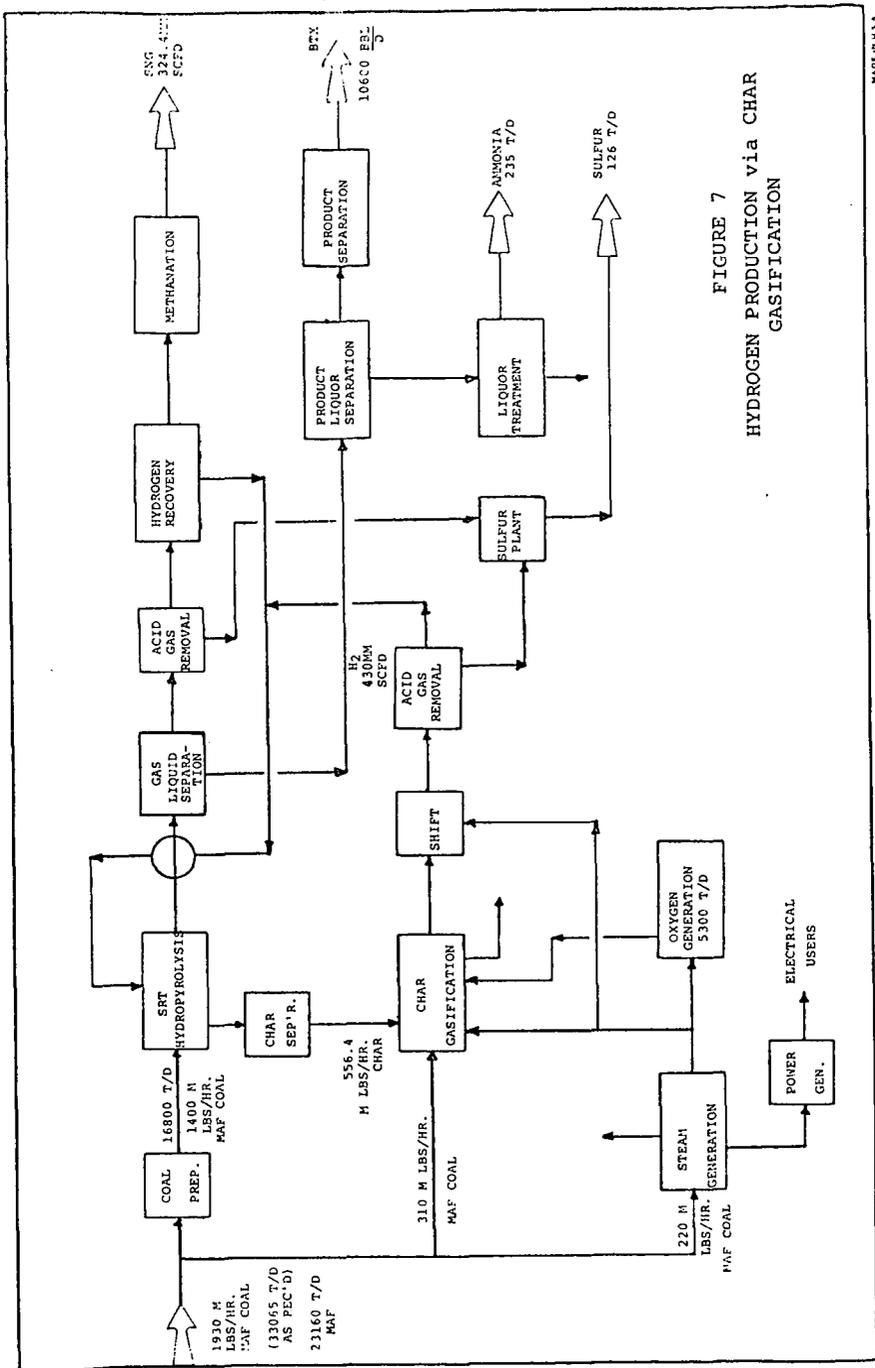


FIGURE 7  
HYDROGEN PRODUCTION via CHAR  
GASIFICATION

SHASTRI, P. S.

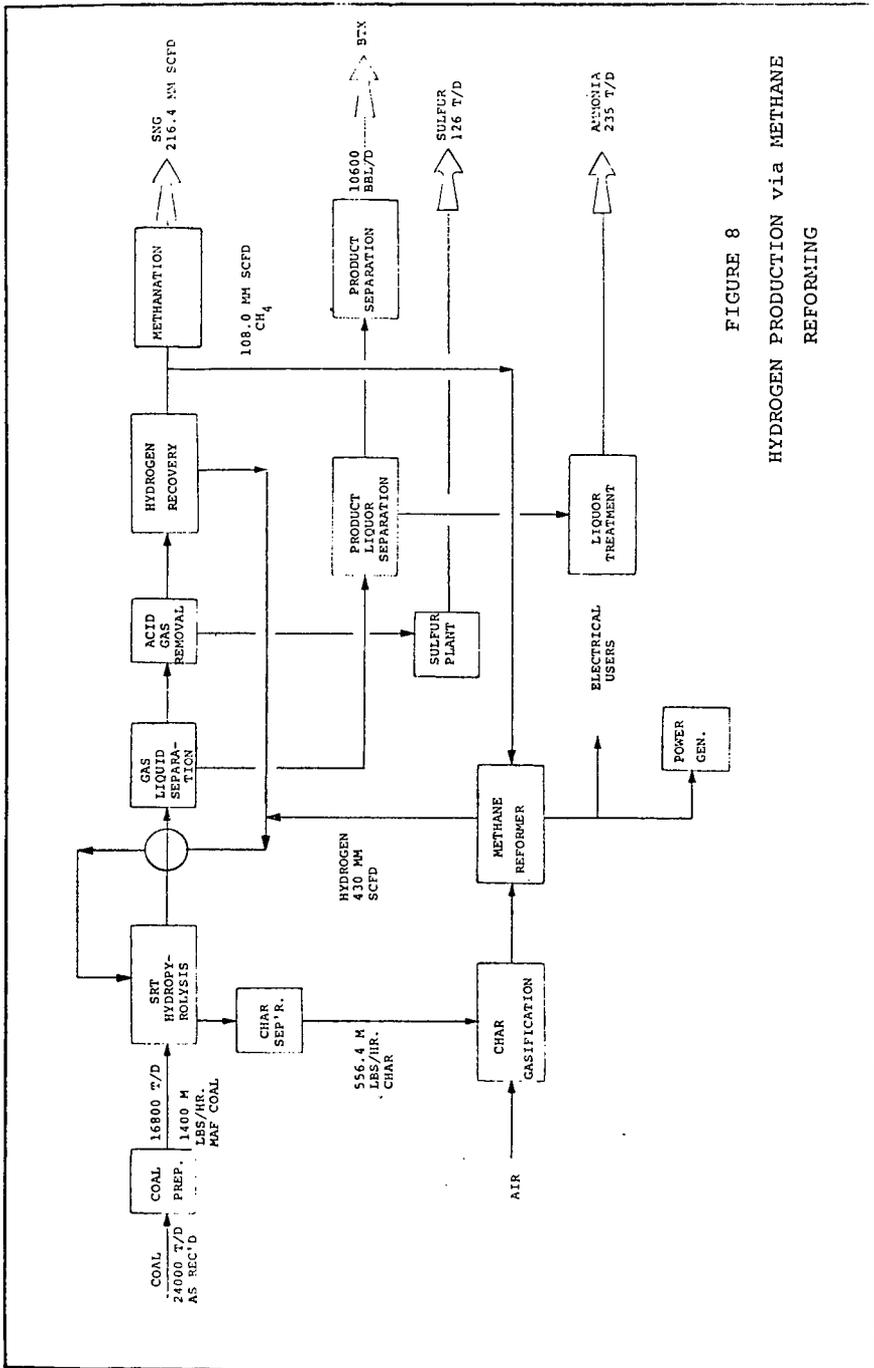


FIGURE 8  
HYDROGEN PRODUCTION via METHANE  
REFORMING

Figure 8 is a flow diagram whereby hydrogen is produced by steam reforming some of the methane that is produced. In this case, the char is gasified with air and the resulting 150 BTU/SCF gas is used to fire the reformer. The thermal efficiency of this scheme is 62% but the capital investment is much less since an oxygen plant is not required. Approximately 9000 SCF of CH<sub>4</sub>/ton of coal are produced. though both schemes are economically attractive, the scheme shown on Figure 8 seems to be the preferred route not only because of the lower capital investment but also because air-blown char gasification is much simpler than char gasification with oxygen and steam.

At present, Cities Service is planning to retain an independent engineering firm to make a detailed engineering analysis so that all alternatives can be evaluated.

ACKNOWLEDGMENT:

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KINETICS AND SOLUBILITY OF HYDROGEN  
IN COAL LIQUEFACTION REACTIONS

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Introduction

There has been considerable interest in investigation of the kinetics of coal dissolution and heteroatom removal in the presence of donor solvents and hydrogen gas. This interest stems not only from an intrinsic desire to understand the process better from a fundamental viewpoint, but also from a need to obtain data and knowledge from which coal liquefaction processes may be intelligently designed. If reliable kinetics expressions can be obtained, the effects of various operating variables quantified, and the trends better established, then data taken in laboratory experiments can be more confidently extrapolated to other conditions with a minimum of experimental investigation.

From work in this laboratory (1,2) and that of others (3,4,5,6) a free radical mechanism for the dissolution of coal in hydrogen donor solvents can be postulated. The initial dissolution of the coal solid is thermally initiated; however, the net rate of depolymerization for a given coal depends upon the nature of the solvent and its effectiveness in stabilizing the free radicals. The higher the hydrogen donating ability of the solvent, the more effective the solvent is in terminating radicals and promoting coal solvation. This is shown by the fact that hydrogenated recycle solvent has been found to facilitate coal solvation much more readily than untreated solvent (18). The overall rate limiting step in the process appears to be the rehydrogenation of the donor vehicle. This latter process can, however, be aided significantly by the action of coal mineral matter (7,8). The separation of these two steps, hydrogen transfer and solvent rehydrogenation, may provide the key to an improved SRC type process, allowing greater reactor throughput and operation at lower temperatures and pressures. Such an arrangement would be similar to the coal conversion process at Cresap, West Virginia.

Considerable research has been conducted concerning the kinetics of coal solvation and sulfur removal. Although performed in the absence of a solvent, the recent study of the nonisothermal kinetics of coal hydrodesulfurization reported by Yervey, *et al.* (9) is of interest. These investigators divided the sulfur in coal into five classes of Organic I, II, III, Pyritic, and Sulfide, and determined pre-exponential and activation energies for the reaction of each of these five types. Of particular interest

was the reverse reaction of  $H_2S$  with the organic matter of coal to produce the Organic III class of coal-contained sulfur. Liebenburg and Potgieter (10), and Potgieter (11), have recently reported studies on the uncatalyzed hydrogenation of coal and on the kinetics of conversion of tetralin during the hydroliquefaction of coal. They concluded that heating and cooling could cause considerable spurious effects in batch autoclave kinetics studies and suggested sampling techniques to avoid these. Kinetic rate constants for the formation of asphalt and oil fractions from the uncatalyzed hydrogenation of coal in tetralin were reported and several different kinetic mechanisms were postulated. Wen and Han (12) have also determined rate constants using coal liquefaction and desulfurization data gathered primarily from studies by Pittsburgh and Midway Coal Mining Co., the University of Utah, and the Colorado School of Mines. These researchers were able to fit data from these sources with an empirical expression for the rate of coal dissolution; however, no kinetic expression was obtained for desulfurization, probably because of lack of sufficient data. Furthermore, the effect of hydrogen partial pressure was not firmly established, and it is likely that the different type reactors and experimental procedures employed in the three laboratories made the data correlation more difficult. Coal liquefaction data using creosote oil together with a  $CO$ -stream gas phase have been reported by Handwerk, et al. (13) at the Colorado School of Mines. In these experiments it was established that reaction temperature had a stronger effect on desulfurization than did hydrogen partial pressure; however, reaction rate expressions were not reported. Similar investigations employing synthesis gas, with the addition of an external catalyst, have been reported by Fu and Illig (14) and Appell, et al. (15). With regard to catalytic studies, the University of Utah studies on hydrocracking and heteroatom removal (16,17) are representative of batch autoclave studies in the presence of an added catalyst, although in these particular studies a coal-derived oil was used as a starting material rather than a coal-solvent slurry. Given et al. (18) at the Pennsylvania State University, in cooperation with Gulf Research and Development Company, have reported recent results of their efforts to correlate coal liquefaction behavior with chemical and physical characteristics of the coal. Although their results are enlightening, it appears that further work will be required to firmly establish the relation between different characteristics of the coal and liquefaction behavior, in view of the large number of interacting variables which are present. Thus, despite the fact that numerous studies have been reported concerning liquefaction kinetics, it appears that the reaction-dissolution process is still not completely understood and that further investigation is needed.

In contrast to the large amount of research on the kinetics of coal solvation and sulfur removal, there is a distinct lack of related information on the kinetics of hydrogen consumption during the coal solvation process. The rate of hydrogen consumption is important in the SRC process where it is desirable to minimize the consumption of costly hydrogen and maximize the yield of the SRC boiler fuel. The production of highly hydrogenated products including  $C_1$ - $C_4$  gases decreases SRC yield and increases the consumption of hydrogen. The synthesis of boiler fuel for use in power plants does not require extensive hydrogenation. It is interesting to note that SRC product usually contains a slightly lower hydrogen/carbon ratio ( $H/C = 0.75$ ) than the feed coal itself ( $H/C=0.8$ )(19,26). Thus, if the production of light gases ( $H/C=6.6$ ), water, and light liquids ( $H/C=1.5$ ) can be minimized, the SRC process has the potential to be self-sufficient in hydrogen which can be recovered from light liquids and gases by steam reforming, if necessary. The SRC pilot plants operated at

Wilsonville, Alabama, and Tacoma, Washington, currently consume about two weight percent of hydrogen per pound of HAF coal feed. Controlling solvent composition and process conditions to optimize selectively the production of SRC product would limit hydrogen consumption to a minimum and still produce an environmentally acceptable boiler fuel. Before optimum conditions can be selected, however, kinetic rate expressions are needed to provide models for process scale-up, simulation, and optimization. This work reports the development of such a model for hydrogen consumption in the dissolver stage of the SRC process.

### Reaction Kinetics Experiments

Reagents and Materials. Kentucky No. 9/14 coal mixture was crushed; and the -170 mesh fraction - having the screen analysis shown in Table 1, and the elemental analysis in Table 2 - was used. The creosote oil used in this work was furnished by Southern Services, Inc., and was used as received from Wilsonville. Typical analysis of this creosote oil by gas chromatography is given in Table 1. The oil is distilled from coal tar in the boiling range 175° to 350°C. The oil was originally obtained from Allied Chemical Company as creosote oil 24-CB; and has a carbon-to-hydrogen ratio of 1.25 (90.72% C and 6.05% H), a specific gravity of 1.10 at 25°C, and a boiling point range of 350 to 650°F. A 3:1 solvent-to-coal weight ratio was used in all experiments reported, and all coal was dried overnight at 100°C and 25 inches of Hg vacuum before use. Hydrogen was obtained from Linde Hydrogen in 6000 psi grade and had a purity of 99.995%. Practical grade mesitylene was obtained from Matheson Coleman and Bell (MCB) and used without further purification.

Procedures. For each run, a 30 gm. of coal/90 gm of solvent slurry was charged into a 300 cc. magnedrive autoclave from Autoclave Engineers, Inc. Reactions were carried out at reaction times of 15, 30, 60, and 120 minutes and at reaction temperatures of 385, 400, 410, and 435°C; a stirrer setting of 1000 rpm was used in all the runs, with the exception of one run in which a stirrer setting of 2000 rpm was used to evaluate mass transfer effects. A heat-up rate of about 20°C per minute was used - requiring only about three minutes for heat-up within the zone in which significant reaction occurs (above 370°C) and a total heat-up time of about 30 - 35 minutes. Prior to heat-up 400 psig of hydrogen was charged to the reactor and at reaction temperature more hydrogen was added to give the desired initial hydrogen partial pressure. During each run reaction temperature was held constant within  $\pm 3^\circ\text{C}$ ; and upon completion, the final hydrogen partial pressure (psia) was determined from gas analysis and total pressure measurement.

### Solubility of Hydrogen in Coal Liquids

Data on the solubility of hydrogen in the coal-solvent slurry and a knowledge of the Henry's law constant is necessary in the kinetic modeling to follow hydrogen consumption. In addition, hydrogen solubility data are of importance for design and analysis of subsequent hydrogen recovery and downstream hydrogenation units in the coal processing train.

The coal-derived process solvent for liquefaction operations is typically a complex mixture consisting largely of partially hydrogenated polynuclear aromatic compounds, capable of transferring hydrogen to the coal structure. The exact chemical composition of the steady-state recycle solvent is dependent upon the characteristics of the feed coal and operational conditions. The creosote oil having the composition given in Table 1 was used as the start-up solvent at the SRC pilot plant in Wilsonville, Alabama, and is reasonably representative of the steady-state

recycle solvent. Solubility data for hydrogen in this oil are determined and used for the kinetics modeling in this investigation.

Determinations of the solubility of hydrogen in coal liquids have not been previously reported at coal liquefaction conditions. Peter and Weinert (20) have determined hydrogen solubility in slack wax, a paraffin oil, under similar conditions as encountered here. Eakin and Devaney (21) have measured hydrogen solubilities in paraffinic, naphthenic, and aromatic solvents as a ternary system with hydrogen sulfide in the temperature range from 100° to 400°F and a pressure range from 500 to 2000 psia. Chappelow and Prausnitz (22) have also made measurements of the Henry's law constants for hydrogen solubility in squalane and octamethylcyclotetrasiloxane between 25° and 200°C. The work presented here provides data on hydrogen solubility in creosote oil solutions at the high partial pressures of hydrogen and high temperatures used in coal liquefaction reactors. Thus, these data may be applied directly to coal conversion systems.

#### Hydrogen Solubility Experiments

The equilibrium cell used was a one gallon Autoclave Engineers 316 Stainless Steel magnedrive autoclave. Equilibrium pressures were monitored with a Heise Bourdon-tube gauge which had been calibrated against a deadweight gauge. The temperature of the cell was measured with a Type K thermocouple inserted into a thermowell extending into the liquid phase. Temperature was controlled within ±1%.

Gases encountered in this experiment were analyzed for H<sub>2</sub>, Air, CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, i-C<sub>4</sub>H<sub>10</sub>, n-C<sub>4</sub>H<sub>10</sub>, i-C<sub>5</sub>H<sub>12</sub>, and n-C<sub>5</sub>H<sub>12</sub>. Hydrogen analyses were carried out on a Varian Model 920 areograph using a 15 foot column packed with 75% molecular sieve 13X and 25% molecular sieve 5A. The column was operated isothermally at 100°C with nitrogen as a carrier gas (40 ml/min). The other gases were analyzed on a Varian model 1800 areograph using a 15 foot column packed with Porapak Q, 80-100 mesh. The column temperature was programmed between 40° and 230°C at approximately 12°C/min. Helium was used as a carrier gas (40 ml/min). Both chromatographs were equipped with thermal conductivity detectors.

The creosote oil was charged into the autoclave and the system purged by evacuation. The autoclave was then brought to the desired temperature and hydrogen added to an amount determined by observation of the pressure. Hydrogen pressure was found to reach an equilibrium state in less than 5 seconds by standard step-response testing. Stirring was carried on during the entire process (2000 rpm), except during sample withdrawal.

Samples of the vapor were withdrawn from the top of the autoclave and analyzed by gas chromatography. From the analysis of the vapor phase and the knowledge of the gauge pressure and the vapor pressure of the creosote oil (Figure 1), the partial pressure of hydrogen in the vapor was calculated.

Liquid samples were withdrawn from the bottom of the autoclave into a stainless steel bomb. The bomb was then fitted to an evacuated glass rack, (Figure 2), in which the volume of the dissolved gases were measured. After volume measurement the gases were passed to a gas chromatograph for analysis. From this analysis,

-knowing the barometric pressure, ambient temperature, and total gas volume - the weight of hydrogen dissolved in the creosote oil was computed using the ideal gas law. By weighing the loaded bomb the weight of the oil was determined inferentially, and the solubility calculated as grams  $H_2$ /gram oil.

#### Result of Hydrogen Solubility Experiments.

To verify the liquid sampling and analytical procedures the solubility of  $H_2$  in mesitylene was determined at 400°F (204°C) at partial pressures of hydrogen between 500 and 2000 psia. A comparison of the data obtained for solubility of hydrogen in mesitylene in this work to the literature values (21) is given in Figure 3. The measured values agree with the previously reported values within a few per cent, thus confirming the techniques used here.

Experimental data for the solubility of hydrogen in creosote oil were obtained at temperatures of 100°, 200°, 300°, and 400°C at partial pressures of hydrogen ranging from 500 to 3000 psia; and the resulting data is shown in Figure 4. Hydrogen solubility exhibits an interesting inverse temperature behavior, with solubility at 400°C being greater than values at 100°C at the same pressure.

The major sources of error in this work are associated with transfer of liquid sample from the autoclave to the gas burette. The sample bomb was massive and determination of the weight of oil withdrawn was the least accurate step in the experiment. Minor errors result from uncertainties in the temperature of the equilibrium cell and the measurement of dissolved gas volume. As a result of these factors, the present data are estimated from least squares analysis to have an experimental accuracy of 4-6% in solubility at a given partial pressure of hydrogen.

It is apparent from these data that hydrogen is appreciably soluble in creosote oil. Thus in a batch autoclave with equal volumes of gas and liquid at 400°C and 2000 psig approximately one-third of the total hydrogen gas present is dissolved in the liquid phase.

In order to determine the effect of coal on the hydrogen solubility, experiments were run in which a slurry of 3:1 ratio of solvent to coal was used instead of creosote oil. The data were taken at 400°C and 2500 psia total pressure after 30 minutes at temperature. Assuming all the organic coal matter to be in the liquid phase, the hydrogen solubility was essentially the same - that is, within experimental error - as that in creosote oil alone at the same conditions. Thus the hydrogen solubility data in Figure 4 may also be used in the subsequent study of coal liquefaction kinetics.

