

HYDROLIQUEFACTION OF AUSTRALIAN COALS

Norbert V.P. Kelvin

Australian Coal Industry Research Laboratories Limited,
North Ryde, N.S.W. 2113. Australia.

Introduction

Australia, like many other nations, faces an increasing demand for liquid transportation fuels with decreasing domestic crude oil production. Accordingly, efforts are now under way to investigate the liquefaction of Australian coals. Hydroliquefaction processes are considered to be likely candidates for initial commercial development because of the abundance of brown and high volatile black coals which are good hydroliquefaction feedstocks. Initial work by ACIRL indicates that a number of Australian coals can be hydrogenated to produce high liquid yields.

Batch Autoclave Screening Tests

Batch autoclave tests were done on several Australian coals ranging from low-volatile high rank to Victorian brown coals (sub lignites) (1-8). These were conducted in 4 litre stirred autoclaves in tetralin solvent under hydrogen pressure at the following conditions:

Total autoclave volume, L		3.78
Coal charge, g		500
Tetralin charge, g		1500
Initial hydrogen pressure (cold), MPa		8.3
Max. temperature °C		400
Hold time at 400°C, h		4

The yields of toluene-soluble oils are plotted against coal composition and petrography in Figures 1, 2 and 3. As expected these data clearly show that coals with high reactive maceral contents, high hydrogen/carbon ratios and high volatile matter are likely to give the highest liquid yields.

Abundance and ease of mining of the highest liquid yielding coals as determined in the batch autoclave tests indicated the most suitable coals for further testing in ACIRL's continuous bench scale reactor unit.

Continuous Reactor

ACIRL's continuous reactor unit has been described in an ACIRL report (8). The flow diagram of the unit is shown in Figure 4. Coal-solvent slurry and hydrogen are fed into the unit which produces a cooled product slurry containing all the water and light oil which is then flash-distilled in 4 kg batches in separate glass-ware. High-pressure exit gases are vented at low pressure through meters and representative samples analysed by GC.

The distillation is carried out in stages to produce light oil, water, medium (atmospheric) distillate, vacuum distillate and a residue of high boilers plus all the unconverted coal solids. Recycle solvent is made by recombining the medium and vacuum distillates. For nearly all runs conducted so far, sufficient solvent has been produced to maintain solvent balance plus a net liquid yield.

The actual excess liquids produced end up as samples for further analysis and evaluation.

The conditions under which the continuous reactor operates are :

Slurry feed rate	0.5 - 3.0 kg/hr
Hydrogen feed rate	0 - 300 g/hr
Solvent:coal ratio	1.7 - 3.0:1
Pressure	10 - 21 MPa
Temperatures :	
- preheater	500 ^o C max.
- stirred reactor	425 ^o C max.
Preheater tube dimensions	6-20 m x 6 mm I.D. x 9.5 mm O.D.
Preheater volume	0.2 - 0.6 L
Stirred reactor liquid holdup	1.5 - 3.6 L

Results

Run conditions and yield data from a batch test and a series of continuous recycle runs on a typical coal selected for continuous tests are presented in Table 1. Analyses of this coal are given in Table 2.

These data indicate that hydrogenation of this coal under recycle solvent conditions will produce about 40% distillate liquids on dry ash-free coal.

Further work is being carried out now to improve these yields to around 50% or better. The configuration of the unit and equipment limitations (temperature, pressure, hydrogen compressor capacity, etc.) for the tests reported here are considered to be in need of upgrading to achieve the higher yields. Moreover, some operational problems are also considered to contribute to lower than desired yields. These problems are discussed below.

Operability

Apart from mechanical and electrical problems that have nothing to do with what goes through the system, the major problem areas are -

1. Large losses relative to the small scale of operation (mainly in distillation).
2. Difficulty in pumping thicker slurries than 2:1 solvent:coal ratio at this small scale.
3. Preheater blockage.
4. High-pressure slurry let-down valve wear.

Losses

Generally, material balances from feed to product slurry and gases over the high-pressure system are good, 97 - 103%. Distillation losses of the order of 5% on coal are usual and almost unavoidable at this small scale. These losses are believed to be caused mainly by evaporation of light hydrocarbons and water from collecting vessels and vaporisation and inadequate trapping of medium boiling materials during vacuum distillation. In addition, some pyrolysis occurs at the later stages (at 400 - 450^oC) of vacuum distillation releasing gases which are not

easy to meter and analyse under vacuum conditions.