#### Controlling Regimes in Coal Liquids Hydrogenation

The three-phase - solid-coal, hydrogen-gas, and donor-solvent - reaction system present in the SRC process is subject to several possible mass transport effects. The fact that coal particles readily disintegrate in the presence of an appropriate donor solvent (1) and that initial particle size seemingly has little effect upon the rate of solvation (23) indicates that pore diffusion and fluid-solid mass transfer play minor roles in the SRC process - though additional research is desirable to fully substantiate this tentative conclusion. Nonetheless, the rate of gaseous hydrogen consumption might be controlled, at least partly, by

mass transfer across the gas-liquid interface. When gas-liquid mass transfer controls the overall reaction rate, the most important factor is the interfacial area, which is governed by the agitation rate. To test for the presence of mass transfer regulation, experiments were performed using autoclave stirring speeds of 1000 and 2000 rpm respectively (24). The experimentally measured gas phase composition indicated no difference in the net rate of hydrogen consumption, thus indicating the absence of mass transfer resistance for the hydrogenation reaction. Further evidence is provided by Figure 5 where, after injecting a pulse of hydrogen gas, a new quasi-equilibrium state is rapidly established, immediately following hydrogen saturation of the liquid phase. The data of Figure 5 were obtained by allowing the reaction mixture of equilibrate at 405°C and 700 psig hydrogen pressure. The pressure was then increased very rapidly to 1870 psig, by opening and closing the hydrogen inlet valve. The pressure rise and decay was followed by a Leeds and Northropp pressure transducer. The rapid approach to equilibrium shown in Figure 5 indicates that at any given time, the gas and liquid phases are in equilibrium with respect to hydrogen concentration, unless the reaction is very fast indeed.

A third and final criterion for the absence of mass transfer influence upon the hydrogen consumption rate is the magnitude of the activation energy subsequently determined. The activation energy of 21 kcal/mole determined experimentally is indicative of kinetic control rather than diffusional control. Thus, it appears that mass transfer is not rate controlling in the noncatalytic (except for mineral matter effects) hydrogenation of coal solutions and that lumped parameter, homogeneous-phase reaction rate expressions are adequate for kinetics modeling.

#### Reaction Kinetics Modeling

The purpose of this section is to determine the magnitude of the parameters in an appropriate kinetic rate expression for hydrogen consumption. Material balances for hydrogen in the gas and liquid phases in the batch autoclave may be written:

$$\frac{dH_g}{dt} = -\dot{m} \quad (1)$$

$$\frac{dH_L}{dt} = -r_A V_L + \dot{m} \quad (2)$$

The mass transfer term  $\dot{m}$  allows for the transfer of hydrogen from the gas to the liquid phase as the reaction proceeds and hydrogen is depleted. The form of the reaction rate  $r_A$  must be determined from experimental data. Addition of Equations 1 and 2 eliminates the mass transfer term  $\dot{m}$  and yields Equation 3 for the rate of disappearance of total hydrogen:

$$\frac{dH_T}{dt} = \frac{d(H_g + H_L)}{dt} = -r_A V_L \quad (3)$$

For a first order reaction of dissolved hydrogen in the liquid phase, the form of  $r_A$  is

$$r_A = k_L H_L / V_L \quad (4)$$

Using the solubility data presented in Figure 4 we may determine the Henry's law constants for use in the relation:

$$\beta = S/P_{H_2} \quad (5)$$

Representative values of  $\beta$  are given in Table 4. Equation 5 may be used together with the experimental parameters to yield Equation 6.

$$\alpha = H_L / H_T \quad (6)$$

Values of  $\alpha$  for the experimental temperatures used herein are presented in Table 5. Employing the assumption of quasi-equilibrium discussed previously, Equations 3, 4, and 6 may be solved to yield the significant result:

$$\frac{H_L}{H_{L0}} = \frac{H_G}{H_{G0}} = \frac{H_T}{H_{T0}} = \exp(-\alpha k_L t) \quad (7)$$

Note that the solubility of hydrogen enters the kinetics model through the parameter  $\alpha$ . Equation 7 gives the amount of hydrogen present in either the gas or liquid phase as a function of time during the reaction. A comparison of Equation 7 with the experimental data is presented in Figure 6. The satisfactory fit verifies the assumption of first-order kinetics made in Equation 4. Values of  $k_L$  obtained from the slopes are presented in the Arrhenius plot of Figure 7, where an activation energy of 21 kcal/mole for the hydrogenation reaction has been determined. The complete experimental data for this investigation is recorded elsewhere (25). The total amount of hydrogen consumed by the reaction at any time may be found according to

$$H_c = H_{T0} [1 - \exp(-\alpha k_L t)] \quad (8)$$

### Conclusions

The rate of consumption of hydrogen in coal solvation can be adequately described by a homogeneous kinetic rate expression first-order in dissolved hydrogen concentration. Mass transfer influence appears to be negligible and the overall hydrogen consumption rate is governed by chemical kinetics alone.

The reaction rate constant has a frequency factor of  $1.06 \times 10^5$  per minute and an activation energy of 21 kcal/mole. It is likely that these numerical values are affected by the mineral matter present in the coal, which can catalyze hydrogenation activity (8).

The solubility of hydrogen in coal liquefaction solutions is appreciable and may be represented adequately by a Henry's law coefficient. The solubility exhibits an inverse temperature-solubility behavior.

#### Notation

H = mass of hydrogen, g  
K = first order rate constant,  $\text{min}^{-1}$   
m = rate of mass transfer from gas to liquid, g/min.  
P = pressure, psia  
S = solubility, g  $\text{H}_2$ /g oil  
 $r_A$  = reaction rate of hydrogen in liquid phase, g/min-cc  
T = temperature,  $^{\circ}\text{K}$   
t = time, min  
V = volume, cc  
 $\alpha$  = parameter defined by Equation (5)  
 $\beta$  = Henry's law constant, g  $\text{H}_2$ /g oil-psia

#### Subscripts

c = amount consumed by reaction  
g = in gas phase  
L = in liquid phase  
T = total amount in both places  
o = amount at  $t = 0$

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TABLE 1

## Gas Chromatographic Analysis of Creosote Oil

Compound	Weight %
coumarone	.10
p-/cymene	.02
indan	.11
phenol	.12
o-cresol	.05
benzonitrile	.12
p-cresol	.37
m-cresol	.16
o-ethylaniline	.03
naphthalene	5.1
thianaphthene	.08
quinoline	.37
2-methylnaphthalene	1.3
isoquinoline	.30
1-methylnaphthalene	.38
4-indanol	.55
2-methylquinoline	.42
indole	.21
diphenyl	.49
1,6-dimethylnaphthalene	.39
2,3-dimethylnaphthalene	.19
acenaphthene	6.0
dibenzofuran	6.7
fluorene	10.3
1-naphthonitrile	.18
3-methyldiphenylene oxide	1.7
2-naphthonitrile	.14
9,10-dihydroanthracene	2.4
2-methylfluorene	.85
diphenylene sulfide	.52
phenanthrene	18.6
anthracene	4.3
acridine	.19
3-methylphenanthrene	.98
carbazole	2.2
4,5-methylenephenanthrene	2.5
2-methylanthracene	.24
9-methylanthracene	1.2
2-methylcarbazole	1.7
fluoranthene	5.5
1,2-benzodiphenylene oxide	.96
pyrene	2.6

Table 2. Screen Analysis of Bituminous Kentucky No. 9/14 Coal Mixture

Mesh Size of Screen	% Retention
170	1.23
200	1.92
230	1.09
270	4.30
325	17.94
400	10.86
-400	62.65
Total	99.99

Table 3. Chemical Analysis of Bituminous Kentucky No. 9/14 Coal Mixture

H	4.9
C	67.8
Total Sulfur	2.55
Organic Sulfur	1.63
FeS <sub>2</sub>	0.79
Sulfate Sulfur	0.13
Total Ash	7.16

Table 4

Henry's Law Constants for Hydrogen in Creosote Oil

$T_1$ °C	$\beta \times 10^7$ , g H <sub>2</sub> /g oil-psia
100 <sup>o</sup>	5.95
200 <sup>o</sup>	6.94
300 <sup>o</sup>	7.75
400 <sup>o</sup>	9.65

Table 5

$T_1$ °C	$\alpha$
385 <sup>o</sup>	0.183
400 <sup>o</sup>	0.193
410 <sup>o</sup>	0.196
435 <sup>o</sup>	0.211

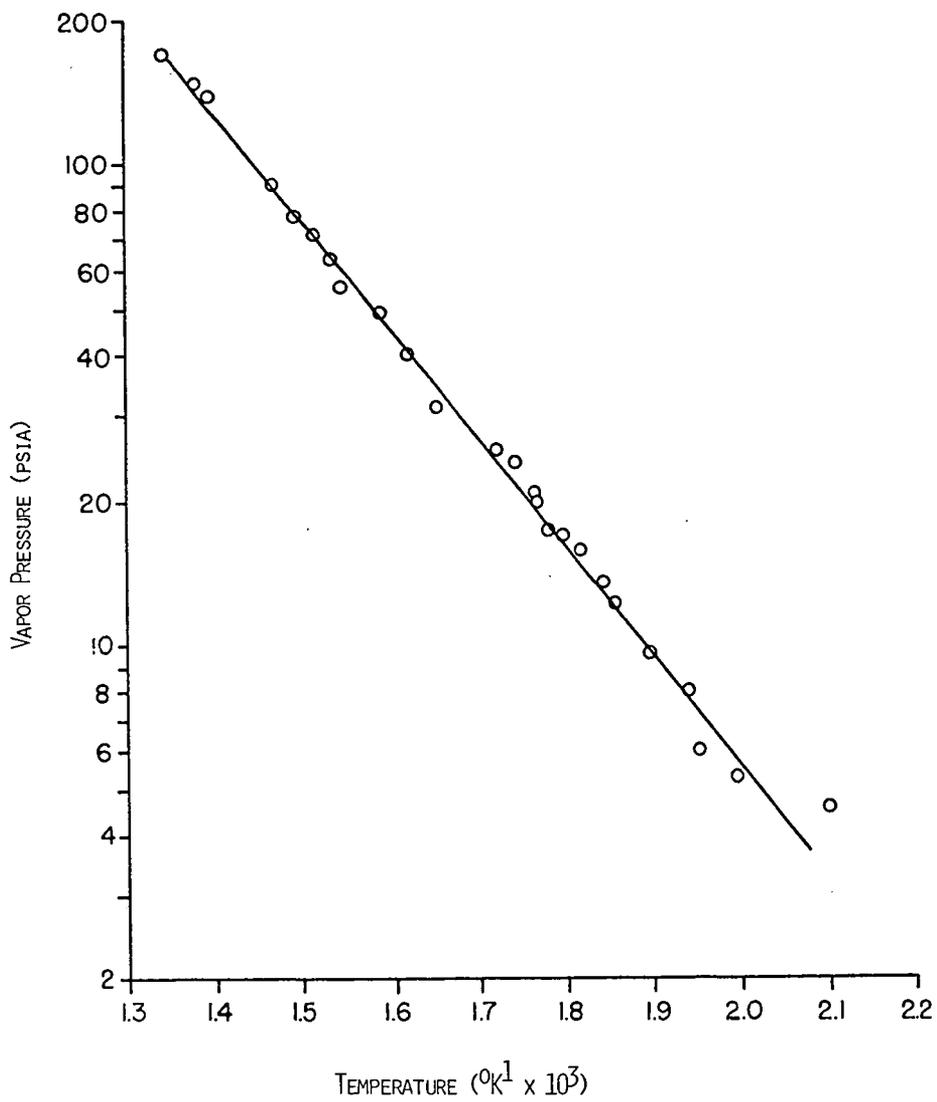


FIGURE 1. VAPOR PRESSURE OF CREOSOTE OIL

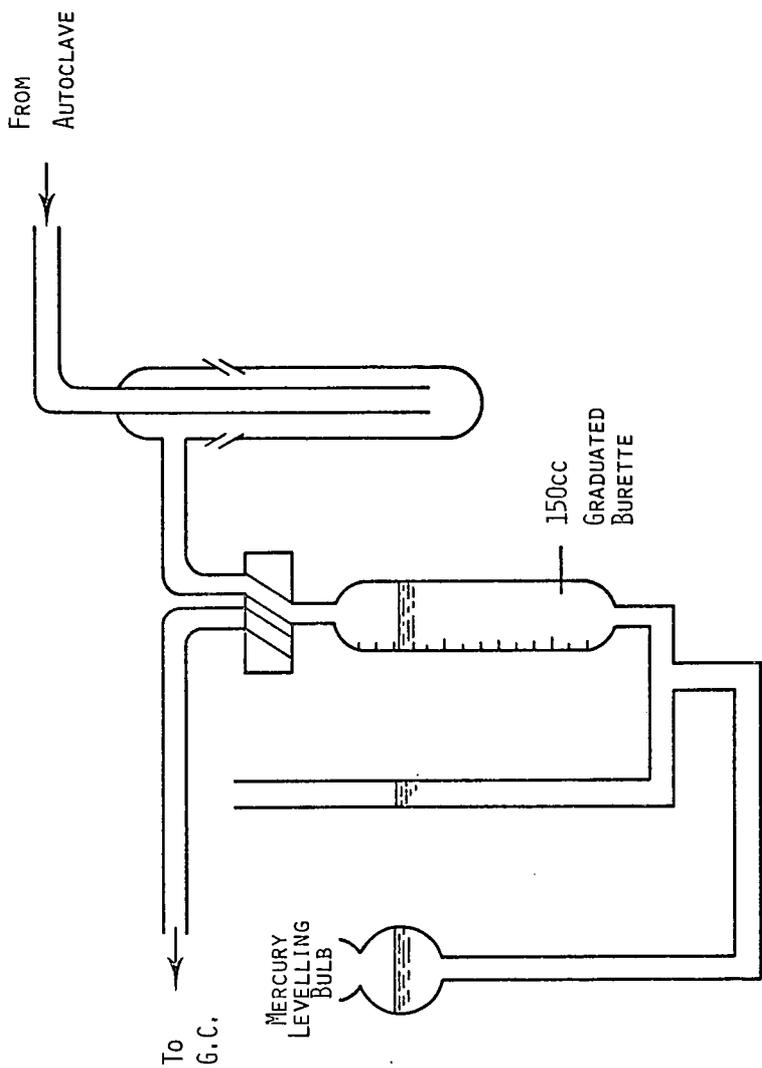


Figure 2. Gas Solubility Measurement Apparatus.

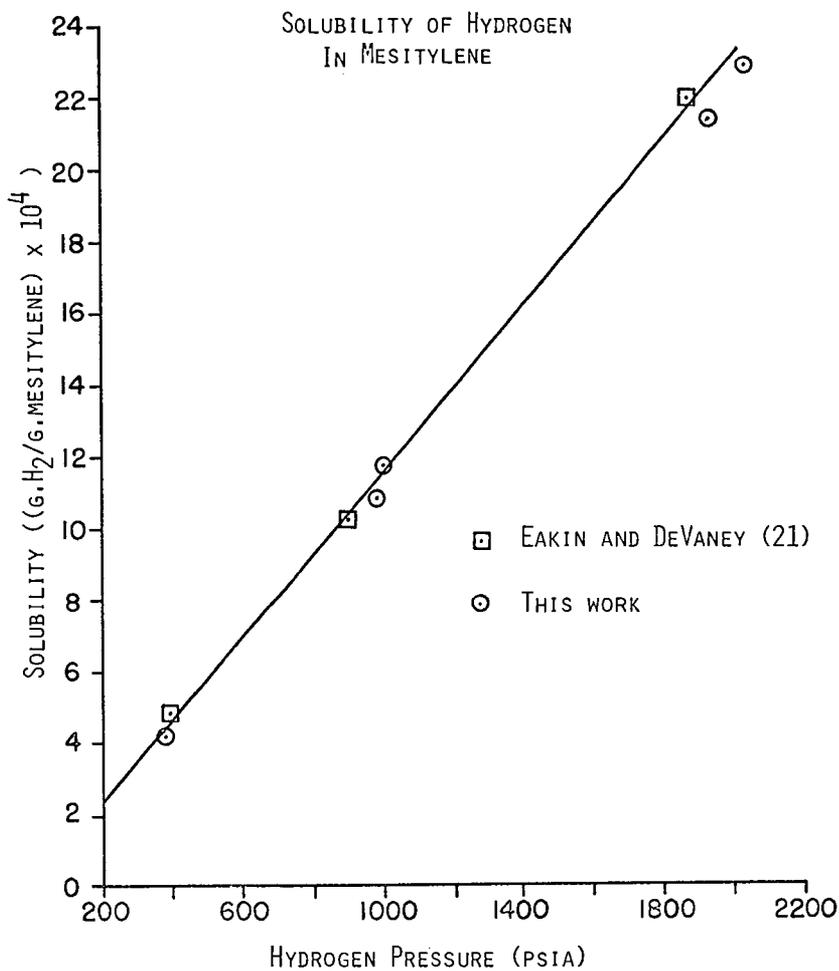


Figure 3. Comparison of this data with previous data for hydrogen solubility in Mesitylene

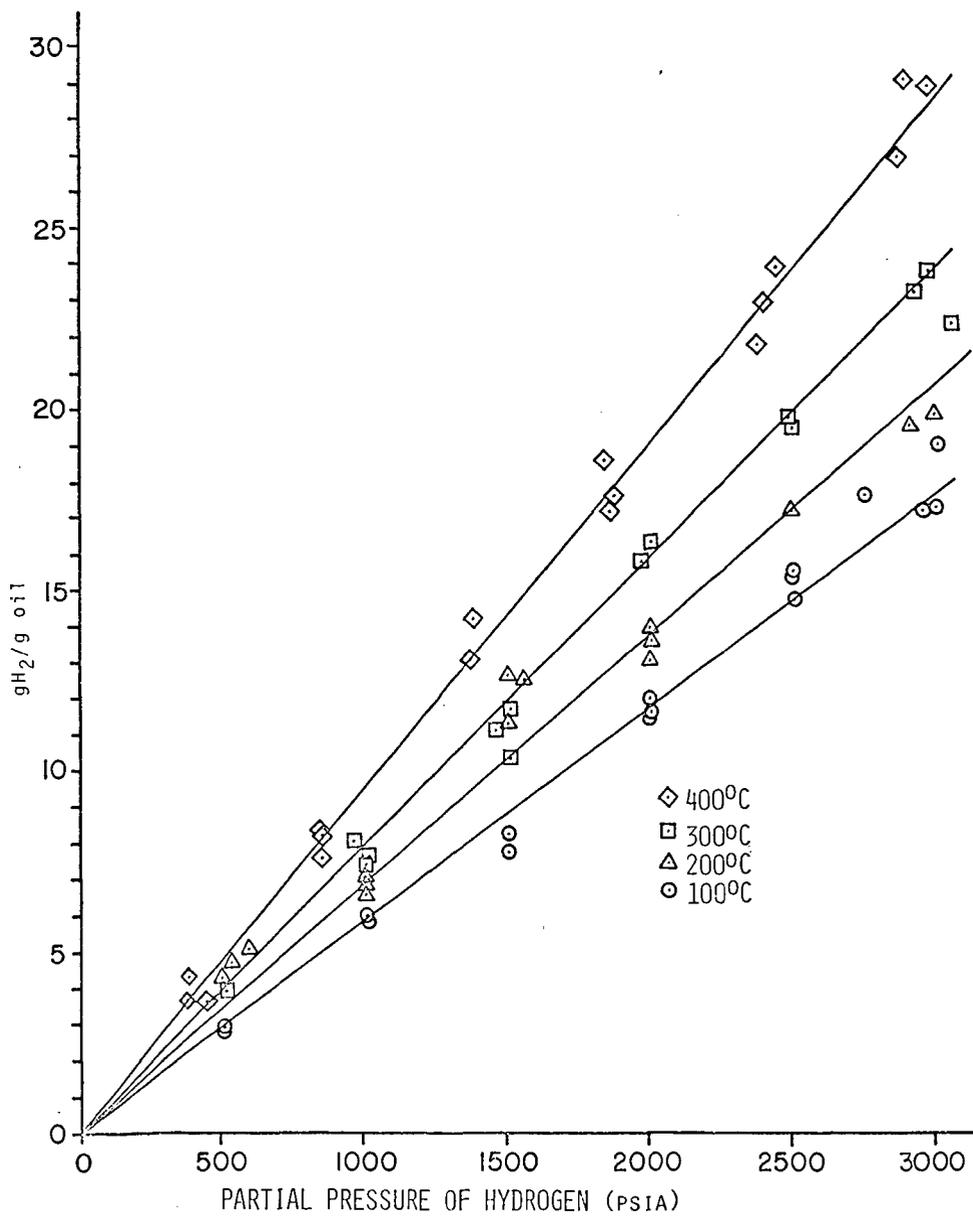


Figure 4. Solubility of H<sub>2</sub> in Creosote Oil

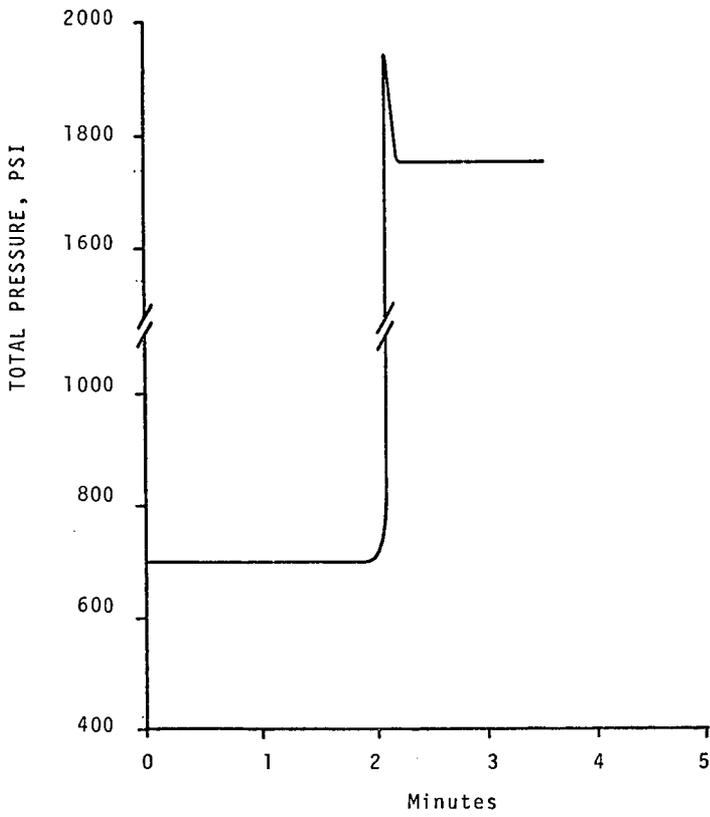


Figure 5. Rate of Approach to Gas + Liquid Equilibrium

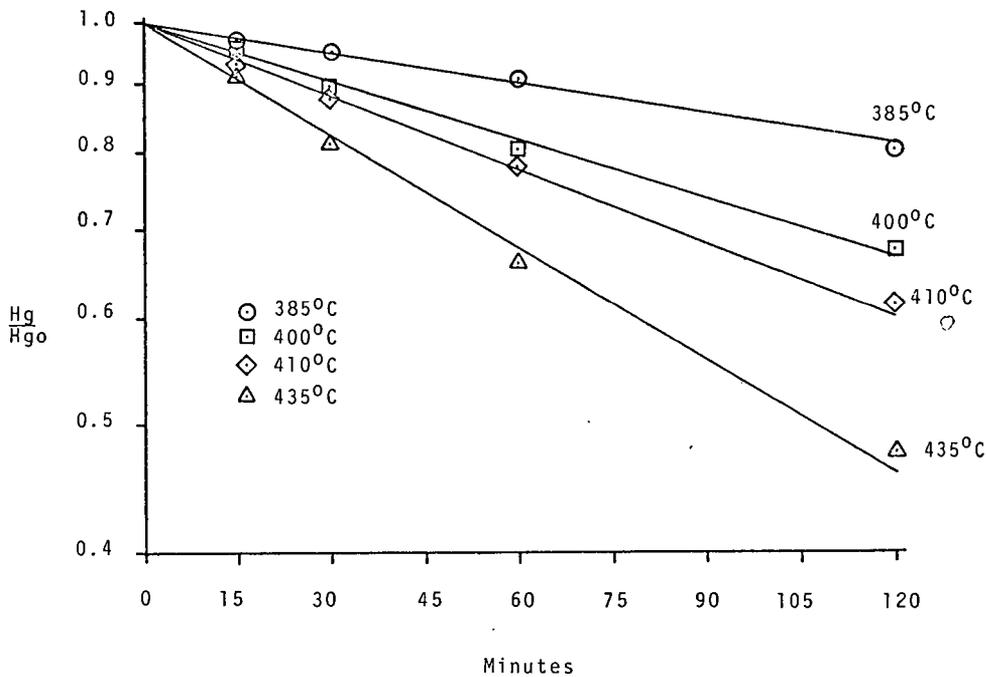
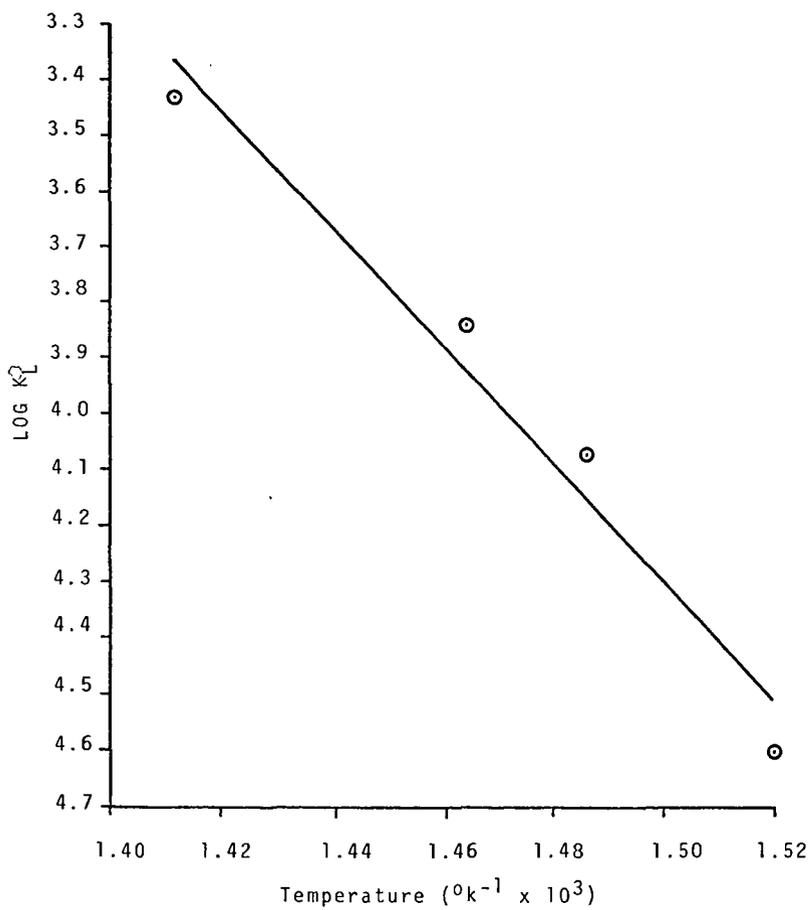


Figure 6. Verification of Hydrogenation Model

Figure 7. Arrhenins plot for hydrogen transfer rates to coal.



# A PETROGRAPHIC CLASSIFICATION OF SOLID RESIDUES DERIVED FROM THE HYDROGENATION OF BITUMINOUS COALS

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## Introduction

Previous optical studies of coal dissolution have shown that the grain size of the organic constituents decreases with increasing reaction temperature (1, 2). These investigations were concerned mainly with chemical aspects of coal hydrogenation as a function of hydrogen transfer and thermal degradation; however no attempt was made to relate these parameters to the changing physical character of coal macerals. The "char" components produced during hydrogenation are known to be optically dissimilar to their original coal constituents. Therefore, it will be necessary to understand the physical mechanisms involved in maceral dissolution as well as the properties of these "char" or residue constituents before the chemical aspects of hydrogenation can be given adequate consideration.

A morphological characterization of solid residues will be a foundation for determining the various physical mechanisms involved in coal maceral degradation. Comparison of the petrography of a feed coal to that of its solid residue derived from hydrogenation is not sufficient for determining the origin of residue components. Understanding these origins, however, can be achieved by interpreting the progressive disintegration of coal macerals. These intermediate steps were observed in optical studies of residues produced by progressive batch hydrogenation and serve to associate the original feedcoal macerals to residue components derived from continuous-flow reaction.

Optical studies reveal that residue constituents are formed as a result of incomplete hydrogenation, repolymerization or carbonization. Those coal macerals which pass through the process unreacted or exhibiting only slight morphological alteration are readily identified. Other constituents are related to their precursory macerals by studying low temperature batch hydrogenation residues and are described on the basis of their morphology, relative reflectance, anisotropy, and grain size.

## Sample Origin

Residues from two coal hydrogenation systems were used in this study. An experimental batch hydrogenation system utilized 20 g of minus 20 mesh coal with four parts by weight of tetralin in a stainless steel reaction vessel (nitrogen atmosphere). These preparations were reacted in a fluidized sand bath for three hours at a selected constant temperature in the range of 300°-450°C at 25°C increments (3). The reaction vessel contents were extracted in benzene and the resulting insoluble fraction was dried, embedded in epoxy resin, and polished.

The second system employed was a proprietary continuous-flow bench-scale reactor. This process used a feed rate of 400 g/hr of minus 200 mesh coal slurried in a 1 to 3 ratio with solvent-recycle or anthracene start-up oil. The slurry was pumped under a pressure of 1500 psig into a reaction column with hydrogen. Reported reaction temperatures of 441°C and 427°C were given for a residence time approximating 30 minutes. Filtration was conducted at regular intervals to determine the product balance for each run. Filter cake materials were extracted in pyridine and the resulting residue was dried, embedded in epoxy resin, and polished.

Solids from a pilot plant continuous-flow reactor were also subjected to optical observation.

### Comparative Optical Results

The petrography of feed coals used for conversion in these hydrogenation systems are summarized in Table I. The more reactive coal constituents, vitrinite and exinite (see Fisher *et al.* (4) and Davis *et al.* (5)) appear in varying concentration. The reactive maceral content of the Indiana #6, West Kentucky #14, and Illinois #6 feed coals are relatively high while those for the Indiana #1 Block and the Australian Callide feed coals are substantially lower. These feed coals are high volatile bituminous in rank with the exception of the subbituminous A Callide seam.

### Vitrinite Contributions to Residues

Table II presents the proposed residue classification and disassociation mechanisms which link the residue components to their original macerals. The most diverse contribution to hydrogenation solid residues is obtained from vitrinite. The fact that this maceral exhibits a capacity to swell or contract within the temperature range of liquefaction is well documented. However, the appearance of unreacted vitrinite in these residues may present an inconsistency with the properties of vitrinite in the temperature range of liquefaction. Plate I, Figure (a) shows a particle of vitrinite containing a spore exine (sporinite) remaining in continuous-flow hydrogenation after reaction of the West Kentucky #14 feed coal at 441°C. Typically, vitrinite that may be distinguished in these residues shows some thermal contraction or expansion along bedding planes. However, the particle illustrated here attained only a slight granularity along one of its edges. The incomplete hydrogenation and apparent lack of thermal degradation of vitrinite suggests that reported reaction temperatures may not be accurate.

Plate I, Figure (b) shows two additional vitrinite-residue components formed as reaction temperatures increase to 350°C in the batch hydrogenation of the Indiana #1 Block feed coal. The appearance of a spherical morphology which is here called "vitroplast", [vitro - derived from vitrinite, refers to the original material and plast - derived from plasty (a combined form meaning from the Greek *plastos*, formed and *plassein*, to mold)] and a submicron material which will be assigned to the "granular residue" category are depicted in Table II. The term "vitroplast" describes a plastic or once-plastic thermal degradation product of vitrinite. It is characterized by flow-structure as well as the spherical morphology seen in Plate I, Figures (b), (d), and (e). Vitroplast also appears as broad (>100 $\mu$ ) isotropic areas containing inclusions of other residue components and as angular fragments. Its identification is often difficult due to its gradual transition to semi-coke.

The dissolution of vitrinite during hydrogenation is demonstrated by Plate I, Figure (c). The batch hydrogenation of the Indiana #6 feed coal at 325°C exhibits the transition from slightly thermally altered vitrinite to the vitroplast flow structure and spherical morphology referred to above. The lower reflectance of vitroplast is an indication of the disruption of the vitrinite lamellae and the resulting amorphous crystallography. Vitroplast formation may also occur during continuous-flow reaction, an example of which is illustrated in Plate I, Figure (d) (West Kentucky #14 residue at 441°C).

The granular residue seen in Plate I, Figure (b) is submicron in size (0.3-1.0 $\mu$ ), approximately spherical in shape, and appears blue and red in polarized reflected light. Its appearance on the surface of vitrinite during progressive hydrogenation resembles the genesis of micrinite from weakly reflecting vitrinite during metamorphic coalification as discussed by Teichmüller (6). Qualitative electron microprobe analyses of the submicron constituents from the continuous-flow residue of Illinois #6 coal indicate that approximately 11 percent of the particles tested were organic.

The remainder of the granular residue is consequently assumed to represent fragments of finely dispersed clay. More work is required before compositional differentiation of the submicron fraction can be achieved.

The continued degradation of vitrinite and the spherical vitroplast derived from it is seen in the development of "cenospheres". This term was first applied to structures formed as a result of rapid heating of pulverized coal by Newall and Sinnatt (7) and later by Street *et al.* (8). Cenosphere is a morphological term defined as a reticulated hollow sphere composed of ribs or frames and windows. In hydrogenation residues simple cenospheres are often observed which lack reticulate texture and the thin membranes or windows. These less complex structures are observed in the continuous-flow residue of the West Kentucky #14 feed coal (Plate I, Figure (d)). Simple cenospheres are seen in close association with the spherical vitroplast, and exhibit related morphologies. This association may be observed for more complex cenospheric structures. Plate I, Figure (e) suggests the development of gas bubbles in the interior of a vitroplast sphere from the continuous-flow residue of West Kentucky #14 coal (427°C). While in the plastic state, gases formed by thermal cracking exert sufficient pressure to cause expansion and eventually lead to the formation of a highly reticulate hollow sphere as seen in Plate I, Figure (f).

Optical observation reveals that as vitrinite is subjected to increasing reaction conditions it may swell and become plastic, forming both a fine-grained residue fraction, inert to further hydrogenation, and a plastic, low-viscosity phase (vitroplast) which is immiscible in the hydrogen-donating solvent. The granular residue constitutes a major portion (>50%) of these residues and may be considered as a semi-quantitative category composed of both inorganic and organic constituents. The vitroplast is more variable in concentration, much like the "unreacted vitrinite" category. Quantitative data will be required to distinguish whether these varying concentrations are due to characteristics of the feed coal or to the reaction conditions.

Vitroplast may not be as reactive to further hydrogenation as unaltered vitrinite, especially when the vitroplast's reflectance increases above that of the precursor vitrinite. The spherical vitroplast generally exhibits reflectances above 1.0 percent, although the reflectance level is variable. Presumably, the immiscibility of the disoriented vitrinite lamellae and a subsequent loss of internal pore structure makes hydrogenation increasingly difficult. A continued increase in temperature may affect the spherical vitroplast, causing internal thermal cracking and expansion to form cenospheres.

During hydrogenation repolymerization of the vitrinite-derived liquids may occur as a result of hydrogen starvation, temperature or pressure drops, or a critical accumulation of solids. This observation is confirmed by the presence of semi-coke formed specifically by the mesophase mechanism. Mesophase is a transient intermediate stage between a unique fluid system (liquid crystals) of high molecular weight and a solid anisotropic carbon such as semi-coke (9). The initial appearance of mesophase can be an anisotropic sphere formed by the lamellar stacking of the liquid-crystal polymers parallel to the sphere's equator. A slight increase in temperature can result in this transient phase being converted irreversibly into semi-coke. A second mode of occurrence of mesophase which is of greater significance to liquefaction processes is the adsorption of nematic liquid crystals on inert surfaces. Marsh *et al.* (10) have shown that liquid crystal (mesophase) development can occur in the carbonization of some coals and coal tar pitches, suggesting that during liquefaction, coal-derived substances can repolymerize to form liquid crystals.

The potentially deleterious effects of nematic liquid crystal nucleation during hydrogenation is seen in Plate II, Figure (a). During a continuous-flow pilot plant reaction of an Illinois #6 feed coal, liquid crystals are shown to have formed in concentric layers on the surface of an inert particle. Whether polymerization occurred

at the surface or within the surrounding fluid can only be speculation. However, as a result of lamellar stacking and subsequent development of cross-link bonding, an anisotropic nucleated carbon is formed which is inert to further hydrogenation. The development of this phase has been associated with reaction vessel coking problems.

#### Liptinite Contributions to Residues

The liptinite group of macerals includes sporinite, resinite, cutinite, and alginite. Of these, sporinite appears in low concentrations in high volatile bituminous coals. Due to the very minor concentrations of the other liptinite components, a systematic study will not be covered here.

Teichmüller (6) suggests that micrinite forms from sporinite and other liptinite macerals during the metamorphosis of coal. She contends that the genesis of spore-derived micrinite occurs only during the high volatile bituminous stage of coalification. This suggests the possibility that sporinite may break down into a granular residue constituent as well as liquid by-products during hydrogenation. Plate II, Figure (b) exhibits a megaspore exine from the Indiana #1 Block coal which, as indicated by its porous and granular surface, may be forming this granular material during the course of coalification. Plate II, Figure (c) is a photomicrograph of the remains of a microspore after batch hydrogenation of the same feed coal at 375°C. A high reflecting granular material is observed along its swollen and partially reacted central cavity. One implication is that during hydrogenation of high volatile bituminous coals, a submicron granular material may be generated from sporinite to become a possible addition to other inert constituents.

#### Inertinite Residue Contributions

The group of coal macerals known as inertinite includes fusinite, semifusinite, macrinite, and micrinite. Their inertness relative to other macerals was determined through their behavior in carbonization; however, the term "inert" does not adequately describe their properties. These macerals are considered by some to be semi-inert even in coke making (11) and the same may be true for liquefaction.

The classic study by Fisher *et al.* (4) and later work by Davis *et al.* (5) indicate that fusinite is less suitable than the other "inertinites" for hydrogenation and may in fact be totally inert during liquefaction. It is observed in moderate concentration in hydrogenation residues and is generally more abundant than in the original feed coal. The difference in fusinite concentration is a result of continuous circulation, mechanical abrasion, and accumulation in the turbulent flow of continuous-flow reactors. Fusinite is usually readily apparent in its dispersed form as high reflecting angular fragments which often exhibit remnant cell structure.

Semifusinite is transitional in reflectance, morphology, and chemistry between vitrinite and fusinite. The partial reactivity of semifusinite has been assumed for carbonization, and may be valid for the liquefaction process. The Australian Callide seam which has an unusually high concentration of semifusinite (Table I), was reacted in the batch hydrogenation system to investigate semifusinite's partial reactivity. The coal gave a 40 percent conversion at 400°C indicating the probability that components other than vitrinite and exinite were involved in the reaction. Optical examination of the Callide residue substantiated the partial reaction of semifusinite. Plate II, Figure (d) shows semifusinite with slightly rounded edges and irregularly shaped cell lumens which may have begun to close when the structure became plastic. The residue also contains a high concentration of spherical vitroplast. Since this coal has a very low vitrinite content, and noting the close association of the vitroplast with the plasticized semifusinite, it seems likely that this vitroplast has been derived from semifusinite. However, it is not possible to make a definite inference as to the source of the vitroplast. At this stage of research, the reactivity of semifusinite must be determined by empirical testing for individual coals.

Another coal constituent which is considered to be inert during carbonization is macrinite. Table I reports a high percentage of this component in the Indiana #1 Block feed coal. Batch hydrogenation of this sample at 450°C resulted in a 72 percent conversion, indicating again that some of the "inert" constituents must have reacted. Microscopic observation of the progressive reaction residues suggests that with increasing temperature, macrinite reacts and that by 425°C no distinguishable residue analog remains. By adding macrinite to the reactive constituents (vitrinite and exinite, Table I) the percentage of reactive macerals now closely corresponds to the 72 percent total conversion. As with semifusinite, the relative reactivity of macrinite must be determined empirically for each feed coal.

Another constituent present in low concentrations in this series of high volatile bituminous coals is micrinite. Due to its fine grain size (0.1-1.0 $\mu$ ), progressive hydrogenation is difficult to assess. There are physical similarities between micrinite and the granular material produced by the degradation of sporinite and weakly reflecting vitrinite during hydrogenation. However, it is not known whether there are any chemical similarities which could account for micrinite's reaction during liquefaction. As with the other members of the inertinite group, micrinite's partial reactivity must be determined empirically for each individual feed coal.

#### Carbonized Residue Constituents

The development of anisotropy in the insoluble organic constituents of hydrogenation can be extensive. Any one of the residue components described above can develop anisotropic domains and, at the same time, retain a distinctive and characteristic morphology. The cenosphere in Plate I, Figure (f) is an example. The outer wall has been carbonized to a fine-grained anisotropic mosaic. Similarly, vitroplast may develop an anisotropy depending on temperature and time. The distinction between this type of semi-coke and that produced specifically as a result of a liquid crystal formation is important, although both types of semi-coke represent a loss of reactive constituents and repolymerization. The appearance of these carbonized particles may indicate that reaction conditions were too severe, or that reactor flow was not efficient and that these particles were subjected to a longer residence time than reported.

#### Summary and Conclusions

It is evident from the preceding discussion that, as a result of optical studies of the residues obtained from progressive batch hydrogenation, insight is gained into the origin of residue components from continuous-flow liquefaction. The result of these optical studies is a classification of organic solid residues (Table II), and some understanding of the physical disintegration of coal macerals. Optical observation of these residues can also provide an alternative method of analyzing run conditions and determining product balance for continuous-flow systems.

The chemical heterogeneity of coal macerals and the various mechanisms by which these macerals disintegrate are reflected in the morphologies and phases observed in the insoluble residues. The fact that vitrinite is a complex organization of different cross-linked polymers may account for the formation of vitroplast and cenospheres rather than the slightly altered vitrinite. Optical examination of coal indicates that there are slight differences in reflectance and morphology between vitrinitic particles within the same sample. The partial reactivity of semifusinite for some coals is a further demonstration of the effects of chemical heterogeneity.

Diversity of thermal environments during liquefaction is definitely reflected by these residues. The appearance of unreacted or slightly altered vitrinite implies that thermal conditions are too low. In contrast, the occurrence of semi-coke or the development of anisotropic domains suggest more severe conditions. The variation

in reflectance of the vitroplast spherical morphologies (Plate I) may indicate that reaction temperatures are variable. The lower reflecting spheres apparently have been less thermally altered than those of higher reflectance.

Further, the classification indicates several constituents which may affect the efficient operation of continuous-flow liquefaction processes. Besides liquid crystal (mesophase) nucleation being responsible for coking during reaction, the spherical vitroplast and cenosphere components are also a potential problem. Increased concentration of these phases could detrimentally affect filtration. Their nearly spherical shape could lead to a very tight packing during filtration, resulting in decreased filtration rate.

The potential of residue microscopy is not yet fully realized. However, by classification of the organic and inorganic constituents, a means of systems product balance may be developed. Comparison of quantitative point-count data derived from this classification should also aid in determining the "optimum-yield" run conditions.