Slurry Pumping

We have found that our slurry circulating gear pumps can only handle slurries up to 35% solids loadings. On a larger scale 45% would be possible. At this scale the larger pumping and piping required would entail too much variable hold up of feed slurry to be able to obtain satisfactory material balances.

Preheater Blockages

Our preheater, a 20 metre length of 9.5 mm O.D. by 6.0 mm I.D. stainless steel tube wound into spirals, is heated in a cylindrical sand bath 270 mm diameter x 300 mm sand depth. We have found that preheater blockage can result from a number of factors including :

- (i) temperatures above 460°C.
- (ii) accidental pressure reduction so that too much solvent evaporates.
- (iii) sudden surges of feed hydrogen which dry out the solvent.
- (iv) stagnant slurry at above 380°C due to pumping stoppage.
- (v) attempting to pump slurry through the preheater when its whole length is at 360 - 390°C, that is when the preheater is full of gelling slurry.

Slurry valve wear

Wear of high pressure slurry let-down valves has been a very serious problem. After discharging about 20 - 100 kg slurry from 21 MPa to atmospheric pressure through our slurry let-down valves these valves are unable to hold pressure satisfactorily. At our small scale, this problem can only be solved by using gas pressure equalisation to reduce the pressure drop across the slurry valves.

Acknowledgments

Financial support for this work was provided by the National Coal Research Advisory Committee. Permission by Mr. A.H. Hams, ACIRL's General Manager and Director of Research, to present this paper is gratefully acknowledged.

The assistance of J.F. Cudmore, R.E. Guyot, I.S. Fletcher, P.A. Bennett and B.P.K. Lim is also gratefully acknowledged.

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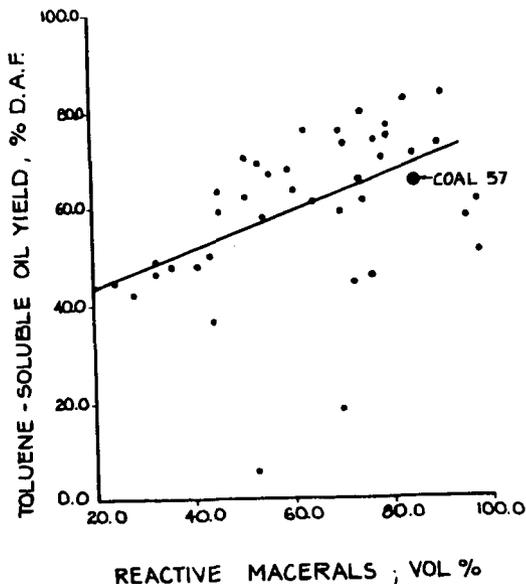