#### Acknowledgments

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TABLE I  
PETROGRAPHIC ANALYSIS OF FEED COALS

Sample No.	Method of Hydrogenation	Seam	State	Macerals, Vol. %							
				Vit.	Fus.	Sf.	Mac.	Mic.	Ex.	Res.	Cut.
PS0C-106	Exp.*	Indiana #1 Block	Ind.	25	10	12	21	6	23	2	1
PS0C-280	Exp.	Indiana #6 Seam	Ind.	92	1	1	0	3	2	1	0
PS0C-303	Exp.	Callide Seam	Queensland, Australia	15	4	73	1	2	2	0.2	3
POC-288	Continuous-Flow**	W. Ky. #14 Seam	Ky.	74	3	5	3	13	2	0	0
POC-289	Continuous-Flow	Ill. #6 Seam	Ill.	91	5	2	0	1	1	0	0

\* Experimental batch-hydrogenation  
 \*\* Continuous-flow reaction

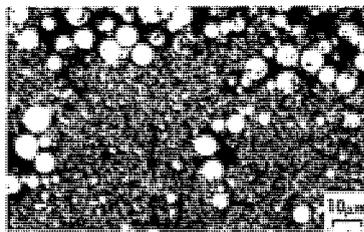
Vit. - vitrinite    Sf. - semifusinite    Mic. - micrinite    Res. - resinite  
 Fus. - fusinite    Mac. - macrinite    Ex. - exinite    Cut. - cutinite

TABLE II  
BEHAVIOR OF COAL ORGANIC CONSTITUENTS DURING LIQUEFACTION

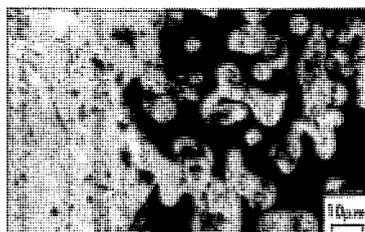
Maceral Precursor	Disassociation Mechanisms	Organic Residue Components
Vitrinite	Slightly altered vitrinite (contracted and/or swollen) Granular residue Vitroplast (high molecular weight) → cenosphere Vitroplast (intermediate molecular weight) → vitroplast Hydrogenated Product (repolymersized) → liquid-crystal ± mesophase → semi-coke	Unreacted vitrinite Granular residue Cenosphere Vitroplast Semi-coke
Fusinite	No observable mechanism	Fusinite
Semifusinite	Possible fractional contribution, mechanism similar to vitroplast	Semifusinite or semi-coke
Macrinite	Possible fractional contribution, mechanism unknown	Unknown
Exinite	Fractional contribution of submicron granular material	Granular residue



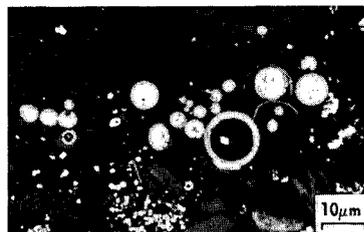
(a)



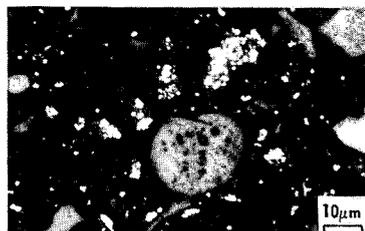
(b)



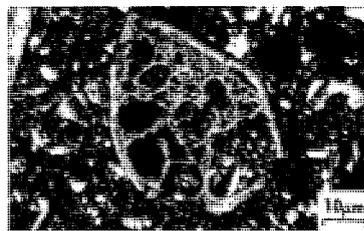
(c)



(d)



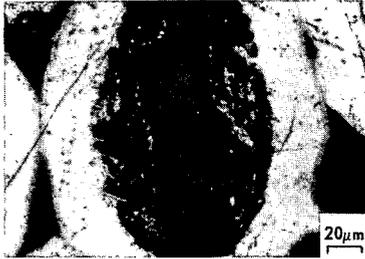
(e)



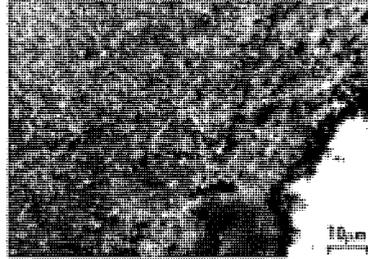
(f)

#### PLATE I: PHOTOMICROGRAPHS OF HYDROGENATION RESIDUES

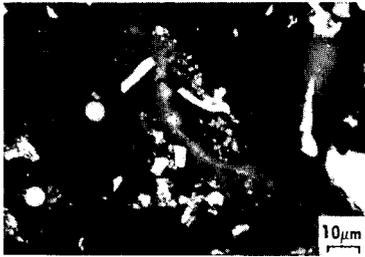
- Figure (a). Unreacted vitrinite containing sporinite from continuous-flow reaction of the West Kentucky #14 (441°C).
- Figure (b). Vitroplast and granular residue produced in batch hydrogenation of Indiana #1 Block at 325°C.
- Figure (c). Vitrinite plasticity and the formation of vitroplost at 325°C, after batch hydrogenation of Indiana #6 seam.
- Figure (d). Vitroplast and a simple cenosphere in the West Kentucky #14 residue (441°C, continuous-flow reactor).
- Figure (e). Vitroplast exhibiting gas bubble generation as a prelude to cenosphere formation. Continuous-flow reaction of West Kentucky #14 (427°C).
- Figure (f). Highly reticulate cenosphere with carbonized outer wall. Continuous flow reaction of the West Kentucky #14 at 441°C.



(a)



(b)



(c)



(d)

**PLATE II: PHOTOMICROGRAPHS OF HYDROGENATION RESIDUES**

- Figure (a). The effect of liquid crystal (mesophase) nucleation on calcite causing semi-coke formation. Pilot plant continuous-flow reaction of Illinois #6 feed coal at 446°C.
- Figure (b). Sporinite observed in the Indiana #1 Block feed coal, showing signs of disintegration during normal coalification.
- Figure (c). Remnant microspore exhibiting granular residue formation in the 375°C batch hydrogenation residue of the Indiana #1 Block.
- Figure (d). The apparent plasticity and partial reaction of semifusinite from the 400°C batch hydrogenation run using the Austroliion Callide seam.

## PRELIMINARY EXAMINATION OF COAL LIQUEFACTION PRODUCTS

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### INTRODUCTION

The three direct general processes for converting coals to liquid fuels are: catalyzed hydrogenation, staged pyrolysis, and solvent refining (1,2). Each of these processes results in the production of a coal liquid which contains a variety of desirable and undesirable components. The desirable coal liquids are the oils-saturated and aromatic hydrocarbons plus nonpolar nonhydrocarbons, and the resins-polar nonhydrocarbons. The undesirable species are the asphaltenes and the carbene-high molecular weight highly aromatic solids, and the carboids-polymerized coke-like materials. The undesirable elements: metals, sulfur, nitrogen, and oxygen are generally present in higher concentration in the asphaltene and carboid fractions. Under hydrogenolysis conditions, the conversion of coal to oil has been suggested to proceed via the following sequence (3): Coal  $\rightarrow$  Asphaltene  $\rightarrow$  Oil. Therefore, asphaltene generation and elimination are of great importance in the liquefaction process. A study of the chemical and physical properties of asphaltenes may lead to the discovery of ways to reduce or eliminate asphaltene build-up in coal liquids and to thereby increase the yields of desirable coal liquefaction products. In this work, coal liquids from representative liquefaction processes have been separated by solvent fractionation, and the fractions are being examined by various analytical and physical techniques. Particular attention is being directed toward asphaltene separation, purification and characterization.

### RESULTS AND DISCUSSION

A solvent fractionation scheme for separating coal liquid products into five fractions (oil, resin, asphaltene, carbene, and carboid) is shown in Figure 1. Representative coal liquid samples produced via the three direct coal liquefaction processes were separated into the five fractions described above. The results are presented in Figure 2. For the catalyzed hydrogenation product produced in the Synthoil process (4), the product composition is about 61% oil, 22% resin, 13% asphaltene, 0.6% carbene, and 3% carboid. The staged pyrolysis filtered product\* from the FMC Corporation's COED process (5) has a product composition of about 26% oil, 48% resin, 15% asphaltene, 1% carbene and 10% carboid. The solvent refined coal (SRC) produced by Catalytic Inc. based on PAMCO's SRC process (6) affords about 4% oil, 15% resin, 45% asphaltene, 2% carbene, and 34% carboid. The results found in this work are in good agreement with those reported recently for solvent fractionation of a Synthoil catalytic hydrogenation product, and a non-catalytic SRC product (7). These workers found for a Synthoil product, 80% pentane soluble material, 15% of pentane insoluble and benzene or toluene soluble material, and 5% of benzene insoluble material. For an SRC product they found 20%, 46% and 34% respectively for the above three fractions. They found their benzene insoluble fraction to be pyridine soluble, and named this fraction 'pre-asphaltene' in the belief that it might be intermediate between coal and classical asphaltene. We feel, however, that the benzene insoluble fractions may arise from reactive coal depolymerization moieties which are not stabilized by hydrogenation, but are repolymerized into materials more difficult to degrade than the original coal substance. More work will have to be done

\*The filtered product is the pyrolysis product produced prior to the final hydro-treating reaction. The FMC-COED Syncrude produced by hydrotreating the filtered product at 3100psi, 775°F consists of about 99% oil, 0.8% resin, and 0.2% asphaltene.

to elucidate the origin of this fraction.

The analyses of the starting coal liquids and the various solvent fractions are given in Tables I, II, and III. Semiquantitative Metal Analyses are presented in Table IV. It may be seen that heteroatoms and metals are generally concentrated in the asphaltene and carboid fractions.

TABLE I. - Synthoil Solvent Fractions Ultimate Analysis, %\*

Fraction	C	H	N	S	O**	Ash	MW***
Coal liquid	87.26	8.44	0.94	0.10	3.26	0.69	
Oil	87.74	9.58	0.60	0.43	1.65	0.02	260
Resin	87.27	7.77	1.30	0.14	3.52	0.30	
Asphaltene	87.27	6.51	1.63	0.66	3.93	0.48	738
Carbene	87.96	5.94	1.72	0.74	3.64	0.56	
Carboid	88.32	5.69	1.64	2.07	2.28	8.80	

\*Moisture and ash free

\*\*By difference

\*\*\*VPO in benzene

TABLE II. - FMC-COED Solvent Fractions Ultimate Analysis, %\*, MW

Fraction	C	H	N	S	O**	Ash	MW***
Coal liquid	83.04	7.68	1.09	1.11	7.08	0.28	
Oil	85.88	9.75	0.42	1.08	2.87	0.01	310
Resin	83.25	7.25	1.06	1.26	7.18	0.39	
Asphaltene	82.14	6.47	1.70	2.58	7.11	0.79	458
Carbene	81.17	6.01	1.69	1.31	9.82	0.11	
Carboid	78.47	5.65	1.95	1.85	12.08	1.31	

\*Moisture and ash free

\*\*By difference

\*\*\*VPO in benzene

TABLE III. - Cat. Inc. SRC Solvent Fractions Ultimate Analysis, %\*

Fraction	C	H	N	S	O**	Ash	MW***
Coal liquid	88.71	5.53	1.26	0.19	4.31	0.29	
Oil	90.99	6.94	0.41	0.57	1.09	0.25	
Resin	89.88	6.64	0.84	0.00	2.64	0.05	
Asphaltene	88.79	5.61	1.25	0.12	4.23	0.78	747
Carbene	89.77	5.03	1.11	0.26	3.83	0.40	
Carboid	87.08	4.70	0.96	0.34	6.92	0.71	

\*Moisture and ash free

\*\*By difference

\*\*\*VPO in benzene

TABLE IV. - Semiquantitative Metal Analysis\*

Major Elements	Synthoil		FMC-COED		Cat, Inc, SRC	
	Asphaltene	Benzene Insoluble	Asphaltene	Benzene Insoluble	Asphaltene	Benzene Insoluble
Si	180	1800	210	100	55	130
Fe	130	420	20	270	7	58
Al	8	760	57	140	6	420
Ti	69	130	12	10	1	71
B	60	77	81	72	5	18
Ca	3	69	39	280	26	96
Mg	1	29	5	14	10	140

\*Results in ppm

Table V. shows the color indices (8) (integrated absorption of a species between 750nm and 400nm) of the various solvent fractions for different coal liquids. Since the color index of an aromatic molecule is a function of the size of the aromatic  $\pi$ -system, it appears reasonable to assume that the increase in the color indices in going from oil, to resin to asphaltene to carbene, reflects an increase in the size of the respective  $\pi$ -systems. The color indices and molecular weights of the carboid fractions have not been determined yet. However, as they are the darkest and most insoluble of the fractions it is expected that they will exhibit high color indices and molecular weights.

TABLE V. - Color Indices, I\* of Solvent Fractions

Fraction	Synthoil	FMC-COED	Cat, Inc, SRC
Oil	0.1	0.1	0.4
Resin	1.7	1.8	1.5
Asphaltene	12.7	4.1	16.6
Carbene	24.7	5.3	48.5
Carboid	-	-	-

$$*I = \int_{400\text{nm}}^{750\text{nm}} \text{Ad}\lambda \text{ in THF}$$

Tables VI, and VII show the carbon aromaticities,  $f_a$  (9) and the hydrogen percentages by proton type (10) for asphaltenes produced in the different processes. Carbon aromaticities are found to be similar in the preliminary measurements.

The solvent refined coals yield asphaltenes which contain a higher percentage of aromatic protons relative to benzyl and saturated protons than do the other types of liquefied coals.

Asphaltenes produced in the Synthoil process have been reported to consist of acidic and basic components (11). These components have been separated by treating the asphaltenes, dissolved in toluene, with dry HCl gas. The basic component precipitates as an HCl adduct in 57% yield, and the acidic and neutral components (43%) remain in solution. In this work we have further separated asphaltenes into two major fractions by solvent elution chromatography. The two major fractions obtained by elution from silica gel with benzene and diethyl ether have different properties although they both may be freeze-dried to brown powders from benzene solutions.

Table VIII, gives the total weight % asphaltenes recovered, and the % distribution of asphaltenes obtained using the eluents benzene and diethyl ether. Table IX, compares the color indices of the solvent eluted fractions with those of the starting asphaltenes. The color indices for all the diethyl ether-eluted fractions are lower than either the starting asphaltenes or the benzene-eluted asphaltenes. This suggests

TABLE VI. - X-Ray Carbon Aromaticity,  $f_a^*$ 

Samples	Asphaltene	Benzene Fraction	Diethyl Ether Fraction
Synthoil	0.49	0.43	0.39
FMC-COED	0.45	0.43	0.41
PAMCO SRC	0.48	0.48	0.52

$$*f_a = C_A/C_{total} = A_{002}/A_{002} + A_r$$

$C_A$  = number of aromatic carbons

$C_{total}$  = number of total carbons

$A_{002}$  = area under peak for aromatic carbons

$A_r$  = area under peak for saturated carbons

TABLE VII. - NMR H-Percentages By Proton Type\*

Asphaltene	$H_{aromatic}$	$H_{benzyl}^{**}$	$H_{sat}^{**}$
Synthoil	33	42	25
FMC-COED	37	43	20
Cat. Inc. SRC	50	34	16
PAMCO SRC	45	38	17

\*Run on Varian T-60 NMR, Solvent 99.8%  $DCCl_3$  + 1% TMS

\*\*Separation point between  $H_{benzyl}$  and  $H_{sat}$  chosen at  $\tau = 8.27$

TABLE VIII. - Silica Gel Chromatography of Asphaltenes

Asphaltene Sample	Total Wt % Recovered	Wt % with Solvent	
		Benzene	Diethyl Ether
Synthoil	84	57	43
FMC-COED	88	38	62
Cat. Inc. SRC	89	66	34
PAMCO SRC	88	51	49

a less extensive  $\pi$ -aromatic structure in these fractions. A comparison of the analyses and molecular weights of the various silica gel chromatography fractions is presented in Table X. The H/C ratios are highest in the diethyl ether-eluted fractions suggesting relatively more aliphatic carbons in this fraction. Table VI also indicates the aromaticity of the diethyl ether fraction is generally lower than the benzene fraction, except the PAMCO sample which could be due to some odd effect. The percentages of the heteroatoms nitrogen and oxygen are also appreciably greater in the diethyl ether-eluted fractions. These results are consistent with the acidic nature of silica gel, and the expectation that silica gel would preferentially adsorb basic molecules. This suggests that silica gel chromatography may provide a mild, chlorine-free procedure for separating asphaltenes into basic and non-basic components.

Actually, the words 'acid' and 'base' as reported by Sternberg et al. (11,7) do not adequately classify or clarify the coal-derived asphaltene. We would suggest acceptor ( $\pi$ -deficient) and donor ( $\pi$ -abundant), since their association and the nature of charge transfer is well known in asphaltene (12). The asphaltene thus formed is a complex and not as a salt in the sense of ionizable species of acid or base. We feel the benzene-eluted fraction could be neutral, the ethyl ether-eluted fraction polar, and by properly selecting adequate solvent, another more polar fraction can also be obtained. All these phenomena can be explained on the basis of charge-transfer. Actually, the existence of different degrees of association of this charge-transfer makes the task of separation of asphaltene difficult.

TABLE IX. - Color Indices, I\*, of Silica Gel Fractions

Sample	Asphaltene	Eluent	
		Benzene	Diethyl Ether
Synthoil	12.7	12.1	8.2
FMC-COED	4.1	5.1	3.5
Cat. Inc. SRC	16.6	13.4	10.7
PAMCO SRC	10.4	9.4	8.8

$$*I = \int_{400\text{nm}}^{750\text{nm}} \text{Ad}\lambda \text{ in THF.}$$

TABLE X. - Silica Gel Chromatography Fractions Ultimate Analysis, %\*, and MW

Sample	C	H	N	S	O**	Ash	MW***
Synthoil Asph.	87.27	6.51	1.64	0.66	3.92	0.48	738
Benzene	89.15	6.57	0.58	0.99	2.71	0.97	614
Diethyl Ether	85.17	6.86	1.60	0.73	5.64	1.19	560
FMC-COED Asph.	82.14	6.47	1.70	2.58	7.11	0.79	458
Benzene	83.83	6.30	1.06	1.93	6.88	1.38	445
Diethyl Ether	79.67	6.48	1.54	1.33	10.98	1.23	340
Cat. Inc. Asph.	88.80	5.61	1.25	0.12	4.22	0.78	747
Benzene	87.66	6.40	0.65	0.65	4.64	1.01	467
Diethyl Ether	84.73	6.33	1.67	0.79	6.48	1.78	490
PAMCO Asph.	86.33	6.15	1.47	1.13	4.92	1.50	432
Benzene	87.27	6.20	0.68	1.20	4.65	1.83	421
Diethyl Ether	83.00	6.52	1.99	1.01	7.48	2.03	465

\*Moisture and Ash free

\*\*By difference

\*\*\*VPO in Benzene

## SUMMARY

A preliminary examination of coal liquefaction products from four different coal liquefaction processes has been carried out. Each coal liquid has been separated into five different fractions by solvent fractionation. Total recoveries ranging from 93 to 97% by weight have been obtained. These solvent fractions are respectively: oil, resin, asphaltene, carbene, and carboid. We have further separated the asphaltene fraction by utilization of solvent elution chromatography with silica gel, into two fractions of different polarities. Unlike the asphaltene separation method described by Sternberg et al. (11), which gives a high chlorine content (4.1-4.5%), the present method does not chemically alter the asphaltenes.

## ACKNOWLEDGEMENTS

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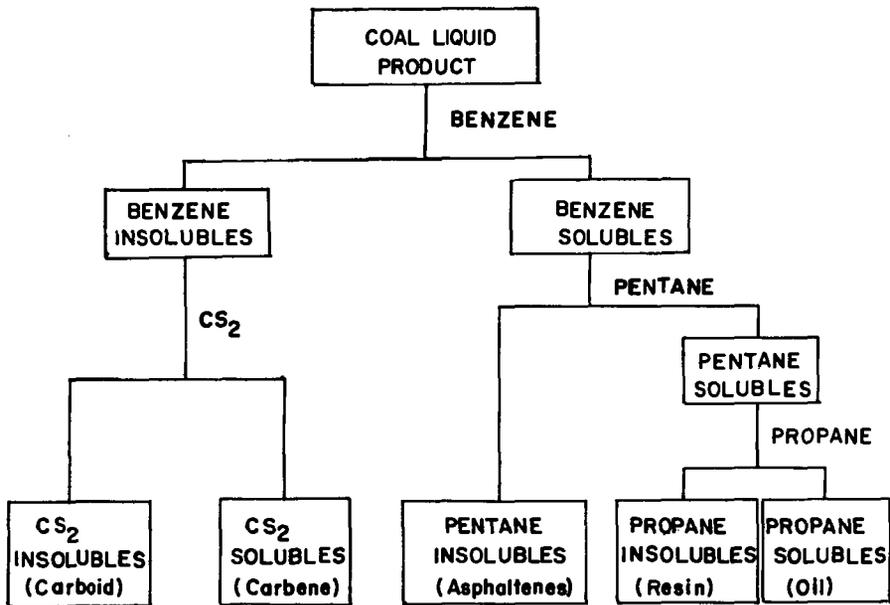


FIGURE 1 SOLVENT FRACTIONATION SCHEME FOR COAL LIQUID PRODUCT

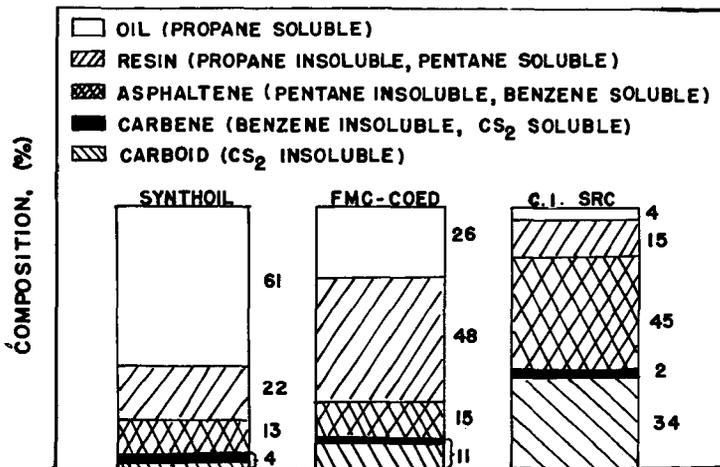


FIGURE 2 SOLVENT FRACTIONATION ANALYSIS OF COAL LIQUID PRODUCTS

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PRODUCTS FROM TWO-STEP COAL LIQUEFACTION  
USING THREE DIFFERENT FIRST-STEP REACTOR PACKINGS

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INTRODUCTION

In the current work, laboratory-scale batch and flow studies have been conducted with various nominally non-catalytic materials as reactor packing for the first-step of a two-step coal hydroliquefaction process being studied at the Morgantown Energy Research Center's Liquid Fuels Research and Development Branch. An examination of the available literature on some three dozen coal liquefaction processes gave no evidence for any previous studies along these lines. Several of the processes have been compared in review articles (1, 2).

The process studied is a two-step coal/recycle oil slurry-feed hydroliquefaction process, with removal of solid residue between the two steps, in which the second-step catalytic reactor is preceded by a first-step reactor containing a nominally non-catalytic material selected for its ability to induce desirable hydrolytic reactions. These reactions are principally the conversion of asphaltene intermediates from the coal feed to oils and/or to asphaltenes of higher hydrogen content. Unconverted asphaltenes will likely result in coke formation in the catalytic reactor, greatly reducing catalyst activity and selectivity. Hydrolytic treatment (thermally induced dissociation or disproportionation of hydrogen) of petroleum residues, before a catalytic desulfurization, is designed to break down the less thermally stable asphaltic compounds so as to give less coke formation on the desulfurization catalyst (3). The presence of a high surface area carbonaceous material apparently accelerates the desired reactions, as in the "Combifining" process in which asphaltic compounds are treated with hydrogen at 30 atm in a fluidized-bed of petroleum coke at 380-410° C (4). The deactivation effect of coal asphaltenes is reduced by hydrolytic splitting on the surface of semi-coke dust (5). Pore diameters between 100 and 1,000 Ångstroms, and larger, appear necessary to allow free access of asphaltenes for their conversion. Conversely, when only small diameter pores are present, asphaltenes are reported to block the pores and the material is rapidly deactivated (6).

The material desired as first-step reactor packing for the process studies must, therefore, in consideration of the pertinent literature, have a moderate surface area with a surface structure allowing or promoting carbon deposition, high porosity, and large pores (0.1 micron, or larger). A nominally non-catalytic material is indicated, to restrict surface reactions to those induced by a carbonaceous deposit. This would appear to rule out silica-alumina and possibly gamma-alumina, while allowing alpha-alumina and silica. Vitrified ceramics would apparently not offer sufficient surface area or porosity, although they are nominally non-catalytic for this reason.