FIGURE 1 - BATCH AUTOCLAVE OIL YIELD VERSUS REACTIVE MACERALS

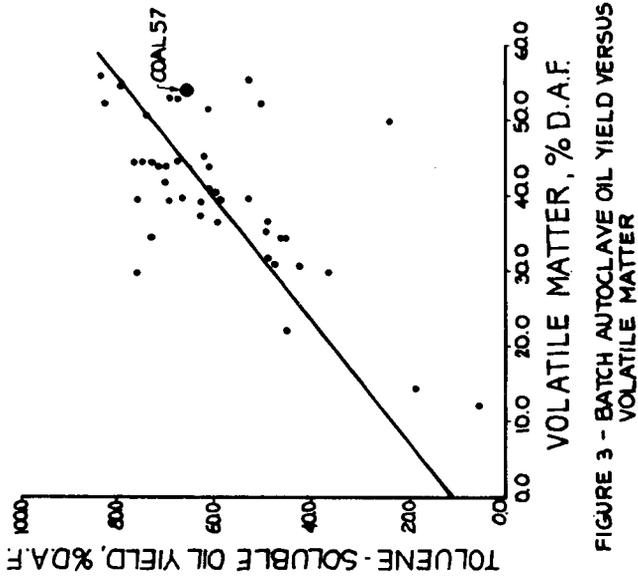


FIGURE 3 - BATCH AUTOCLAVE OIL YIELD VERSUS VOLATILE MATTER

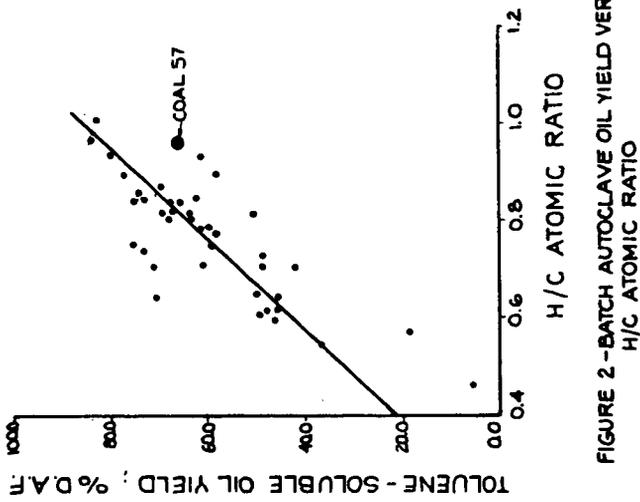


FIGURE 2 - BATCH AUTOCLAVE OIL YIELD VERSUS H/C ATOMIC RATIO

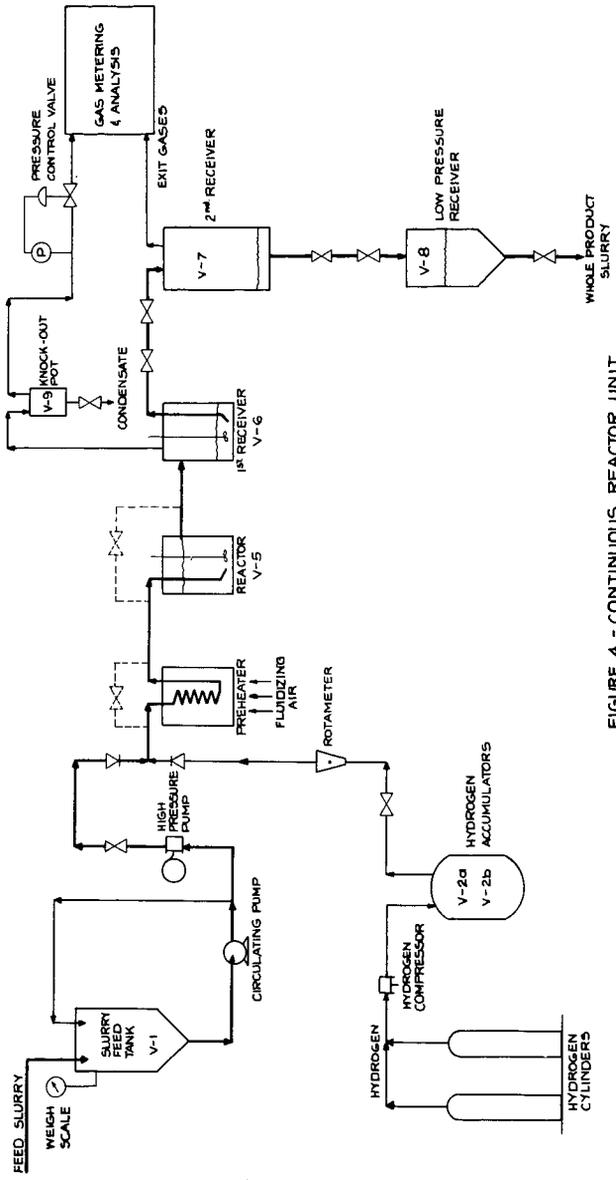


FIGURE 4 - CONTINUOUS REACTOR UNIT FLOW DIAGRAM

TABLE 1

Yield Data for Coal 57

Process Parameters	Batch	Continuous Reactor Runs			
	Test	23	25	26A	26B
Run time, h	4	83	100	216	(216)
Solvent	(T)	(R)	(R)	(R)	(R)
Solvent:coal ratio	3	2	2	2	2
Red mud, % coal	0	3	3	3	3
Feed H ₂ , % d.a.f. coal	2.6	5.5	9.6	27	43
Pressure MPa	~19	21	21	21	21
Temperatures, °C					
- preheater	-	425	440	425	425
- reactor	400	425	425	400	400
Est.slurry hold time,h	4	2	3.2	4.2	4.2
Slurry feed rate,kg/h	static	1.0	1.0	0.5	1.0
<u>Results</u>					
Product recovery,					
% of feeds	~95	100	93	99	99
Toluene conversion,	91	75	82	87	80
(% d.a.f.)					
Total distillate oil	20	30.4	29.4	36.8	35.1
yield, (% d.a.f.)					
Distillation residue,	54	61.3	47.9	41.8	54.2
(% d.a.f.)					
Water & Gases, (% d.a.f.)	26	8.2	9.7	16.2	8.4
Losses (% d.a.f.)	(N)	0.1	13.0	5.2	2.3
Est. residue pyrolysis	3	3.1	2.4	2.1	2.7
oil yield, % d.a.f.					
Total estimated oil	23	33.5	38.3	41.5	39.0
yield, % d.a.f. (E)					

Notes: (T) Tetralin solvent
 (R) Recycled distillate (ca. 200 - 600°C B.P.)
 (N) Batch data normalised to 100%
 (E) Sum of total distillate yield, 50% of losses and estimated pyrolysis oil.

TABLE 2

Analyses of Coal 57

<u>Proximate</u>	%	<u>Elemental</u>	% d.a.f.
Moisture	2.0	Carbon	78.7
Ash	18.3	Hydrogen	6.38
Volatile Matter	42.2	Nitrogen	1.25
Fixed carbon	37.5	Sulphur	0.63
		Oxygen	13.0
		(by diff.)	
<u>Petrography</u>	Vol. %	<u>Forms of Sulphur</u>	% d.a.f.
Vitrinite	67	Pyritic	0.09
Suberinite	15	Sulphate	0.01
Exinite	4	Organic	0.43
Inertinite	4		
Mineral Matter	15		

Mean maximum reflectance of vitrinite 0.54%

The Effect of Solvent Quality on Coal Conversion

C.W. Curtis, J.A. Guin, J.F. Jeng and A.R. Tarrer

Chemical Engineering Department
Auburn University
Auburn, Alabama 36830

Introduction

One factor governing the success or failure of a coal liquefaction process is the ability of the process to generate and sustain an adequate amount of a sufficiently high quality recycle solvent for continuous operation. To insure continued operability of the plant and to recognize when solvent quality is declining it is useful to have a quantitative measure of the solvent's ability to liquefy some given coal under a prescribed set of operating conditions, i.e. the solvent quality. It is obvious that the solvent quality will depend to a high degree on the solvent composition - as determined by a variety of techniques - however, the solvent's performance will also vary with coal type and operating conditions. That is, the best solvent for coal A will not necessarily be the best solvent for coal B. Extension of this idea to temperature, pressure, residence time, etc. is obvious. Thus, when speaking of solvent quality, one must, of necessity refer to a prescribed set of conditions. In general, however, there will be some finite range of solvent parameters which are more beneficial for coal conversion for a rather wide variety of coals and processing conditions.

The purpose of this study is to begin to define such a range of solvent parameters. While this set of parameters will not apply to all situations, it is hoped that they will allow a distinction to be made between a truly poor solvent and one which is satisfactory for coal liquefaction operations and perhaps some inclination as to the efficacy of a particular solvent under certain conditions.

Experimental

Coal Dissolution

Coal dissolution reactions were performed in a tubing bomb reactor which has previously been described. (1) These reactions used Western Kentucky 9/14 and Amax coals under the following conditions: temperatures - 385°C, 410°C and 450°C; reaction time - thirty minutes; agitation rate - 1000 rpm; solvent to coal ratio - 2 to 1; and an air atmosphere. The conversion of the coal was determined by comparison of the ash content of the cresol insoluble filter cake with the original ash content of the coal.

Solvents and Solvent Preparation

Four light recycle oils (LRO) from the SRC processing of Indiana V, Monterey and Amax coals were obtained from the Wilsonville SRC Pilot Plant and were used in this study. Three distillation cuts were obtained from Western Kentucky LRO: <140°C, 140°-200°C, 200°-290°C pot temperature at 1 torr. Creosote oil was successively hydrogenated to hydrogen contents between 7% and 10% in a commercial 300 cc magne-drive autoclave (Autoclave Engineers) using a commercial Co-Mo-Al catalyst and hydrogen pressures from 1000 to 3500 psi for periods of time ranging from 1 to 13 hours. Also, one solvent was prepared by dehydrogenation of cresote oil under nitrogen atmosphere.