Dissolution of the coal in the first-step reactors allows separation of the mineral residues. Although coal minerals have been suspected to have substantial coal-liquefaction catalytic behavior (7), these same minerals, or trace metals in them, act as strong poisons for hydrogenation catalysts (8). In addition, the sub-micron, clay-derived mineral residues plug the pores of

the catalyst. Massive plugging between catalyst pellets occurs when the mineral residues settle out. In the initial developmental work on the Synthoil Process for making low-sulfur fuel oil from coal it was demonstrated that this type of plugging could be prevented by a highly turbulent flow of hydrogen through the catalyst bed (9). However, if the density of the product oil is reduced from that of a fuel oil to that of a kerosine and gasoline rich product, massive plugging occurs even with highly turbulent hydrogen flow, because the light kerosine and gasoline flash off into the gas phase, leaving insufficient liquid vehicle to carry residual solids through the fixed bed.

By introducing an effective hydroxyprolytic step followed by separation of the mineral matter, the catalyst, such as the widely used cobalt molybdate catalysts on silica-promoted alumina supports, can have a longer life, and can be used at the milder temperatures and pressures for which they were designed, rather than at more rigorous conditions necessary for trying to maintain some degree of activity.

With regard to pressure, as the hydrogen pressure increases, there is a maximum in the overall yield of hydrocracking product (10). In a two-step coal hydrocarbonization-tar vapor catalytic hydrogenation laboratory-scale study, the maximum yield of product was obtained at a hydrogen pressure of 40 atm (11). With an increase in temperature above 400° C, thermal splitting by a free radical mechanism starts to be significant, leading to the formation of coke-like materials. High hydrogen pressures will reduce coking to some extent, but are economically unfavorable, while resulting in decreased yield of liquid product. At 375°-400° C and 1,500 psig, catalytic hydrogenation of a low-temperature coal tar gave a product with high aliphatic character and a high diesel index (12).

## EXPERIMENTAL

### Stirred Batch Reactor Runs

Coal-oil slurries were made up with one part by weight of run of mine coal (Pittsburgh No. 8 seam, Ireland mine, 33.06 weight percent volatile matter, 0.72 weight percent moisture, 19.51 weight percent high-temperature ash, carbon 60.42, hydrogen 4.32, nitrogen 0.92, oxygen 7.96, and sulfur 4.62 weight percent, all by analysis) and two parts of hydrogenated Reilly tar oil. This hydrogenated oil was prepared in a one-gallon stirred batch reactor with hydrogen gas at 390° C and 1,800 psig for three hours, using about 1,800 ml oil and about 32 g presulfided cobalt molybdate on silica-promoted alumina 1/8-inch pellets (Harshaw CoMo-0402T 1/8") in two baskets attached to the stirrer, as shown in figure 1. The catalyst was presulfided in situ with a flow of 10-15 percent hydrogen sulfide in hydrogen at 3-4 liters per hour per 100 g catalyst for 1.5 hours at 400° C and atmospheric pressure. Gas chromatographic/mass spectrometric analysis showed about 20 percent identifiable hydroaromatics, or hydrogen donors, in the hydrogenated oil, compared to none in the original oil. The identities of these are discussed under Results.

These coal/oil slurries were examined for their behavior over two different kinds of packing that could be tried in the first-step reactor of the two-step process. These were a vitrified ceramic (Norton "Denstone 57" catalyst bed support,<sup>1/</sup> consisting of 1/4-inch balls having a silica content of 56.4 weight percent, with a surface area of about 0.01 m<sup>2</sup>/g and a very low porosity),

<sup>1/</sup> Use of trade names or company names is for identification only and does not imply endorsement by ERDA.

and alpha-alumina (Girdler catalyst carrier T-375, consisting of 1/8-inch pellets having a silica content of only 0.02 weight percent, with a surface area of about 5.3 m<sup>2</sup>/g, and 0.06-0.8 micron pores). A series of runs was made in a one-gallon stirred batch reactor, using 36.15 g of "Denstone" or alpha-alumina in two baskets attached to the stirrer, and about 900 g slurry at 450° C and 1,800 psig for three hours, or about 1,800 g slurry at 430° C and 1,500 psig for three hours, the reactor being brought up to the desired pressure with hydrogen gas. Air was flushed from the system with nitrogen gas and nitrogen purged from the system with hydrogen gas before partial pressurizing, heating, and then any final pressurizing. As hydrogen was consumed the pressure was maintained with additional hydrogen.

Half of each first-step product from all runs was filtered to remove mineral residue, and the filtered and unfiltered portions were then hydrogenated over the same catalyst used to prepare the hydrogenated tar oil (Harshaw CoMo-0402T 1/8"). The second-step run conditions for all eight runs were identical, namely, 1,500 psig (achieved with hydrogen gas) at 380° C for one hour in a one-gallon stirred reactor, using about 200 g feed and 0.4 g presulfided cobalt molybdate on silica-promoted alumina in two baskets attached to the stirrer. The quantity of catalyst was chosen to approximate 500 hours operation at a liquid hourly space velocity of one in a fixed bed process.

The products were analyzed by 1) solvent extraction to recover benzene insolubles, asphaltenes (benzene-soluble, cyclohexane-insoluble), and oils (cyclohexane-soluble); 2) liquid elution chromatography of the oils from activated alumina with cyclohexane and benzene (to remove colored resins); 3) gas chromatographic mass spectrometric analysis of the cleaned oil to identify and quantify individual compounds; 4) elemental analysis for determination of the atomic hydrogen-to-carbon ratio in various samples; 5) gas chromatographic analysis of the gaseous products for the amounts of the individual hydrocarbons; and 6) physical property determinations (density and distillation curves) on the filtered products. Differences due to different operators, procedures, or equipment were avoided. The separation procedures were similar to those previously used for analysis of low-temperature coal tars (13).

#### 0.2 Pounds Coal/Hour Flow System

A schematic flow diagram of this system is detailed in figure 2. Interchangeable reactors packed for either first-step runs, or with catalyst for second-step runs, were used in the clam shell heaters. This laboratory-scale equipment was used in a run of nearly 48 hours duration to prepare about five gallons of hydrogenated tar oil for slurry preparation. The Reilly tar oil was fed at a rate of about 375 ml/hr (LHSV=1.4) through presulfided cobalt molybdate on silica-promoted alumina at 380° C and 1,500 psig hydrogen. Product sample collected at 44 hours analyzed for 26.26 weight percent hydroaromatics, while the hydrogen donor content for the composite five gallon product was 26.88 weight percent, showing no significant decline in catalyst activity over about 48 hours operation. The tar oil feed contained no hydrogen donors.

Hydropyrolytic first-step runs were made in the same reactor (1-inch, schedule 80, 304 stainless steel pipe), with the first seven inches packed with 1/2-inch lengths of 1/4-inch O.D. 304 stainless steel tubing and the remaining 21 inches packed with either 1/8-inch alpha-alumina pellets, or a 99.5 weight percent alpha-quartz packing (Girdler catalyst carrier T-1571, consisting of 3/16-inch silica spheres with a surface area of about 131 m<sup>2</sup>/g, and 1-18 micron pores). The total volume of the reactor was 270 ml. The slurry feed was made

from one part by weight of 70 percent minus 200 mesh, 100 percent minus 100 mesh, Ireland Mine coal (Pittsburgh No. 8 seam), and three parts of the hydrogenated Reilly tar oil, made as described above. The slurry was fed at a rate between 245 and 375 g/hr at 440° C, 1,500 psig, and a hydrogen flow rate of about 7.0 scfh. Total run time with each first-step packing was nearly 16 hours. The faster feed rate for the bed packed with spheres compensated for the larger void volume for the spheres.

The products from both runs were filtered to remove mineral residue, and the residue washed with benzene to remove adhering oil, dried, and weighed. The filtered products were then subjected to catalytic hydrogenation in the second-step reactor under conditions essentially the same as those used to prepare the hydrogenated tar oil. The second-step reactor was identical to the first-step reactor, except for the packing, which was entirely sulfided cobalt molybdate on silica-promoted alumina. The liquid feed was introduced at a rate between 250 and 350 g/hr at 380° C, 1,500 psig, and a hydrogen flow rate of about 7.0 scfh. Total run time was up to about 11 hours.

## RESULTS AND DISCUSSION

### Stirred Batch Reactor Runs

Mass, hydrogen, and carbon balances for the stirred batch reactor runs, including data on the four first-step runs and the four corresponding second-step runs with unfiltered first-step product as feed, are presented in tables 1 through 3. The process conditions for all stirred batch reactor runs are summarized in table 4.

Mass balances varied between 90.4 and 99.6 percent, with an average of 96.7 percent. Six of the eight runs had mass balances between 97.7 and 99.6 percent. Ammonia, hydrogen sulfide, and water were determined by calculating the decrease in elemental nitrogen, sulfur, and oxygen in going from solids and liquids in the feed to those in the product, and converting to the equivalent weights of the three compounds. Essentially all the water, and nearly all of the hydrogen sulfide, were evolved in the first-step runs. The alpha-alumina appeared to favor a greater production of water and hydrogen sulfide than the Denstone vitrified ceramic, except for hydrogen sulfide at the more rigorous conditions.

Hydrogen balances varied between 93.5 and 108.6 percent, with five of the eight runs between 98.7 and 103.8 percent. Hydrogen usage was estimated from the pressure gauges on the cylinder regulators, but temperature variations restricted the accuracy of this approach because the cylinders were mounted outside the high pressure cell building. A better estimate of hydrogen usage was obtained by assuming a balance of 100 percent and correcting the grams H<sub>2</sub> gas in, accordingly. The gas chromatographic analyses of product gases showed that the alpha-alumina favored a greater production of hydrocarbon gases than the Denstone vitrified ceramic. This coupled with the greater production of H<sub>2</sub>O and H<sub>2</sub>S would be expected to require a greater consumption of hydrogen with alpha-alumina. The corrected values for grams H<sub>2</sub> gas in come much closer to showing this than the uncorrected values, which appear to be generally unreliable.

Carbon balances varied between 90.5 and 106.9 percent, with half the values between 97.1 and 106 percent. The amounts of CO and CO<sub>2</sub> in the product gases from the first-step runs appeared to be somewhat high compared to the previous work, and may account for the 104.5 to 106.9 percent carbon recoveries for the first-step runs, as opposed to the 90.5 to 99 percent recoveries for the second-step runs.

The mass, hydrogen, and carbon balances for the stirred batch reactor runs fall within the range of values generally found for such laboratory-scale operations.

The results of the solvent extraction analysis of the products from the stirred batch reactor runs are summarized for all eight runs in table 4, with the data for the paired "Denstone" and alpha-alumina first-step reactor materials placed together for ease of comparison. A large, but noncalculable, part of the oils comes directly from the compounds in the oil used to make the coal/oil slurry, while the rest of the oil comes from hydroliquefaction of the coal and the asphaltic constituents. Assuming that the lowest oil yield from the coal was only about one percent, with almost 90 percent recovery of vehicle oil (10 percent conversion to gas and light oils), it can be seen that in most instances the amount of oils was increased from 20 percent to as much as three-fold by using alpha-alumina instead of vitrified ceramic. In one instance, even though the oil yields were essentially the same, the atomic hydrogen-to-carbon ratio for the alpha-alumina-derived oil was much higher, as shown later, demonstrating a higher total hydrogen gain for the alpha-alumina-derived oil.

In line with the larger amounts of coal-derived oil, using the alpha-alumina, larger amounts of identifiable coal-derived compounds were obtained (table 5), with the compounds arranged according to increasing boiling point. These six compounds are all polycyclic aromatic hydrocarbons which were not detectable in the hydrogenated tar oil, and therefore probably came from the coal via the asphaltenes. The slightly lower concentration at the higher temperature and pressure may be explained by the dilution with a little more of other coal-derived compounds. There was about 50 or 60 percent more coal-derived, or more correctly, asphaltene-derived compounds in the second-step product oil using first-step product from the alpha-alumina bed as feed. Possibly this is because this feed did not deactivate the cobalt molybdate catalyst as much as the first-step product from the vitrified ceramic.

The higher activity of alpha-alumina for producing low-boiling hydrocarbons directly from coal or asphaltenes was also demonstrated by the gaseous hydrocarbons collected during the first-step runs. The volume of methane, ethane, propane, and butanes per pound of coal was in each instance greater for each hydrocarbon compound when using alpha-alumina (table 6). The yields of hydrocarbon gas are also greater at 450° C than at 430° C, because this is the temperature range in which bituminous coals show a rapid increase in thermal decomposition. The greater yields of hydrocarbon gas with alpha-alumina are not due to increased dealkylation of alkylated polycyclics in the oil (table 5). In fact, somewhat greater yields of alkylated compounds were obtained at both operating temperatures, using alpha-alumina.

The yields of asphaltenes (table 4) were less with alpha-alumina, generally down to about one-half the quantity obtained with the vitrified ceramic. In the one instance in which the yields were close, the atomic hydrogen-to-carbon ratio was substantially higher for the alpha-alumina-derived asphaltene (table 7). Under both of the first-step run conditions the atomic hydrogen-to-carbon ratios for the asphaltenes were clearly higher using alpha-alumina, as shown in table 7. In one instance, the oil derived in the presence of alpha-alumina was distinctly higher in atomic H/C. In the other, the two oils had nearly identical values of atomic H/C. The yield of oil in the latter was greater with alpha-alumina (table 4), demonstrating a higher total hydrogen uptake.

The total amounts of nine important classes of alkylated polycyclic aromatics were greater for the products obtained using alpha-alumina (table 5), under both first-step run conditions. Larger amounts were obtained with both

first-step materials at the more rigorous conditions, due to more reaction of the coal, and the percent increase for alpha-alumina was considerably greater.

The identities and amounts of the eight identifiable hydroaromatics, or hydrogen donors, in the hydrogenated tar oil used to make up the slurry for the stirred batch reactor runs are shown in table 8. Analysis of the oil in the two different first-step products showed nearly double the consumption of hydrogen donors in the presence of alpha-alumina, compared to the vitrified ceramic.

It is possible that the much greater surface area and pore volume of the alpha-alumina compared to the vitrified ceramic could offer more carbonaceous surface for the hydrogen donors to react. Examination of the spent materials visually, and by scanning electron microscopy, showed that a black, carbonaceous deposit covered the exterior of the ceramic balls, but extended throughout the interior of the alpha-alumina pellets.

In all instances, the presence of mineral residue in the second-step reactor gave improved results (table 4) as regards decreased yields of asphaltenes and increased yields of oils. As mentioned in the Introduction, this apparent advantage is outweighed by several serious disadvantages.

Because the slurry feed to the stirred batch reactor runs was 67 percent by weight of hydrogenated tar oil, the distillation curves to a final boiling point of 495° C of the first-step products and the vehicle oils were rather similar. However, some differences were evident which reflected the differences in activity of the two different reactor packings and the two different reactor conditions, as shown in table 9. The largest cut, the median boiling diesel oil fraction, was essentially identical for the two tar oils and three of the four products. The fourth product, obtained with the alpha-alumina packing under the rigorous conditions, showed a substantial decrease in this major fraction, with a corresponding substantial increase in the lowest molecular weight fraction, the gasoline cut. At the milder conditions, there was only a little more gasoline range fraction with the alpha-alumina packing than with the vitrified ceramic packing, and as expected both packings gave substantially less gasoline cut than under the more rigorous conditions.

#### 0.2 Pounds Coal/Hour Flow System

The process conditions for all flow reactor runs, the results of the first-step product filtration, the solvent extraction analysis, and the product gas analysis are summarized for all four runs in table 10. The residue filtered off from the first-step products, after washing with benzene to remove adsorbed oil, essentially equalled the calculated mineral matter in the coal feed, demonstrating essentially complete dissolution of the organic part of the coal. The benzene insolubles in the filtered product from the silica balls was more than twice that from the alpha-alumina pellets.

The total yield of total hydrocarbon gases from the alpha-alumina bed reactor was nearly four times that from the silica bed reactor. Conversely, there was a nearly fourfold greater yield of hydrocarbon gases from the catalytic reactor, using the silica bed product as feed. Thus, most of the hydrocracking to give gas occurs in the alpha-alumina bed, where the concomitant carbon deposit formation does little harm, whereas a little over half of the gas formation occurs in the catalytic bed used after the silica bed, where carbon deposits are undesirable. The conversion of benzene insolubles to asphaltenes in this catalytic bed may be undesirable for similar reasons. The residence time for the liquid phase in the first-step reactor was estimated to be less than 20

minutes, compared to a residence time (not the time of contact with the packing in the baskets) of three hours in the stirred batch reactor. This probably explains the considerably lower yield of hydrocarbon gases in the flow system compared to the batch system.

In line with the larger amounts of coal-derived oil from the alpha-alumina bed, compared to the silica bed, somewhat larger amounts of identifiable coal-derived compounds were also obtained in the first-step product, as shown in table 11, with the compounds arranged according to increasing boiling point. The alkylated compounds in the first-step product from alpha-alumina were about the same as those from silica. Thus, the greater yields of hydrocarbon gas with alpha-alumina are not due to increased dealkylation. It should be noted that some of the compounds identified were both coal-derived and alkylated.

The identities and amounts of the ten identifiable hydroaromatics, or hydrogen donors, in the hydrogenated tar oil used to make up the slurry for the flow system are shown in table 8. There was a substantially greater consumption of hydrogen donors in the alpha-alumina bed than in the silica bed, in line with the better quality first-step product from the alpha-alumina. The proportion of hydrogen donors consumed in the flow system alpha-alumina first-step run was actually greater than that in the corresponding batch system first-step run because of the higher ratio of tar oil to coal in the flow system, as well as the higher initial concentration of hydrogen donors.

Examination of the used first-step packings showed a much greater degree of carbon deposition on the alpha-alumina than on the silica. Even though the silica packing had a much greater surface area, all of the analytical results on the products indicated greater activity with the alpha-alumina. The structure of the alpha-alumina surface may be such as to allow or promote the type of carbonaceous deposit promoting the desired hydrolytic reactions of the coal/hydrogenated tar oil slurry.

Scanning electron microscopy showed random stacks of flat crystallites of carbon. It is suggested that the carbon level reaches an equilibrium due to reduction by hydrogen, and physical attrition. Small amounts of carbonaceous material were found in the benzene-washed residue from filtration of the first-step products.

The filtered first-step product from the flow system using alpha-alumina packing at 1,500 psig and 440° C had an appreciably lower density than the corresponding product using silica packing (table 12). This was not due to less coal dissolved (table 10), but probably was because of the smaller amounts of benzene insolubles and asphaltenes in the product. As shown in table 12, the filtered first-step product from the batch system using alpha-alumina packing at 1,500 psig and 430° C also had an appreciably lower density than the corresponding product using Denstone vitrified ceramic. For both the batch and flow systems the density increase of the product over that of the slurry vehicle oil was only about half as great for alpha-alumina as for the silica, or Denstone.

Because the first-step reactor did not contain any material capable of catalyzing extensive hydrodesulfurization or hydrodenitrification reactions, the filtered first-step products from both the batch and flow systems, with vitrified ceramic, silica, and alpha-alumina packings, all showed retention of heteroatoms (table 13). There was essentially no reduction in nitrogen content. Identifiable nitrogen compounds included pyridines, quinolines, and carbazoles. Alpha-alumina packing in the batch system was slightly better than the vitrified ceramic for reduction of heteroatoms, and this, along with the much greater yield of hydrocarbon gases and oils, required a much greater consumption of

hydrogen from hydroaromatics. Thus, in the first-step product from the alpha-alumina bed there was a little less hydrogen because of loss as hydrogen sulfide, ammonia, water, hydrocarbon gases, and volatile light oils. Silica packing was slightly better than alpha-alumina for reduction of heteroatoms in the flow system, but much inferior for the production of hydrocarbon gases and oils, so that the alpha-alumina product showed a greater consumption of hydrogen donors, and a slight lowering of hydrogen content thereby.

Conversely, the alpha-alumina bed first-step product, when processed at 1,500 psig hydrogen and 380° C in the second-step cobalt molybdate bed, gave a second-step product with fewer heteroatoms, a higher hydrogen content and a higher atomic hydrogen to carbon ratio than that from the first-step product from the silica bed (table 14). The second-step catalyst was more active in converting first-step product from the alpha-alumina bed. A greater second-step gas yield (table 10) with its concomitant greater carbon deposition on the catalyst was observed in converting first-step product from the silica bed. The second-step product, starting with alpha-alumina for first-step packing, had three times the increase in hydrogen content, and atomic H/C, and three times the decrease in nitrogen content as compared to the second-step product starting with silica for first-step packing.

#### CONCLUSIONS

In the two-step coal hydroliquefaction process studied there were large differences in the behavior between various first-step nominally non-catalytic reactor packings. These results may be due to differences in the ability of the packing surface to promote or allow a sufficient amount of the type of carbonaceous deposit on which desired hydroxylytic conversions of coal and/or asphaltene molecules could occur by interaction with hydrogen donors (and hydrogen). The preferred packing produced asphaltene with higher atomic H/C ratios and/or increased conversion to oils. These products appeared less likely to deactivate the cobalt molybdate catalyst used in the second-step reactor. The greater activity of the catalyst was indicated by the production of a second-step product with lower heteroatom content and higher atomic H/C, with negligible hydrocarbon gas formation and concomitant carbon deposition.

The preferred first-step packing was shown to be a moderate surface area, large pore size, very low silica content alpha-alumina. A high surface area, large pore size, pure silica, and a very low surface area, negligible porosity vitrified ceramic were less effective. The chemical as well as the surface properties of the packing appeared to affect performance. The alpha-alumina produced more first-step hydrocarbon gas, without increasing dealkylation, giving more first-step light oil, more total oil of a lower density, and less asphaltene, along with a greater consumption of hydrogen from hydrogen donors.