Solvent Characterization

The solvents were characterized using standard analytical techniques. Carbon and hydrogen percentages in each solvent were determined using a Perkin Elmer 240 Elemental Analyzer. The infrared spectra of the solvents were obtained neat, in CCl_4 and in CS_2 using a Digilab FTS10 Fourier Transform Infrared Spectrometer. A Varian EM390 NMR spectrometer was used to obtain the ^1H nmr spectrum of each solvent both neat and in CCl_4 .

Results and Discussion

Dissolution Behavior of Western Kentucky Coal

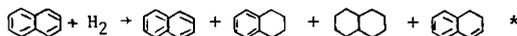
The dissolution behavior of Western Kentucky 9/14 coal was examined in the solvents listed in Table I. The dissolution behavior in each solvent is reported together with the hydrogen content of each solvent. Other conditions were the same for all reactions. Both the creosote oil solvent series and the light recycle oils are listed in order of increasing conversion.

Solvent Character

The solvents used in this study were characterized by infrared analysis, by NMR and by gas chromatographic analysis. For each solvent, the infrared aromatic C-H stretch at 3050cm^{-1} , methyl asymmetric C-H stretch at 2960cm^{-1} , and methylene in-phase stretch at 2925cm^{-1} were measured. The infrared absorbance ratios of aromatic/aliphatic (CH_3) and aromatic/aliphatic (CH_2) were calculated and are given in Table II. In every solvent, except the 90-weight petroleum oil, the aromatic absorption at 3050cm^{-1} is present. The methylene absorption at 2925cm^{-1} is present in both the creosote oil solvent series and in the light recycle oils. The methyl absorption at 2960cm^{-1} is present in the light recycle oils and in the original creosote oil, HCl, HClI and HClII, all of which contain 7% hydrogen or less. The methyl absorption is absent in the neat spectra of the more highly hydrogenated oils.

The hydrogen distribution of each solvent is given in Table III. The hydrogen distributions range from being predominately aromatic as in the creosote oil and HCl solvent to being nearly totally aliphatic as in the 90-weight petroleum oil. Average hydrogen values for three ranges of conversion, 32.8% to 48.1% (low), 64.2% to 70.0% (medium) and 79.7% to 84.5% (high) are shown in Table IV. At low conversion levels, the aromatic hydrogen is the greatest compared to other conversion levels. The α and β hydrogens increase substantially from low conversion to high conversion levels; a significant increase is also seen for the γ hydrogens. Calculation of the average chemical shift from the integrated hydrogen distribution provides a means for determining the effect of the total hydrogen distribution on conversion as shown in Figure 1. A roughly normal shaped distribution is observed for the hydrogenated creosote solvent series. As the hydrogen distribution becomes predominately aliphatic (low ppm) or aromatic (high ppm) coal conversion is adversely affected.

The weight percents of naphthalene, hydrogenated naphthalenes and decalin, in selected solvents were determined by gas chromatographic analysis. This compound series was chosen to provide an indication of the effect of degree of hydrogenation on an aromatic species that readily accepts hydrogen to form hydroaromatic and alicyclic compounds. In the oils studied, the naphthalene appeared to produce three reaction products



The weight percents of these compounds in the selected oils are shown in Table V. The original creosote oil contains 11% naphthalene with no tetralin present. As

*Retention behavior similar to dihydronaphthalene. Further identification work planned.

the creosote oil becomes increasingly hydrogenated, tetralin, decalin and a compound with retention behavior similar to dihydronaphthalene is formed. (Further work is being conducted to identify this compound.) The most hydrogenated oils, HCIV and HCIX, contain a significant percentage of decalin, 7.6% and 5.7%, respectively.

Solvent Character and Coal Dissolution

Coal dissolution behavior is a function of the character of the solvent. The solvents used in this study, characterized by the methods described, provide some indication as to the type of solvent necessary for effective coal dissolution.