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Table 1. - Mass Balance for Stirred Batch Reactor Runs

Run conditions	Grams In			Grams Out							Ratio total grams out, total grams in	
	Coal	Hydrogenated oil or 1st stage product	H <sub>2</sub> gas	Total	Liquid product	Tars <sup>1</sup>	Monitored gases <sup>2</sup>	NH <sub>3</sub>	Unmonitored components <sup>3</sup> H <sub>2</sub> S H <sub>2</sub> O	Total		
First-step <sup>4</sup> Denstone extreme	298.70	597.30	24.24	920.20	792.10	5.45	82.08	0.19	15.69	20.89	916.40	0.9959
First-step <sup>5</sup> Denstone mild	601.30	1202.70	26.45	1830.45	1673.69	16.90	53.27	-1.12	20.51	35.83	1798.99	0.9828
First-step <sup>4</sup> alpha-alumina extreme	307.67	612.33	19.41	939.41	791.70	24.50	78.41	-0.12	12.80	21.79	929.08	0.9890
First-step <sup>5</sup> alpha-alumina mild	599.20	1198.60	13.22	1811.02	1635.90	23.15	64.31	-3.14	21.83	36.89	1778.94	0.9823
Second-step <sup>6</sup> Denstone extreme	---	233.30	13.23	246.53	222.60	---	19.19	0.11	0.06	-0.04	241.92	0.9813
Second-step Denstone mild	---	233.00	13.23	246.23	209.50	---	15.98	0.22	0.43	0.79	226.92	0.9216
Second-step alpha-alumina extreme	---	222.00	13.22	235.22	198.20	---	12.70	1.00	0.22	0.45	212.57	0.9037
Second-step alpha-alumina mild	---	213.00	13.22	226.22	205.40	---	14.88	0.41	0.32	-0.08	220.93	0.9766

<sup>1</sup>Residual products sticking to equipment.<sup>2</sup>Monitored gases: H<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub> by gas chromatography.<sup>3</sup>Unmonitored components: NH<sub>3</sub>, H<sub>2</sub>S, H<sub>2</sub>O. Amounts of these components were calculated from the differences between input and output N, S, and O.<sup>4</sup>Hydrolytic first-step with Denstone vitreous ceramic packing, at 1,800 psig and 450° C.<sup>5</sup>1,500 psig, 430° C.<sup>6</sup>All four second-step runs with the cobalt molybdate catalyst, at 1,500 psig and 380° C, using unfiltered first-step product as feed.

Table 2. - Hydrogen Balances for Stirred Batch Reactor Runs

Run conditions	Grams H <sub>2</sub> In			Grams H <sub>2</sub> Out			Ratio, total grams out, H <sub>2</sub> gas in, total grams in, corrected				
	Coal stage product	Hydrogenated oil or 1st stage product	H <sub>2</sub> gas	Total product	Liquid product	Tars		Monitored gases <sup>2</sup>	Unmonitored <sup>3</sup> components <sup>3</sup>	Total	
First-step <sup>4</sup> Denstone extreme	12.90	41.81	24.25	78.96	55.45	0.22	18.98	3.27	77.92	0.9868	23.21
First-step <sup>5</sup> Denstone mild	25.98	84.19	26.45	136.62	112.13	0.68	12.90	5.19	130.90	0.9581	20.73
First-step <sup>4</sup> alpha-alumina extreme	13.29	42.86	19.41	75.56	54.23	1.47	19.31	3.17	78.18	1.0347	22.03
First-step <sup>5</sup> alpha-alumina mild	25.89	83.90	13.22	123.01	113.04	0.92	14.28	5.38	133.62	1.0863	23.44
Second-step <sup>6</sup> Denstone extreme	---	16.33	13.22	29.55	16.03	--	13.51	0.02	29.56	1.0003	13.23
Second-step Denstone mild	---	15.61	13.22	28.83	15.21	--	14.56	0.16	29.93	1.0382	14.32
Second-step alpha-alumina extreme	---	15.21	13.22	28.43	13.81	--	12.54	0.24	26.59	0.9353	11.38
Second-step alpha-alumina mild	---	14.72	13.22	27.94	14.17	--	14.64	0.09	28.90	1.0344	14.18

<sup>1</sup>Residual products sticking to equipment.

<sup>2</sup>Monitored gases: CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub> by gas chromatography.

<sup>3</sup>Unmonitored components: NH<sub>3</sub>, H<sub>2</sub>S, and H<sub>2</sub>O. Amounts of H<sub>2</sub> consumed by forming these components were calculated from the difference between input and output N, S, and O.

<sup>4</sup>Hydrolytic first-step with Denstone vitreous ceramic packing, at 1,800 psig and 450° C.

<sup>5</sup>1,500 psig, 430° C.

<sup>6</sup>All four second-step runs with the cobalt molybdate catalyst at 1,500 psig and 380° C, using unfiltered first-step product as feed.

Table 3. - Carbon Balances for Stirred Batch Reactor Runs

Run conditions	Grams C In			Grams C Out				Ratio, total grams out, total grams in
	Coal	Hydrogenated oil or lst stage product	Total	Liquid product	Tars <sup>1</sup>	Monitored gases <sup>2</sup>	Total	
First-step <sup>3</sup> Denstone extreme	180.33	539.36	719.69	706.71	5.18	54.21	766.10	1.0645
First-step <sup>4</sup> Denstone mild	363.01	1086.04	1449.04	1496.65	16.06	36.23	1548.94	1.0689
First-step <sup>3</sup> alpha-alumina extreme	185.74	552.93	748.67	707.46	22.05	52.46	781.97	1.0445
First-step <sup>4</sup> alpha-alumina mild	361.74	1082.34	1441.18	1463.64	21.99	44.97	1530.60	1.0599
Second-step <sup>5</sup> Denstone extreme	---	208.15	208.15	200.36	--	5.61	205.97	0.9895
Second-step Denstone mild	---	208.12	208.12	187.50	--	1.04	188.54	0.9059
Second-step alpha-alumina extreme	---	198.38	198.38	179.39	--	0.13	179.52	0.9049
Second-step alpha-alumina mild	---	190.57	190.57	184.80	--	0.19	184.99	0.9707

<sup>1</sup>Residual products sticking to equipment.

<sup>2</sup>Monitored gases: CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub> by gas chromatography.

<sup>3</sup>Hydrolytic first-step with Denstone vitreous ceramic packing, at 1,800 psig and 450° C.

<sup>4</sup>1,500 psig, 430° C.

<sup>5</sup>All four second-step runs with the cobalt molybdate catalyst at 1,500 psig and 380° C, using unfiltered first-step product as feed.

Table 4. - Solvent Extraction Analysis of Product from Two-Step Coal Liquefaction in Stirred Batch Reactor

	Weight percent							
	1,800 psig, 450°C, 3 hrs				1,500 psig, 430°C, 3 hrs			
	Not filtered between steps		Filtered		Not filtered between steps		Filtered	
First-step run conditions <sup>1</sup>	Denstone	Alpha-alumina	Denstone	Alpha-alumina	Denstone	Alpha-alumina	Denstone	Alpha-alumina
Mineral residue								
First-step reactor material								
Fraction								
Benzene insolubles	11.3	11.5	9.2	10.5	12.3	14.4	15.0	18.6
Asphaltenes (benzene-soluble, cyclohexane-insoluble)	9.3	5.2	26.1	11.6	16.3	14.4	26.0	16.5
Oils <sup>2</sup> (cyclohexane-soluble)	79.4	83.3	64.7	77.9	71.4	71.2	59.0	64.9

<sup>1</sup> Second-step run conditions of all eight runs: 1,500 psig, 380°C, 1 hr, presulfided cobalt-molybdenum on silica-promoted alumina.

<sup>2</sup> Includes the bulk of the oil used to make up the coal/oil slurry (ratio 1:2).

Table 5. - Coal-Derived Compounds and Alkylated Compounds in Two-Step Products, Using Filtered Feed for Second-Step

First-step run conditions First-step reactor material	Weight percent <sup>1</sup>			
	1,800 psig, 450°C		1,500 psig, 430°C	
	Denstone	Alpha- alumina	Denstone	Alpha- alumina
Trimethylbenzenes	0.40	0.40	0.23	0.08
Methyl-, Dimethyl-, and Ethylnaphthalenes	11.58	14.04	9.95	9.73
Methylbiphenyls	0.43	0.44	0.32	0.37
Methyldibenzofurans	3.10	2.91	2.71	3.65
Methylfluorenes <sup>2</sup>	1.07	1.16	0.85	1.40
Methylphenanthrenes	2.60	2.92	2.79	2.93
Methylpyrenes	0.45	0.50	0.35	0.54
Benz(c)phenanthrene <sup>2</sup>	0.10	0.14	0.18	0.37
Methylchrysene <sup>2</sup>	0.18	0.42	0.09	0.23
Benz(h,j,k)fluoranthene <sup>2</sup>	0.19	0.53	0.29	0.40
Benz(a & e) pyrene <sup>2</sup>	0.11	0.17	0.20	0.25
Methylbenz(a & e)pyrene <sup>2</sup>	0.04	0.07	0.04	0.06
Total coal-derived compounds	1.69	2.49	1.65	2.71
Percent Increase <sup>3</sup>		47.3		64.3
Total alkylated compounds	20.54	22.86	17.33	18.99
Percent Increase		11.3		9.6

<sup>1</sup> Calculated on the basis of the oil in the coal/oil slurry.

<sup>2</sup> Compounds not detected in the hydrogenated tar oil used for slurry, hence derived from coal.

<sup>3</sup> Percent increase in going from Denstone to alpha-alumina packing.

Table 6. - First-Step Hydrocarbon Gas Yields

Run conditions	Scf/lb coal			
	1,800 psig, 450°C		1,500 psig, 430°C	
Reactor material	Denstone	Alpha-alumina	Denstone	Alpha-alumina
Methane	1.645	1.890	0.835	0.985
Ethane	0.619	0.810	0.246	0.308
Propane	0.274	0.449	0.131	0.188
Butanes	0.043	0.070	0.022	0.025
Total	2.581	3.219	1.234	1.506
Percent increase	24.7		22.2	

Table 7. - Elemental Analysis of Two-Step Products,  
Using Unfiltered Feed for Second Step

First-step run conditions	Atomic H/C			
	1,800 psig, 450°C		1,500 psig, 430°C	
First-step reactor material	Denstone	Alpha-alumina	Denstone	Alpha-alumina
Benzene insolubles	0.62	0.65	0.72	0.73
Asphaltenes	0.64	0.70	0.75	0.78
Oils	0.95	0.94	0.95	0.99

Table 8. - Hydrogen Donors in Hydrogenated Tar Oil for Slurry  
Before and After Reaction with Coal:  
Analysis of First-Step Products

Type reactor	Weight percent					
	Batch			Flow		
Reactor conditions	1,800 psig, 450°C			1,500 psig, 440°C		
Reactor packing	Denstone	Alpha-alumina		Silica	Alpha-alumina	
Hydrogenated tar oil	Lot A		Lot B-F			
Compound						
Indan	1.22	1.51	1.25	1.63	0.72	0.83
Methylindans	0.35	2.94	2.59	0.40	0.32	0.60
Tetralin	7.34	6.61	4.62	9.11	6.58	6.37
Methyltetralins	1.93	2.09	1.00	4.29	3.87	3.35
Dihydrophenanthrene	3.08	1.32	1.11	2.00	1.28	1.17
Octahydrophenanthrene	---	---	---	2.04	1.66	1.89
Tetrahydrophenanthrene	2.42	1.18	1.12	4.30	4.09	2.92
Tetrahydropyrene	3.27	0.59	0.84	2.11	0.44	0.45
Hexahydropyrene	---	---	---	0.20	0.12	0.12
Dihydropyrene	0.97	0.60	0.69	0.80	0.40	0.40
Total	20.58	16.84	13.22	26.88	19.48	18.10
Percent reacted		18.2	35.8		27.5	32.6

Table 9. - Distillation of Slurry Vehicle Oils Compared With  
Distillation of Filtered First-Step Products  
from Stirred Batch Reactor Runs

Reactor conditions	Weight percent <sup>1</sup>					
	1,800 psig, 450°C			1,500 psig, 430°C		
Reactor packing	Denstone	Alpha-alumina		Denstone	Alpha-alumina	
Hydrogenated tar oil	Lot A		Lot B			
Distillate range, °C						
40-202 (gasoline)	10.9	17.1	21.0	13.8	11.1	12.2
202-265 (kerosine)	34.0	27.9	28.4	32.5	28.1	26.7
265-340 (diesel oil)	40.9	39.7	33.1	40.6	40.3	41.4
340-392 (fuel oil)	13.1	12.5	13.9	12.0	15.9	16.2
392-495 (heavy oil)	1.1	2.8	3.6	1.1	4.6	3.5

<sup>1</sup> Based on distillation curve to FBP 495°C.

Table 10. - 0.2 Lb Coal/Hr Flow System

Reactor Packing	First-Step		Second-Step	
	Alpha-alumina	Silica	Co/Mo on SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	
Reactor vol., ml	270	270	270 <sup>1</sup>	270 <sup>2</sup>
Temp., °C	440	440	380	380
Press., psig	1,500	1,500	1,500	1,500
H <sub>2</sub> , scfh	7	7	7	7
Feed, g/hr	246	374	250	350
Coal/oil ratio	1:3	1:3	---	---
Run time, hrs	15.75	15.75	10.5	6.08
<u>Product Analysis</u>				
Filter residue, pct.	3.64	5.55	---	---
Calcd. ash, pct.	4.88	4.88	---	---
Coal dissolved, pct.	100	97	---	---
<u>Filtered</u> <u>As received</u>				
Benzene insolubles, %	5.1	12.4	4.5	4.4
Asphaltenes, pct.	10.6	12.4	2.3	7.7
Oil, pct.	84.3	75.2	93.2	87.9
<u>Hydrocarbon Gas Yields, scf/lb Coal</u>				
Methane	0.638	0.140	0.025	0.189
Ethane	0.150	0.043	0.017	0.041
Propane	0.047	0.018	0.025	0.038
Butanes	0.023	0.006	0.005	0.002
TOTAL	0.858	0.207	0.072	0.268

<sup>1</sup> Filtered product from alpha-alumina run as feed.

<sup>2</sup> Filtered product from silica run as feed.

Table 11. - Coal-Derived Compounds and Alkylated Compounds  
in First-Step Product from Flow System First-Step Reactor

First-step packing	Weight percent <sup>1</sup>	
	alpha-alumina	silica
Trimethylbenzenes	0.33	0.15
Methyl-, Dimethyl-, and Ethlynaphthalenes	12.98	13.09
Methylbiphenyls	1.29	1.16
Methyl- and Dimethyldibenzofurans	4.97	3.95
<u>Methylfluorenes</u> <sup>2</sup>	0.30	0.25
Methyl- and Dimethylphenanthrenes	3.60	3.21
<u>Methylpyrenes</u> <sup>2</sup>	0.55	0.94
<u>Benz(c)phenanthrene</u> <sup>2</sup>	0.13	0.37
<u>Methylchrysene</u> <sup>2</sup>	0.32	0.16
<u>Benz(b,j,k)fluoranthene</u> <sup>2</sup>	0.57	0.21
<u>Benz(a&amp;e)pyrene</u> <sup>2</sup>	0.28	0.07
<u>Methylbenz(a&amp;e)pyrene</u> <sup>2</sup>	0.09	0.00
Total coal-derived compounds	2.24	2.00
Total alkylated compounds	24.43	22.91

<sup>1</sup> Calculated on the basis of the oil in the coal/oil slurry.

<sup>2</sup> Compounds not detected in the hydrogenated tar oil used for slurry,  
hence derived from coal.

Table 12. - Densities of Slurry Vehicle Oils Compared With Densities of Filtered First-Step Products from Stirred Batch Reactor and Flow Reactor Runs

Type reactor	Density, at 20°C	
	Batch	Flow
Reactor conditions	1,500 psig, 430°C	1,500 psig, 440°C
Reactor packing	Denstone alumina	Alpha-alumina
Hydrogenated tar oil	Lot B	Lot B-F
Density increase	1.0589 1.1000 1.0824 1.0056 1.1133 1.0600	0.0411 0.0235 0.1077 0.0544

Table 13. - Elemental Analysis of Filtered First-Step Products from Batch and Flow Systems

Type reactor	Elemental Weight Percents <sup>1</sup>			
	Batch		Flow	
Reactor conditions	1,800 psig, 450°C		1,500 psig, 440°C	
Reactor packing	Denstone alumina		Alpha-alumina	
Coal/oil slurry <sup>2</sup>	Lot A	Lot B-F	Lot B-F	Lot B-F
Sulfur	1.70	0.37	0.30	1.29 0.16 0.37
Nitrogen	0.76	0.78	0.71	0.52 0.40 0.52
Oxygen	3.77	0.55	0.32	2.81 1.58 1.78
Carbon	86.38	90.98	92.17	87.03 90.05 89.91
Hydrogen	$\frac{6.37}{98.98}$	$\frac{7.07}{99.75}$	$\frac{6.71}{100.21}$	$\frac{7.61}{99.26}$ $\frac{7.71}{99.90}$ $\frac{7.28}{99.86}$
Donors reacted <sup>3</sup>	18.2	35.8	27.5	32.6

<sup>1</sup> All elements by analysis.

<sup>2</sup> Moisture and ash free basis.

<sup>3</sup> Weight percent hydrogen donors reacted.

Table 14. - Flow System Second-Step Products,  
Elemental Analyses, Weight Percent

Second-step Reactor conditions	Cobalt molybdate 1,500 psig, 380°C			
First-step packing	Silica	Alpha-alumina		
Hydrogenated tar oil	Lot B-F			
Coal/oil slurry <sup>1</sup>	1:3			
Sulfur	0.09	1.29	0.20	0.13
Nitrogen	0.35	0.52	0.30	0.18
Percent decrease <sup>2</sup>			14.3	48.6
Oxygen	0.90	2.81	1.17	1.00
Hydrogen	8.18	7.61	8.44	8.97
Percent increase <sup>2</sup>			3.2	9.7
Carbon	90.03	87.03	89.56	89.53
Atomic H/C	1.09	1.05	1.13	1.20
Percent increase <sup>2</sup>			3.7	10.1

<sup>1</sup> Coal/hydrogenated tar oil, m.a.f. basis.

<sup>2</sup> Percent change of second-step product compared to hydrogenated tar oil.

HYDROGENATION OF PHENANTHRENE OVER A COMMERCIAL  
COBALT MOLYBDENUM SULFIDE CATALYST UNDER SEVERE REACTION CONDITIONS

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Introduction

While it is true that cobalt molybdenum catalysts were developed primarily for the hydrodesulfurization of petroleum residuum streams, they have been applied extensively in laboratory and pilot plant investigations of the production of quality synthetic fuels from coal, oil shale and tar sands. In these applications the catalyst has been of interest not just because of its desulfurization capabilities, but also because of its high activity in hydrogenation, stabilization and conversion reactions. The remarkable feature of cobalt molybdenum catalysts is their ability to remain active despite the presence of notorious catalyst poisons, in particular organic sulfur and nitrogen compounds, in the feedstocks undergoing treatment.

Phenanthrene is typical of the hydrocarbons produced during the liquefaction of coal. The staggered phenanthrene-like compounds are thermodynamically more stable (6) than the linear anthracene-like isomers and they are usually present in greater abundance in coal derived liquids (e.g. 1). Partially hydrogenated derivatives of phenanthrene are very active hydrogen donors in coal extraction. In one study 9, 10-dihydrophenanthrene was reported to be slightly superior to tetralin in hydrogen donor activity (2). Perhydrophenanthrene was much less active, and the possibility of over hydrogenating the solvent in a hydrogen donor coal liquefaction scheme is widely recognized. The extent to which phenanthrene is hydrogenated in a catalytic solvent hydrogenation reactor is therefore of considerable interest.

In addition some conversion to lower molecular weight species (hydrocracking) is usually desirable. While cobalt molybdenum is much less active in this regard as compared with catalysts containing an acidic component, it has proven superior in terms of hydrocracking selectivity in at least one instance. Gardner and Hutchinson found cobalt molybdenum to be active and selective for hydrocracking polyphenyls including biphenyl (4). Catalysts on acidic supports were less selective and produced mostly coke. Penninger and Slotboom observed substantial quantities of 2-ethylbiphenyl and biphenyl in the reaction products from the thermal high pressure hydrogenolysis of phenanthrene indicating that hydrogenation and  $\alpha$ -ring-opening at the 9, 10-position was in fact taking place (7). The product distribution from cracking over nonacidic or low acidity catalysts frequently resembles that obtained in thermal cracking processes. Since cobalt molybdenum catalysts are known to be selective in the hydrocracking of biphenyl, and it might be speculated that biphenyls can be formed from phenanthrene over cobalt molybdenum in a manner similar to that observed in thermal cracking, it was hoped that some cracking at the central ring of phenanthrene might be accomplished. This speculation was a major driving force behind the present investigation. The economic advantages of hydrocracking at the inner rings of condensed ring aromatics as compared with terminal ring cleavage are readily apparent in terms of reduced hydrogen consumption, higher yields and in some cases higher quality products.

It was evident from the very beginning of this investigation that much higher temperatures than normally encountered in packed bed reactors would be required in order to obtain substantial yields of cracked products. Catalyst

deactivation due to carbon formation on the catalyst surface would likely be a problem. However, liquid fluidized beds have been employed on a commercial scale in the hydrodesulfurization of petroleum residuum streams (H-Oil) and on the pilot plant scale in the liquefaction of coal (H-Coal). One of the advantages of the liquid fluidized bed reactor is that provisions can be made for the continuous addition and withdrawal of catalyst. The addition of fresh catalyst could conceivably overcome the deactivation problem when operating at high severity.

#### Experimental

The catalyst employed in this investigation was supplied by the Nalco Chemical Company and carries the designation Nalcom-471. According to the manufacturer's specifications the catalyst consists of 12.5%  $\text{MoO}_3$  and 3.5%  $\text{CoO}$  supported on an alumina base. The surface area and total pore volume are 295  $\text{m}^2/\text{gm}$  and 0.55  $\text{cc}/\text{gm}$  respectively. High purity hydrogen (99.995% according to the supplier's specifications) was obtained from the Matheson Gas Products Company in 3500 psig cylinders. Phenanthrene, 98% purity, melting point 99-101°C was purchased from the Aldrich Chemical Company. An elemental analysis of the phenanthrene (Galbraith Laboratories, Knoxville, TN) indicated that the sample consisted of Carbon: 93.69%, Hydrogen: 5.48%, Nitrogen: 0.01%, Sulfur: 0.42%, and Oxygen: 0.39% by weight.

The reactor, Figure 1, is a steady flow type constructed of a 1/2 inch heavy wall (0.083 inch) Type 316 stainless steel tube and heated by a Marshall tubular furnace, model 1016. The reactor charges approximately five grams of catalyst. Thermocouples were inserted about 1/2 inch into both ends of the catalyst bed, and a preheat zone of glass chips was provided at the bed inlet. Liquid phenanthrene was metered into the reactor by a precision Ruska proportioning pump, model 2252-BI, with a heated barrel. Various discharge rates from 2  $\text{cc}/\text{hr}$  to 240  $\text{cc}/\text{hr}$  could be obtained by selecting the proper choice of gear ratios. The hydrogen flowrate was monitored by a flow meter constructed of a 29 inch length of 0.009 inch I.D. capillary tubing and a Barton model 200 differential pressure cell. The capillary pressure and reactor pressure were controlled respectively by a Tescom pressure regulator, model 26-1023-002 and a Tescom back pressure regulator model 26-1723-24. Flow rates were controlled with a Hoke Milli-Mite needle valve. Liquid products were collected in two high pressure accumulators constructed of one inch schedule 80 stainless steel pipe and Swagelok butt weld connectors. Product gases were vented through a low pressure accumulator in dry ice-propanol, through a wet test meter, and collected in a polyethylene gas bag.