The infrared ratios of the hydrogenated creosote oil series obtained from CCl_4 solution spectra show that solvents which produce conversions in the 80% range have IR aromatic to aliphatic methylene ratios ranging 0.42 to 0.27. Solvents with infrared ratios either greater or less than these values show poorer coal conversion. In general, the light recycle oils show lower conversions than do the hydrogenated creosote oils and have infrared ratios obtained from CCl_4 solution spectra ranging from 0.15 (Indiana V) to 0.50 (Western Kentucky II).

Through the hydrogen distribution of the solvents, the aromatic and aliphatic nature of the oils can be examined. From Figure 1, it is apparent that an optimum combination of aromatic and aliphatic hydrogens exists to dissolve ~80% of the Western Kentucky coal.

Brown and Ladner (2) determined that a quantitative relationship between the hydrogen distributions obtained through NMR and the infrared ratios supports the value of 0.5 which they adopted for the ratio of the extinction coefficient of the aromatic C-H stretch to the aliphatic C-H stretch. We performed a similar calculation using IR absorbance ratios obtained from neat spectra:

$$\frac{A_{AR}}{A_{CH_2}} = \frac{\epsilon_{AR}}{\epsilon_{CH_2}} \frac{(C-H_{AR})}{(C-H_{CH_2})} = \frac{\epsilon_{AR}}{\epsilon_{CH_2}} \frac{H_{AR}}{H_{\alpha+\beta}}$$

All of the light recycle oils have extinction coefficient ratios ranging between 0.59 and 0.44. Indiana V LRO has a higher ratio value of 0.77.

Through the study of the naphthalene + tetralin hydrogen donor system, the effect of the level of hydrogen donor within one such series on coal dissolution can be examined. The naphthalene-tetralin compound series is a dynamic system within the hydrogenated creosote oils in that the total weight percent of these compounds changes with degree of hydrogenation. The total amount present in the original creosote oil is 11.3% while in oils HCIV, and HCIX the total weight present is 19.78 and 14.95, respectively. Solvents with high hydrogen contents like HCIV and HCIX are likely forming naphthalene from higher molecular weight compounds. The hydrogenated creosote oils which showed coal dissolution of ~80% have a larger portion of hydrogen donors in the two ring series than do the less effective solvents.

A plot of coal conversion vs. H content is presented in Figure 2. For the creosote oil series there is an optimum in the degree of hydrogenation, probably corresponding to maximum H-donor content. For the LRO solvents, there is no clear optimum and all conversions lie below those of the hydrogenated creosote oils. The implications of the optimum range of solvent hydrogenation in plant operations are obvious. A balance between aromatic and aliphatic character must be maintained for acceptable solvent quality.

Effect of Coal Type and Temperature on Coal Dissolution Behavior

The effect of coal type on the dissolution behavior of coal was studied through a comparison of the dissolution behavior of a slow dissolving coal, Amax, and a faster dissolving coal, Western Kentucky (3). For the creosote oil solvent series, the conversion of Western Kentucky coal is consistently higher than for the Amax coal as shown in Figure 2. In addition, two light recycle oils, Indiana V and Amax, were also tested with the two coals. Indiana V shows essentially the same dissolution for both coals 54.3% for Amax and 53.1% for Western Kentucky. Amax LRO, however, was a better solvent for Amax coal (44.5% conversion) than for Western Kentucky (38.4% conversion).

Three solvents, creosote oil, HCIV and HCIX, were used to examine the effect of reaction temperature on the conversion behavior of Amax and Western Kentucky coal. Figure 3 shows that the dissolution for both coals was minimal in the creosote oil with maximum conversion occurring at 410°C. The conversion of Amax increased with increasing temperatures for both HCIV and HCIX. In contrast, in the HCIV solvent Western Kentucky coal shows lower conversion at 450°C than at 410°C. In HCIX, the conversion of Western Kentucky appears to level out between 410°C and 450°C. Even though HCIV and HVIX differ by only 0.5% hydrogen, the conversion of both Amax and Western Kentucky is lower in HCIV at the three different temperatures than HCIX. The solvent character of HCIV is somewhat more aliphatic than HCIX according to Table V and falls outside the optimum range of aromatic and aliphatic hydrogen combinations (Figure 1).

Conclusions

From the results presented above it is seen that solvent quality can be adversely affected by limited or excess hydrogenation, for example, HCl vs. HCIV. In the hydrogenated creosote oil series the decalin content provides a fairly good indication of the degree of solvent hydrogenation. However, this is not a general result since the most hydrogenated light recycle oil, Indiana V, contains no decalin and virtually none of the two ring system, in contrast to the other light recycle oils studied. Since Indiana V is the best LRO solvent for Western Kentucky coal, the absence of the two ring system strongly indicates the probable presence of additional donor species.

Examination of the various solvent parameters: hydrogen content, infrared absorbance ratio, average proton chemical shift, and proton distribution shows an optimum range for maximal conversion and are given in Table VI. It is hoped that these ranges will provide a means for evaluating solvents for effective coal dissolution.

Acknowledgements

The authors are grateful to the U.S. Department of Energy Fossil Energy Division for support of this work.

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Table I
Dissolution Behavior of Western Kentucky Coal in Creosote Oil,
Hydrogenated Creosote Oil and Light Recycle Oil

Experimental Conditions: Temperature = 410° Reaction Time = 15 minutes

Creosote Oil and Hydrogenated Creosote Oil	Hydrogen Content of Solvent H %	Dissolution Behavior of Solvent % Conversion
Creosote Oil	6.74 ± 0.26	32.8 ± 2.37
HC I ^a	6.24 ± 0.13	36.9 ± 0.24
HC II	6.98 ± 0.22	48.1 ± 0.93
HC III	7.20 ± 0.30	64.2 ± 1.82
HC IV	10.00 ± 0.22	66.3 ± 1.11
HC V	7.78 ± 0.07	70.0 ± 1.11
HC VI	8.14 ± 0.22	79.7 ± 0.15
HC VII	9.41 ± 0.21	81.5 ± 0.94
HC VIII	8.34 ± 0.19	82.3 ± 0.61
HC IX	9.54 ± 0.09	82.4 ± 0.63
HC X	8.00 ± 0.22	84.5 ± 0.06
Light Recycle Oil		
Amax	7.97 ± 0.10	38.4 ± 1.4
Monterey	7.26 ± 0.49	40.0 ± 0.55
Western Kentucky I	8.74 ± 0.09	44.2 ± 0.61
Western Kentucky II	8.31 ± 0.40	46.0 ± 1.24
Indiana V	9.72 ± 0.26	53.1 ± 0.14
Western Kentucky Distillation Cuts		
I. < 140°	8.76 ± 0.09	41.0 ± 0.34
II. 140° - 200°	8.08 ± 0.14	57.9 ± 0.58
III. 200° - 290°	8.17 ± 0.27	59.1 ± 3.1
90 - Weight Petroleum Oil	12.47 ± 0.10	28.8 ± 1.4

a) reacted under N₂ atmosphere b) pot temperature, 1 mm of Hg

Table II
Infrared Absorbance Ratios of the Hydrogenated Creosote Solvents and the
Light Recycle Solvents in order of Increasing Dissolution

Solvent:	IR Absorbance Ratios ^e		
	$\frac{\text{Aromatic C-H}}{\text{Aliphatic CH}_3}$ 3050/2960	$\frac{\text{Aromatic C-H}}{\text{Aliphatic CH}_2}$ 3050/2925 ²	$\frac{\text{Aliphatic CH}_3}{\text{Aliphatic CH}_2}$ 2960/2925 ²
Creosote Oil and Hydrogenated Creosote Oils ^e			
Creosote Oil	2.23 ^b	1.54	0.68
HC I ^a	2.30 ^b	1.70	0.74
HC II	1.89 ^b	1.24	0.66
HC III	-- ^c	0.76	-- ^c
HC IV	--	0.18	--
HC V	--	0.62	--
HC VI	--	0.42	--
HC VII	--	0.27	--
HC VIII	--	0.36	--
HC IX	--	0.27	--
HC X	--	0.32	0.24
Light Recycle Oils ^f	3050/2960	3050/2925	2960/2925
Amax	0.70	0.62	0.89
Monterey	0.59	0.54	0.90
Western Kentucky I	0.55	0.48	0.88
Western Kentucky II	0.67	0.59	0.88
Indiana	0.38	0.34	0.88
Distillation Cuts			
<140° C I	0.56	0.51	0.90
140° - 200° C II	0.52	0.45	0.87
200 - 290° C III	0.43	0.34	0.79
90 Weight Petroleum Oil	-- ^d	-- ^d	0.76