The catalyst was crushed and sieved to 20/30 mesh and calcined at 1000°F in air for four hours. After calcining the catalyst was charged to the reactor and the system pressure tested with hydrogen. Presulfiding was carried out at 250 psig using a hydrogen sulfide (2%) - hydrogen (98%) mixture. During presulfiding the gas flow was set at 5  $\text{l}/\text{hr}/\text{gm}$  catalyst and the reactor temperature was maintained at 400°F for 5 hours. After this period the temperature was raised at a rate of 2°F/min to 600°F and held for 1 hour. Then with sulfiding gas flowing at a minimal rate the reactor was cooled to room temperature.

The phenanthrene feed was spiked with elemental sulfur to a total sulfur content of 1.0% by weight. During startup the spiked feed was cut in with the hydrogen sulfide-hydrogen mixture flowing at 1000 psig and 500°F. Once liquid product was detected in the high pressure accumulator the gas mixture was replaced with pure hydrogen and the reactor was brought to operating conditions. After a period of time sufficient for three displacements of the reactor volume the reaction products were directed to a second high pressure accumulator and a yield period begun. At the termination of a yield period the liquid product was collected and stored in a freezer, and the gas product was immediately analyzed.

The system was brought to a new set of run conditions and the procedure repeated. During all adjustments care was taken to assure that the rate of temperature rise never exceeded 120°F/hr and that the catalyst was at all times in contact with sulfur.

The products were analyzed on a gas chromatograph which utilized a hydrogen flame ionization detector and possessed temperature programming capabilities. The column for the liquid product analysis was packed with 5% SE-30 on 60/80 mesh Chromosorb P, AW. The gas analysis column was packed with Chromosorb 102. The identification of the various product peaks was accomplished by measuring the retention time of pure compounds and by a GC-mass spectral analysis. The former method was used to identify most of the lower molecular weight hydrocarbons and the latter method was relied upon for identification of many of the high molecular weight peaks. The mass spectra of some of the more important product peaks are presented in Figure 2. Additional information on the analytical methods used in this investigation is available in masters theses by Huang (5) and Early (3).

### Results

A total of eighteen yield periods were successfully completed in two series of experiments. The operating conditions and product yields are presented in Tables 1 and 2, respectively. These yields have been adjusted to meet a 100% carbon material balance. Before discussing these results it must be pointed out that problems were encountered in two areas.

Because of the large heat effect it was not possible in some instances to operate the reactor isothermally. In the most extreme case the temperature difference between top and bottom of the reactor was of the order of 90°F. Thus the reported temperatures at the milder operating conditions must be considered nominal values only. (The reported temperature is the numerical average of the reactor top and bottom temperatures.) In nonadiabatic-nonisothermal reactors it is not uncommon that the temperature at some point within the reactor will exceed either the top or bottom temperature. Such a phenomenon would go undetected in our experimental set-up since thermocouples were only located at the bed inlet and exit. The actual upper and lower temperatures are presented in Table 1.

The second problem was encountered in the analytical portion of the investigation. Three peaks on the chromatogram were found to be mixtures of two components. The unresolved pairs were: 1. asym-Octahydrophenanthrene isomer and n-Butylnaphthalene, 2. Perhydrophenanthrene isomer and n-Butyltetralin and 3. Octahydrophenanthrene isomer and Dihydrophenanthrene. The unresolved "component" yield known to consist of asym-Octahydrophenanthrene and n-Butyltetralin is plotted as a function of temperature (pressure, space velocity constant) in Figure 3. The curve exhibits two maxima. Thermodynamics considerations suggest that the high temperature maximum is due principally to n-Butylnaphthalene; whereas, the low temperature maximum is due principally to Octahydrophenanthrene. The mass spectra of this unresolved peak from products of the 750°F run and the 800°F run are consistent with this contention. The dotted line in Figure 10 is an estimate of the magnitude of each individual contribution to the unresolved peak drawn in such a manner that the sum of the individual component estimates is equal to the total. Similar estimates were made for the other unresolved pairs (5). Separation of the unresolved components in this manner is admittedly speculative and qualitative. Nevertheless this procedure does provide a simplification which is consistent with the observed data and aids greatly in the qualitative interpretation of the data.

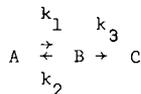
Since rapid deactivation of the catalyst was expected, especially at the more severe operating conditions, it was necessary to maintain a record of declining catalyst activity. This was done by repeating the selected base conditions, of 850°F, 2000 psi, and 2.0 gm/hr/gm in the first set of experiments and 600°F,

2000 psi, 2.0 gm/hr/gm in the second. While no significant deactivation was observed in the second set of experiments (WH-09), Figure 4 shows that both the conversion of phenanthrene and the conversion to  $C_{13}$  decreased with respect to grams of oil on catalyst in the first set of experiments (WH-08). As expected, the sharpest decline in catalyst activity was observed when the more severe operating conditions (1000°F, 1500-2500 psi) were examined.

Yields of the various hydrogenation products of phenanthrene are presented in Table 2 and Figure 5. Large quantities of octahydrophenanthrene and perhydrophenanthrene isomers were observed in many of the products. (The various isomers are lumped together in the figures). At 2000 psig and a space velocity of 2 gm/hr/gm, octahydrophenanthrenes are produced in 82% yield at 600°F. With increasing temperatures the octahydrophenanthrenes are further hydrogenated to perhydrophenanthrenes until a maximum yield of approximately 62% perhydrophenanthrenes is reached at 750°F. Beyond this temperature the yield of perhydrophenanthrenes decreases as the thermodynamic equilibrium is shifted to favor the less saturated species. Cracking reactions are also a factor at the elevated temperatures as illustrated in Figures 6, 7, and 8. The presence of n-butyldecalin and decalin in the products indicates that some cracking of perhydrophenanthrene is taking place. However it appears that at the temperatures required to hydrocrack perhydrophenanthrene (at 2 gm/hr/gm and 2000 psig) the equilibrium is shifted away from perhydrophenanthrene formation. No evidence of large branched paraffins that might be anticipated from mechanisms involving ring opening of perhydrophenanthrene were uncovered in the mass spectral analyses. Large quantities of tetralins and naphthalenes were observed in the cracked products. The presence of large quantities of n-butane and n-butyl substituted tetralin, naphthalene and decalin indicates that the major reaction paths involve saturation and cleavage of terminal rings. In Figure 9 various grouped product yields at 950°F and 2000 psig are plotted versus space time. Again it is evident that the formation of two ring compounds precedes the formation of one ring compounds.

The only evidence of cracking at the central ring was the presence of trace quantities (less than 1 mole % yield) of biphenyl and cyclohexylbenzene in some of the reaction products. Slightly higher yields of 2-ethylbiphenyl were obtained. The maximum occurred at about 900°F (WH-08-02) and corresponded to the maximum in dihydrophenanthrene yield. It should be pointed out that these data do not entirely dispel the possibility of cracking at the central ring. It would be interesting to conduct some experimentation in the same temperature range but at much lower pressures than employed in the present investigation where the equilibrium yields of dihydrophenanthrene would be higher. Of course catalyst deactivation would likely be even more serious a problem than encountered in the present study.

Because of the near isothermal behavior of the high temperature runs it is possible to perform a crude analysis of the reaction kinetics. A simple model which appears to describe our system is:



where A represents phenanthrene, B represents hydrogenated product and C represents cracked products ( $C_{13}$ ). If it is assumed that the equilibrium reaction is rapid in comparison with the cracking reaction, then one can show that the overall conversion of phenanthrene to cracked products should follow first order kinetics (5). But before a meaningful analysis of the data can be undertaken it is necessary that the rate constants be corrected for the observed decline in catalyst activity.

This was done by defining the activity as the ratio of the observed first order rate constant to the first order rate constant obtained by extrapolating the deactivation plot, Figure 4, to zero grams of oil on catalyst. The activity was then calculated for each yield period using the deactivation curve of Figure 4. A plot of  $\ln(1-x)$  versus  $a(\text{activity}) \times \tau(\text{space velocity})$ , Figure 10, confirms that the hydrocracking reaction is indeed correlated with first order kinetics. The activation energy was calculated to be 40 kcal/gmole. Comparison of his value with an activation energy of 65 kcal/gmole estimated from Penninger Slotboom's thermal data (7) indicates that some catalysis of the cracking reactions is operative.

#### ACKNOWLEDGEMENTS

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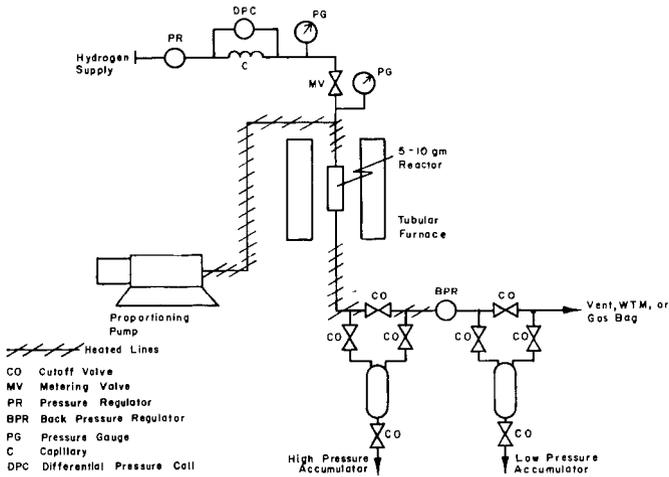


Figure 1 - Simplified Flow Diagram of Apparatus.

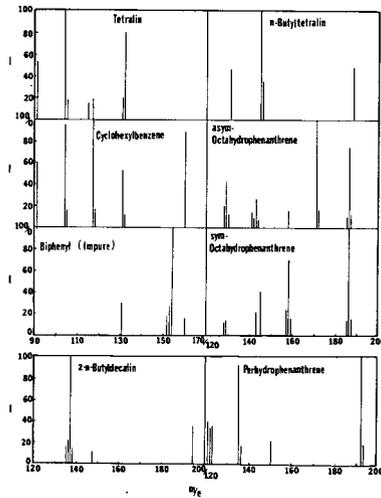


Figure 2 - Mass Spectra of Selected Product Peaks.

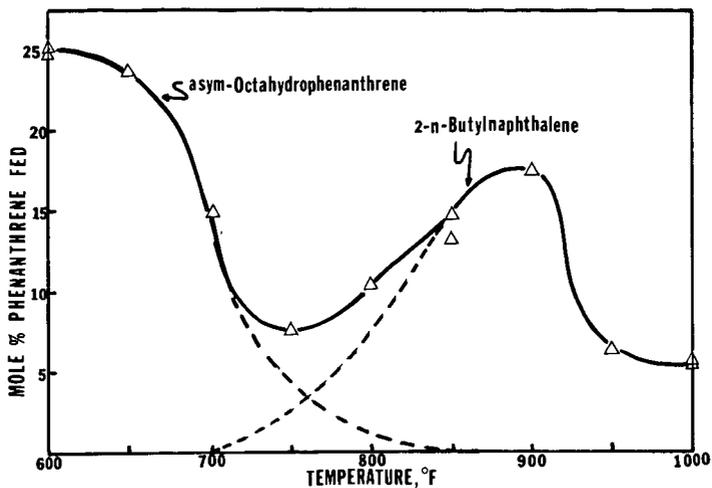


Figure 3 - Yields of Unresolved asym-Octahydrophenanthrene - n-Butylnaphthalene Product Peak.

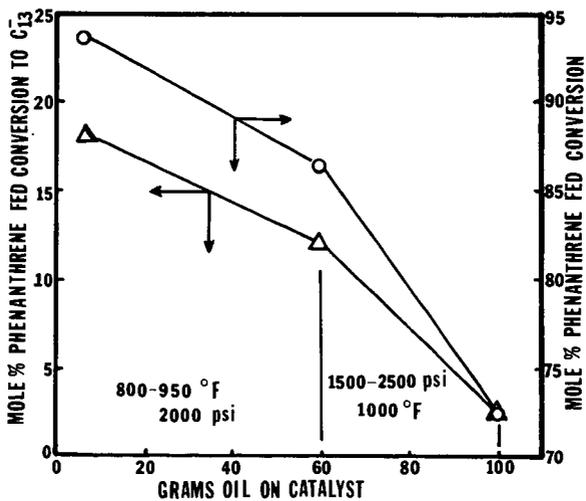


Figure 4 - Conversions at Base Conditions (2000 psig, 850°F, 2 gm/hr/gm).

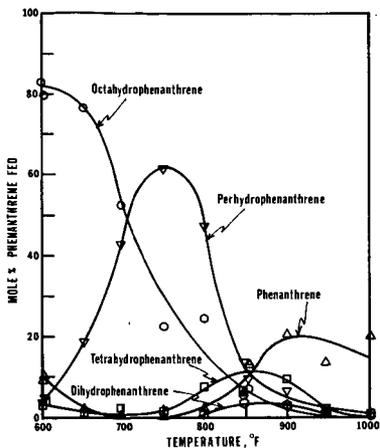


Figure 5 - Yields from the Hydrogenation of Phenanthrene at 2000 psig, 2.0 gm/hr/gm.

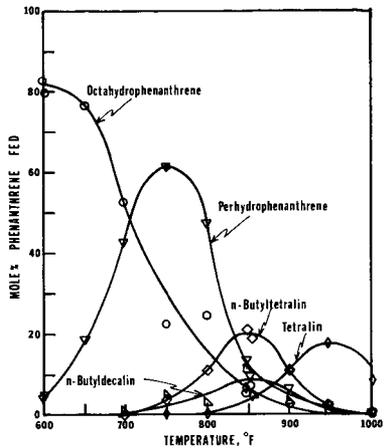


Figure 6 - Yields from the Hydrogenation of Phenanthrene at 2000 psig, 2.0 gm/hr/gm.

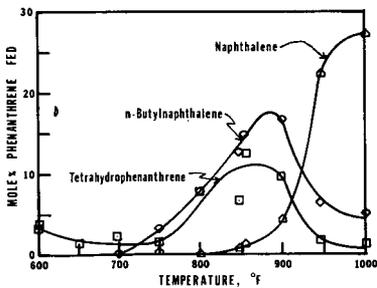


Figure 7 - Yields from the Hydrogenation of Phenanthrene at 2000 psig, 2.0 gm/hr/gm.

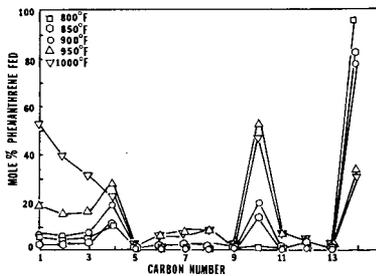


Figure 8 - Product Yields by Carbon Number.

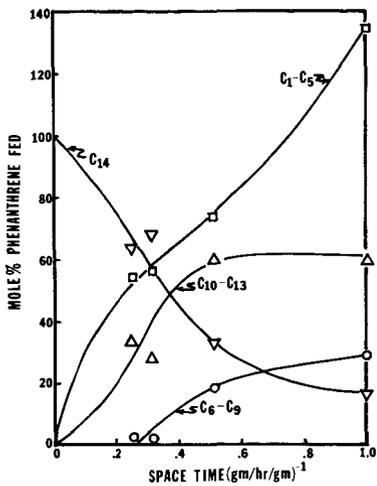


Figure 9 - Product Yields at 2000 psig, 950°F.

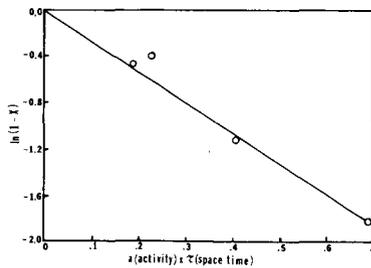


Figure 10 - First Order Plot for Conversion to C<sub>13</sub>.

TABLE 1

RUN 84-09, HYDROCRACKING OF PHENANTHRENE OVER 5.3566 GRAMS OF SULFIDEC  
 CO-MO/ALUMINA CATALYST-----NALCOWO 471.474-5372.  
 RUN SUPPLY

	1.	2.	3.	4.	5.	6.	7.
YIELD PERIOD NO.	3,000	2,000	1,500	3,000	1,500	2,400	4,000
YIELD PERIOD LENGTH, HRS.	960.9	901.6	811.8	946.8	946.8	945.0	949.5
TOP TEMPERATURE, F	936.0	887.4	788.9	946.8	945.1	948.3	945.1
BOTTLE TEMPERATURE, F	936.0	887.4	788.9	946.8	945.1	948.3	945.1
PRESSURE, PSIG	102.1	200.2	101.2	200.2	200.6	186.4	200.6
LIQUID SPACE VELOCITY, CC/HR	1,542	1,933	1,939	1,936	3,897	3,112	0,972
LIQUID SPACE VELOCITY, CM/HR/CM	0.515	0.517	0.516	0.517	1.257	0.221	1.028
APPROX. R2 TREAT PAISE, L(STP)/HR	15.0	29.5	31.5	17.0	28.5	17.5	12.0
APPROX. R2 TREAT PAISE, L(STP)/CM	1.842	2.933	2.933	1.931	2.933	1.715	2.933
CUMULATIVE HRS ON CATALYST	3.75	7.90	11.00	19.50	23.75	27.30	32.75
CUMULATIVE GAS OIL/CM CATALYST	104.6	100.5	18.85	33.84	42.78	46.29	52.88
LIQUID MATERIAL BALANCE, MTG	104.6	100.5	101.6	91.7	95.9	97.3	90.4
CARBON MATERIAL BALANCE, MTG	101.1	104.0	100.3	99.9	99.9	104.3	102.8

CORRECTED YIELDS BASED ON LIQUID FEED

FEED CONVERSION, MOLE%	91.720	79.398	97.837	86.072	95.578	66.215	94.486
CONVERSION TO C13+, MOLE%	17.879	22.332	5.244	67.345	91.644	31.560	83.768
HYDROGEN CONSUMPTION, L(STP)/CM	0.688	0.535	0.721	0.581	0.622	0.444	0.805
HYDROGEN CONSUMPTION, WT%	0.188	0.183	0.183	0.183	0.183	0.183	0.183
GAS OIL YIELD, WT%	101.533	95.457	101.800	88.732	95.584	91.307	77.184
CS-C8 YIELD, MOLE%	2.960	1.195	0.000	18.134	0.282	0.981	27.032
CS-C12 YIELD, MOLE%	19.752	19.120	0.947	60.508	57.343	28.123	61.281
C13-C18 YIELD, MOLE%	84.121	77.068	94.756	32.659	46.356	69.040	16.222
SELECTIVITY, %	51.0	51.0	51.0	51.0	51.0	51.0	51.0
SELECTIVITY, S2	93.70	89.62	18.06	89.85	106.72	87.99	71.17

TABLE I. (contd.)

RUN NR-08, HYDROGENATION OF PHENANTHRENE OVER 5.3566 GRAMS OF SULFIDE  
 CO-C/ALUMINA CATALYST-----NALCOC 471, #74-5372.

RUN SUMMARY	8.	9.	10.	11.	12.	13.
YIELD PERIOD NO.	3,000	3,000	3,000	3,000	4,000	3,000
YIELD PERIOD LENGTH, HRS.	841.1	1003.4	997.1	1002.7	1003.3	858.3
TOP TEMPERATURE, F	846.0	1000.3	1002.0	998.2	1002.7	844.3
BOTTOM TEMPERATURE, F	200.0	200.0	190.0	180.0	200.0	200.0
LIQUID FEED RATE, CC/HR	1.939	1.937	1.932	1.945	1.914	1.916
LIQUID SPACE VELOCITY, CV/HR/GM	0.516	0.516	0.512	0.514	0.523	0.517
SPACE TIME, (CV/HR/CC)-1	16.0	16.0	12.0	20.5	15.5	14.5
APPROX. N2 TRAIL RATE, L(STP)/HR	11.9	11.2	10.9	16.4	11.2	10.3
EXIT GAS RATE, L(STP)/HR	38.00	43.00	50.50	55.34	60.33	67.83
CUMULATIVE HRS ON CATALYST	59.45	67.46	71.75	79.64	87.02	96.68
CUMULATIVE GMS C11/GM CATALYST	90.0	83.1	90.4	87.8	183.7	186.4
LIQUID MATERIAL BALANCE, NTA	89.9	100.3	93.7	98.0	103.0	104.8
CANEX MATERIAL BALANCE, NTA						

CORRECTED YIELDS BASED ON LIQUID FEED	8.	9.	10.	11.	12.	13.
FEED CONVERSION, MOLES	86.323	79.998	45.904	89.006	74.961	68.178
CONVERSION TO C13-, MOLES	12.230	69.751	30.732	80.144	59.093	2.715
HYDROGEN CONSUMPTION, L(STP)/GM	0.594	0.641	0.319	0.632	0.502	0.313
HYDROGEN CONSUMPTION, WT%	5.140	5.764	2.865	5.893	5.414	2.898
LIQUID YIELD (C5+), NTA	98.882	89.003	96.389	86.641	80.721	101.444
C5-C8 YIELD, MOLES	0.000	18.052	0.911	28.578	7.376	0.270
C9-C12 YIELD, MOLES	8.891	53.353	26.455	68.320	45.771	1.904
C13-C14 YIELD, MOLES	87.770	30.249	69.288	13.856	40.507	97.285
SELECTIVITY, %	90.0	78.4	93.7	98.0	103.0	104.8
SELECTIVITY, S2	92.70	78.49	84.98	83.29	77.48	70.11

TABLE 1 (cont'd.)

	1.	2.	3.	4.	5.
RUN #1-09, HYDROGENATION OF PHENANTHRENE OVER 5,1645 GRAMS OF SULFIDOC CO-MC/ALLPINA CATALYST-----NALCONC 471,774-5372.					
RUN SUMMARY					
YIELD PERIOD NO.	1.	2.	3.	4.	5.
YIELD PERIOD LENGTH, HRS.	3,000	3,000	3,000	3,000	3,000
TOP TEMPERATURE, F	616.8	682.8	743.7	791.4	817.3
BOTTEM TEMPERATURE, F	582.8	619.5	682.6	708.9	700.9
PRESSURE, PSIA	20.2	20.2	20.2	20.2	20.2
LIQUID SPACE VELOCITY, CM/HR	2,010	2,009	2,024	2,011	2,011
SPACE TIME, (GM/HR/CM) <sup>3</sup> -1	0.498	0.498	0.494	0.497	0.497
APPROX. H2 TREAT RATE, L(STP)/HR	13.5	14.8	13.5	14.8	13.5
APPROX. H2 TREAT RATE, L(STP)/CM <sup>3</sup>	10.8	10.3	10.8	10.8	10.5
CUMULATIVE HRS ON CATALYST	3,318	8,71	13,38	18,38	23,38
CUMULATIVE GMS LIL/GM CATALYST	9.05	17.92	25.88	34.05	42.52
LIQUID MATERIAL BALANCE, WT%	106.2	105.1	109.0	107.3	106.5
CAMPEN MATERIAL BALANCE, WT%	102.0	100.1	102.3	100.4	100.5
CORRECTED YIELDS BASED ON LIQUID FEED					
FEED CONVERSION, MOLES	90.831	97.639	99.492	99.277	89.398
CONVERSION TO C13+, MOLES	1,284	1,258	1,365	1,498	1,001
HYDROGEN CONSUMPTION, L(STP)/GM	0.460	0.554	0.656	0.770	0.456
LIQUID YIELD (C2+), WT%	0.34	4.993	0.011	0.265	0.011
LIQUID YIELD (C2+), WT%	104.103	104.965	105.989	105.628	104.693
C5-C8 YIELD, MOLES	0.000	0.000	0.000	0.000	0.000
C9-C12 YIELD, MOLES	1.567	1.485	1.680	1.525	1.157
C13-C14 YIELD, MOLES	98.716	98.722	98.695	98.500	98.690
SELECTIVITY, %	114.25	115.80	115.78	101.77	115.63

TABLE 2

RUN W-08, HYDROGENATION OF PHEMANTHRENE OVER 5.3566 GRAMS OF SULFIDED  
 CO-M/MU-LINA CATALYST-----NALCO# 471,174-5372.  
 CORRECTED PRODUCT YIELDS BASED ON LIQUID FEED, MULEY

YIELD PERIOD NO.	1.	2.	3.	4.	5.	6.	7.
C 1F 4	2.223	6.434	4.559	17.443	11.431	13.162	32.874
C 1F 6	2.066	0.708	0.567	0.000	0.000	0.000	0.000
C 2H 6	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C 3H 4	7.970	7.087	3.776	15.421	11.536	12.525	27.540
C 3H 8	0.000	0.066	0.000	0.215	0.200	0.272	0.000
C 4H 10	10.334	18.446	9.977	26.368	13.917	20.151	49.540
C 5H 10	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C 5H 12	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C 6H 14	0.000	0.000	0.000	1.094	0.621	0.000	0.000
C 6H 6	0.971	0.635	0.000	3.119	0.647	0.088	4.911
C 7H 16	0.000	0.000	0.000	0.943	0.000	0.000	1.477
C 7H 18	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C 7H 16	0.518	0.725	0.000	4.184	0.110	0.421	5.394
C 7H 18	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C 8H 10	0.239	0.000	0.000	2.453	0.024	0.031	0.871
C 8H 10	0.000	0.000	0.000	0.000	0.000	0.000	1.407
C 8H 18	0.182	0.000	0.000	0.000	0.000	0.000	0.000
C 8H 18	0.000	0.000	0.000	0.589	0.000	0.000	2.141
C 8H 10	0.430	0.435	0.000	2.895	0.680	0.741	6.362
C 10H 14	4.227	2.576	0.000	6.525	0.325	1.606	8.329
C 10H 18	1.759	0.612	0.000	5.683	0.353	2.384	8.757
C 10H 18	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C 10H 18	0.558	1.010	0.338	17.818	1.293	8.744	17.018
C 10H 8	0.711	4.189	0.000	22.235	1.519	10.158	17.420
C 10H 12	0.118	0.000	0.000	0.000	0.072	0.407	0.735
C 11H 14	0.592	0.143	0.000	0.952	0.137	0.385	1.289
C 11H 14	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C 12H 16	1.002	0.177	0.594	0.682	0.070	0.281	1.678
C 12H 16	0.046	0.032	0.000	0.000	92.940	0.035	0.855
C 12H 10	0.349	0.065	0.026	0.614	0.066	0.179	0.000
C 12H 12	1.145	0.195	0.000	0.741	0.148	0.328	0.671
C 14H 18	1.509	1.990	2.213	1.104	0.000	1.256	0.560
C 14H 24	4.509	1.990	2.213	1.104	0.000	1.256	0.560
C 14H 24	4.742	1.443	20.414	1.230	0.186	1.048	0.672
C 14H 24	2.452	3.184	8.034	0.032	0.117	0.689	0.000
C 14H 24	22.994	11.056	16.566	2.743	0.511	3.694	1.083
C 14H 18	12.822	16.747	10.600	6.348	1.481	12.438	4.246
C 14H 16	1.379	2.935	0.000	0.298	0.453	4.160	0.945
C 14H 14	3.732	3.493	2.058	1.860	0.354	3.729	0.982
C 14H 18	5.173	2.925	22.044	1.204	0.151	0.939	0.404
C 14H 18	6.723	9.609	7.784	1.930	0.524	0.738	5.062
C 14H 10	6.280	20.602	2.163	13.928	4.422	33.785	5.514
ICTALS	119,426	135,364	117,482	185,160	152,200	153,561	238,717

\* MASS SPECTRAL DATA INDICATES THAT THIS PEAK WAS OVERLAPPED BY THE PRECEDING PEAK.

TABLE 2 (cont'd.)

RUN W4-08, HYDROGENATION OF PRENANTHRENE OVER 5.3566 GRAMS OF SULFIDED  
 CO-MOLYBDENA CATALYST-----NALCOM 471,874-5372,  
 CORRECTED PRODUCT YIELDS BASED ON LIQUID FEED, MG/GR

YIELD PERIOD NO.	8	9	10	11	12	13
C 2H 4	4.859	32.374	26.171	32.433	46.617	1.082
C 2H 6	4.193	58.156	19.738	26.413	34.768	1.451
C 2H 8	0.000	0.000	0.000	0.000	0.000	0.000
C 3H 4	5.262	30.432	16.061	20.984	34.340	1.571
C 4H10	5.900	0.147	0.222	0.585	0.586	1.991
C 4H12	0.000	2.040	0.000	0.480	0.000	0.000
C 5H10	0.000	0.282	0.000	0.072	0.000	0.000
C 6H14	0.000	1.222	0.000	2.383	0.506	0.000
C 6H 6	0.000	3.129	0.000	0.000	0.000	0.000
C 7H 8	0.000	0.000	0.000	0.000	0.000	0.000
C 7H 6	0.000	0.000	0.000	1.040	0.000	0.000
C 7H 8	0.000	4.963	0.634	7.166	2.316	0.098
C 7H16	0.000	0.000	0.000	0.260	0.000	0.000
C 8H10	0.000	2.919	0.000	0.708	1.008	0.085
C 8H12	0.000	1.188	0.000	0.000	0.102	0.000
C 9H12	0.000	0.303	0.000	2.335	0.000	0.000
C 8H10	0.000	3.481	0.000	1.417	0.000	0.000
C 10H 8	0.000	0.000	0.000	0.777	6.466	7.623
C 10H 6	0.000	5.697	0.012	0.000	0.000	0.000
C 11H16	0.000	0.054	0.015	4.172	4.178	0.000
C 10H12	0.000	0.537	0.000	1.316	0.113	0.000
C 10H 8	4.340	8.656	2.437	16.555	6.890	1.564
C 10H 8	1.249	27.350	16.085	25.493	21.401	0.000
C 10H12	0.000	0.000	0.000	0.000	0.000	0.000
C 11H12	0.371	0.534	0.094	0.988	0.539	0.225
C 11H10	0.242	4.174	3.933	3.656	6.161	0.116
C 12H16	0.918	0.620	0.364	1.104	0.445	0.000
C 12H16	0.042	0.000	0.000	0.497	0.095	0.000
C 12H10	0.546	0.831	0.311	0.876	1.926	0.000
C 14H26	4.939	0.064	0.125	0.257	0.594	0.000
C 14H24	2.284	0.065	0.127	0.022	0.425	0.078
C 14H24	3.539	0.325	0.760	0.607	1.100	0.000
C 14H24	1.995	0.000	0.000	0.000	0.000	0.000
C 14H20	20.939	0.583	0.098	0.894	1.100	3.757
C 14H20	14.920	4.999	6.469	4.522	5.423	15.080
C 14H16	1.556	1.463	1.603	0.807	1.451	0.894
C 14H16	4.195	1.953	3.594	0.851	1.626	6.530
C 14H12	0.000	0.000	0.000	0.000	0.000	0.000
C 14H12	0.000	0.000	0.000	0.000	0.000	0.000
C 14H14	7.376	0.302	0.261	0.201	0.413	13.274
C 14H14	12.346	1.269	1.536	0.732	1.636	24.481
C 14H14	13.677	20.802	54.096	10.994	27.039	31.822
C 14H10	0.000	0.000	0.000	0.000	0.000	0.000
TOTALS	*123,276	244,028	166,761	215,450	230,430	105,534

\* MASS SPECTRAL DATA INDICATES THAT THIS PEAK WAS OVERLAPPED BY THE PRECEDING PEAK.



# THE ANALYSIS OF LIQUIDS FROM COAL CONVERSION PROCESSES

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## INTRODUCTION

Major coal-conversion processes under consideration (1) for development by U.S. interests are capable of producing a wide variety of products. Processing and using these materials in future applications will require a better understanding of their composition than has been necessary with conventional energy sources. To provide basic data, the Bartlesville Energy Research Center has been studying liquid products derived from various coal-conversion processes.

Depending upon the material to be processed and the information desired, numerous approaches to appropriate characterization may be taken. Some investigators have used mass spectrometry as a single technique to analyze materials of wide boiling range without prior separations (2,3). These mass spectral methods are well conceived and furnish useful information, but cannot provide the compositional detail that is possible with prior separations. Further, more accurate type assignment and quantitation are possible with preliminary separations. Limited analytical data that provide physical characteristics (4) such as percent oil, asphaltenes, gravity, viscosity, etc. may be satisfactory for monitoring coal liquefaction process operations and for comparing materials that will satisfy utility type fuel requirements. However, the composition of coal liquids to be further upgraded such as those to be used for transportation, needs to be determined in more detail to provide the refiner with the necessary basis for processing these materials.

The Bartlesville Energy Research Center is using the approach of physical and chemical separation, followed by instrumental characterization, to provide considerable detailed data on the composition of coal liquefaction products. The key to the identification procedure for those materials boiling above 200° C lies in the GPC-mass spectral correlation method developed at Bartlesville (5,6). Most of the procedures used were developed for the analysis of high-boiling petroleum fractions during a cooperative project between the U.S. Bureau of Mines and the American Petroleum Institute (7). Some minor modifications have been necessary to adapt the procedures to the products of coal liquefaction.

Materials from three different coals and two liquefaction processes were studied: two COED materials produced from Utah and western Kentucky coals and a third material from the Synthoil process using West Virginia coal. The COED process involves pyrolysis of the coal followed by catalytic hydrogenation of the crude liquid, whereas the Synthoil process is a direct catalytic hydrogenation of coal slurried in a recycle liquid. Although process conditions are not available for the two COED products, the Synthoil product was prepared by processing the coal at 450° C and 4,000 psig (8). Hydrogen and a slurry of 35 percent coal in recycle oil were fed at 25 pounds per hour into a nominally half-ton (slurry) per-day unit with a 14.5-foot-long catalytic reactor. The catalyst was 1/8-inch pellets of cobalt molybdate on silica alumina. Two other liquid products from the H-Coal process are under current investigation, and will be completed soon.

## EXPERIMENTAL

The general procedure used in the study of full-boiling-range coal liquid products is shown in Figure 1. Boiling ranges of distillates were checked by simulated distillation (9) to establish the approximate boiling ranges desired. In previous work with petroleum crudes, care was exercised to prepare distillates having identical boiling ranges so that more precise comparisons of data could be made. However, smaller samples of the available coal liquids have precluded adjustment of still conditions to any great extent, and the boiling ranges as determined by simulated distillation for the distillates prepared are not exactly the same. This was not considered essential for these initial studies because the primary interest was to determine whether the procedure might be effective and the adjustments necessary to make an effective characterization. All distillates were prepared in a 4-inch-diameter Rota-Film molecular still. The still, a continuous-flow, wiped-well vessel, provides minimum residence time of the sample at elevated temperatures, thus limiting thermal degradation of the material being processed. Material is passed through the still for each set of conditions of temperature and pressure at the rate of 600 to 1,000 ml/hr.

After the distillates were prepared, the material boiling below about 200° C was separated further into acids, bases, and hydrocarbon-neutral fractions for analysis by gas chromatography (GC), ultraviolet (UV) fluorescence, and mass spectrometry. Distillates boiling from about 200° C to 370° C and 370° C to 540° C were processed through adsorption columns (10) to produce four concentrates for each distillate: saturates, monoaromatics, diaromatics, and polyaromatic-polar material. The saturates were analyzed directly by mass spectrometry; monoaromatics and diaromatics were separated by gel permeation chromatography (GPC) and analyzed by GPC-mass spectral correlations (5,6); and the polyaromatic-polar concentrate was separated into acids, bases, and hydrocarbon-neutrals. The polyaromatic-polar concentrate less acids and bases was then separated by GPC and characterized in the same manner as the monoaromatics and diaromatics.

The adsorption columns used were about 8 feet long by 1 inch diameter, packed with 28 to 200 mesh, Davison grade 12 silica gel in the top half and 80 to 200 mesh Alcoa F-20 alumina in the bottom half, and were operated downflow. The GPC column was about 16 feet long by 1 inch diameter, packed with 100Å polystyrene gel in the top half and 400Å polystyrene gel in the bottom half, and was operated downflow. The mass spectrometer used for these studies was a CEC 21-103C low-resolution instrument; saturates were analyzed by high-ionizing voltage spectra and aromatics by low-ionizing voltage spectra. High-resolution mass spectrometers, the AEI MS-30 and CEC 110, were also used to resolve certain heteroatomic species that overlapped the same nominal hydrocarbon series. NMR spectra from a Varian A-60 instrument were obtained to determine the proton distributions across the GPC runs and thereby confirm and enhance the findings of the GPC-mass spectral correlations.

## RESULTS AND DISCUSSION

Summary data shown in Tables I and II were selected from comprehensive characterization studies (11-13) that have been completed for each coal liquid. Table IA summarizes distillate distributions, Table IB shows totals for major compound classes, and Table II lists ring number distributions by compound class for each distillate. As shown by the distillate distributions data in Table IA, the Synthoil material from West Virginia coal is the highest boiling of the three, having 95.6 percent boiling above about 200° C and 25.7 percent residuum (boiling above about 540° C). Utah syncrude is rated second in higher-boiling material with 85.7 percent boiling above about 200° C. Western Kentucky shows 78.4 percent boiling above 200° C.

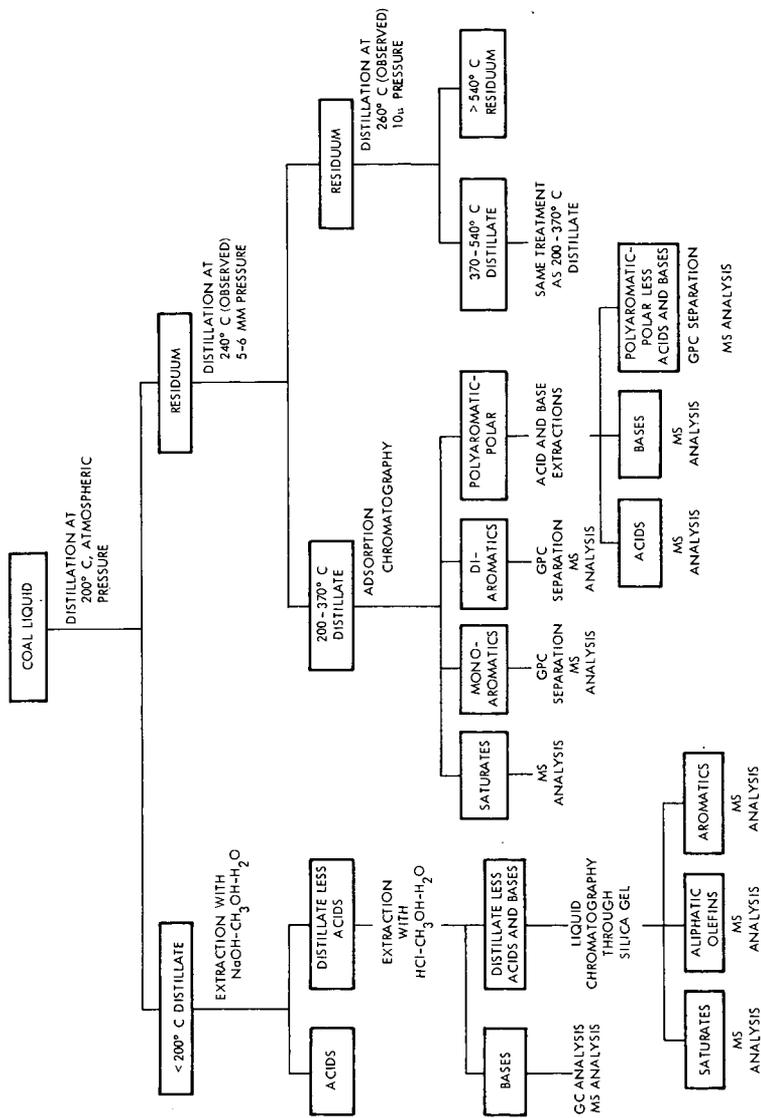


FIGURE 1. Procedure for Characterizing Coal Liquids.

TABLE I  
DISTILLATES AND MAJOR COMPOUND TYPES SEPARATED  
FROM THREE COAL LIQUIDS

A. COAL LIQUIDS AND DISTILLATES

	COED Syncrude Utah Coal	COED Syncrude Western Kentucky Coal	Synthoil West Virginia Coal
	Wt. Pct.	Wt. Pct.	Wt. Pct.
<b>COAL LIQUIDS:</b>			
Sulfur	0.05	0.08	0.42
Nitrogen	0.48	0.23	0.79
<b>DISTILLATE DISTRIBUTIONS:</b>			
< 200° C Distillate <sup>1</sup>	13.3	21.0	4.4
200 - 370° C Distillate <sup>2</sup>	45.4	54.2	42.6
370 - 540° C Distillate <sup>3</sup>	40.3	24.2	27.3
540° C+ Residuum <sup>4</sup>	-	-	25.7
Losses	1.0	0.6	-
<b>B. MAJOR COMPOUND TYPE DISTRIBUTIONS</b>			
Total Saturates	30.10	33.42	10.65
Total Monoaromatics	20.06	33.64	14.23
Total Diaromatics	14.41	12.77	15.53
Total Polyaromatics	14.48	7.91	14.61
Heteroatomic Species	1.50	0.29	2.24
Acids	8.17	3.11	10.40
Bases	1.30	1.05	2.75
Residuum (Not Analyzed)	None	None	25.7
Other Material Not Analyzed	9.98	7.81	3.89
Totals	100.00	100.00	100.00

<sup>1</sup> < 204° C for Utah, < 205° C for western Kentucky, and < 207° C for Synthoil.

<sup>2</sup> 204 - 381° C for Utah, 205 - 380° C for western Kentucky, and 207 - 363° C for Synthoil.

<sup>3</sup> 381° C+ residuum for Utah, 380° C+ residuum for western Kentucky, and 363 - 531° C for Synthoil.

<sup>4</sup> Utah and western Kentucky syncrudes had no material boiling above about 540° C.





Table 1B shows some indication of the degree of aromaticity for each syncrude. For example, assuming the 25.7 percent residuum shown for Synthoil is mostly aromatic, Synthoil then would be the most aromatic of the three having a total aromatic hydrocarbon content near 70 percent, whereas western Kentucky and Utah syncrudes are about 54 percent and 49 percent, respectively.

The quantities of sulfur and nitrogen determined for each coal liquid shown in Table 1A and the amounts of acids, bases, and saturates listed in Table 1B reflect, to some extent, the degree of hydrogenation for each product. For example, the data suggest that the western Kentucky COED product probably was more severely hydrogenated than the Utah COED product, although coal structure or other processing conditions could account for some of the differences in composition. No direct comparison of the Synthoil product with the COED products could be made because of the substantial differences in processing as well as the coal source.

Further insight can be gained into the cyclics present in the hydrocarbon structures of the three coal liquids by examination of the data in Table 11. From the data on saturates, note the lower concentrations of total paraffins as compared to total cyclics. For the Utah syncrude, total paraffins in the saturates amount to about 8.7 percent of the syncrude and cyclics about 14.3 percent, which means the total saturates are about 63 percent cyclic. Western Kentucky syncrude saturates show about 4.3 percent of the syncrude as total paraffins and 14.8 percent as cyclics, or about 78 percent of the saturates are cyclic. The Synthoil product saturates show a paraffin content of 1.9 percent of the total liquid and cyclics content of 7.6 percent, giving an approximate value of 80 percent cyclics in the saturate concentrates. Since Utah syncrude and western Kentucky syncrude were produced by the same process, the significant difference in the amount of paraffins produced would indicate some possible differences in the structures of the coal sources, although the lack of details on the processing of both coals makes this observation tentative. From the distributions shown in Table 11, the aromatics which contain four or more total rings add up to about 23.1, 22.6, and 14.4 percent of the Utah syncrude, western Kentucky syncrude, and Synthoil product, respectively. These data would indicate that the Utah and western Kentucky syncrudes may contain more of the larger aromatic ring systems than the Synthoil product; however, as shown in Table 1B, 25.7 percent of the Synthoil product is residuum that was not analyzed (and probably is composed of multi-ring systems), and about 13.2 percent of the product is in acids and bases. Total ring number distributions shown for each major compound class indicate the two-, three-, four-, and five-ring systems to be predominant in all three syncrudes, Synthoil having material up to 11 total rings. Mass spectral and GPC correlation data and NMR data for these materials indicate structures somewhat more condensed, with more short alkyl groups attached to the cyclic nucleus, than those found in similar boiling ranges of petroleum (14-18). We expect to establish soon the amount of condensation and structural arrangement of materials in the GPC fractions to provide more useful information on the cyclic structures for determining proper refining processes.

## CONCLUSIONS

In general, the scheme followed in separation of syncrude materials for characterization studies has provided data for determining appropriate refining processes for these materials. The preliminary separations provide more meaningful fractions for accurate analysis by mass spectrometry and other instrumental techniques by type identification and quantification. The refiner should find this type of data useful in the selection and development of processes for upgrading coal liquids to finished products.

For the three materials examined, Synthoil product appears to be the most aromatic, with ring systems having up to about 11 total rings. Differences between the two COED syncrudes

may be attributable to the severity of hydrogenation of the crude pyrolysis liquids, although insufficient information is available to distinguish between the effects of process conditions and character of coal used as raw material. In continued studies, the characterization and analysis of additional liquids from known combinations of coal source, liquefaction process, and degree of upgrading will provide a more meaningful basis for future refining processes. For more meaningful data, future studies will require access to information such as the coal source and process conditions.

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