- a) reacted under N₂ atmosphere
b) 2960 cm⁻¹ peak is a shoulder
c) 2960 cm⁻¹ is absent
d) 3050 cm⁻¹ peak is absent
e) solution spectra in CCl₄
f) neat spectra

Table III
Hydrogen Distribution (% H) of Hydrogenated
Creosote Solvents and Light Recycle Solvents

Solvent Creosote Oil Hydrogenated Creosote Oils	% Conversion	Hydrogen Distribution Actual Hydrogen Content in Each Fraction			
		H _{AR}	H _α	H _β	H _γ
Creosote Oil	32.8	5.0	0.74	0.74	0.22
HC I	36.9	4.7	0.75	0.75	0.13
HC II	48.1	5.0	1.0	0.70	0.26
HC III	64.2	4.5	1.2	1.1	0.43
HC IV	66.3	2.3	2.0	4.0	1.6
HC V	70.0	4.7	1.5	1.2	0.39
HC VI	79.7	4.3	1.6	1.6	0.55
HC VII	81.5	2.9	2.1	3.1	1.2
HC VIII	82.3	4.2	1.6	1.8	0.72
HC IX	82.4	2.6	2.3	3.5	1.2
HC X	84.5	3.8	1.8	1.8	0.59
Light Recycle Oils					
Amax	38.4	3.7	1.4	1.8	0.96
Monterey	40.0	3.6	1.3	1.6	0.73
Western Kentucky I	44.2	3.4	1.7	2.4	1.1
Western Kentucky II	46.0	4.3	1.5	1.8	0.66
Indiana	53.1	2.4	2.4	3.5	1.7
Western Kentucky Distillation Cuts					
I	41.0	3.7	1.8	2.2	1.1
II	57.9	3.2	1.8	2.5	0.5
III	59.1	2.5	2.2	2.5	1.1
90 Weight Petroleum Oil	28.8	0.87	0.5	5.4	3.6

H_{AR} = 6.0 to 9.2 ppm

H_β = 1.0 to 2.0 ppm

H_α = 2.0 to 3.3 ppm

H_γ = 0.5 to 1.0 ppm

Table IV
Average Hydrogen Distributions for
the Three Conversion Ranges

Conversion Range % Conversion	Average Hydrogen Distributions			
	H _{AR}	H _α	H _β	H _γ
32.8 to 48.1	4.9	0.83	0.69	0.20
64.2 to 70.0	3.8	1.3	1.8	0.81
79.7 to 84.5	3.5	1.9	2.4	0.85

Table V
Weight Percent of Decalin, Tetralin, Naphthalene and a
Hydrogenerated Naphthalene in Creosote Oils and Light Recycle Oils

Creosote Oil		Hydrogenerated			
Solvent Series	% Conversion	Naphthalene	Naphthalene	Tetralin	Decalin
Creosote Oil	32.8	11.2	0	0	0.11
HC I	36.9	10.2	0	0	0
HC II	48.0	5.7	0.45	0	0
HC III	64.2	8.4	0.25	1.7	0.085
HC IV	66.3	2.4	2.66	7.14	7.58
HC V	70.0	6.9	0.99	3.2	0.093
HC VII	81.5	1.92	1.87	7.64	5.70
HC IX	82.4	0.082	4.05	8.88	1.20
HC X	84.5	2.67	1.40	4.01	1.40
Light Recycle Oil					
Amax	38.4	18.1	0.438	4.4	0.77
Monterey	40.0	14.5	0.43	5.62	1.71
Western Kentucky I	44.2	12.3	4.8	6.03	0.61
Western Kentucky II	46.0	15.8	0.55	5.50	0.83
Indiana	53.1	2.81	0	0.093	0

Table VI

Optimum Parameter Ranges for Effective Dissolution (Conversions > 80%)
for the Hydrogenerated Creosote Oil Solvent Series

<u>Parameter</u>	<u>Range</u>
Hydrogen Content (H%)	8.00 to 9.60
Aromatic Hydrogen ($H_{AR}\%$)	2.75 to 4.3
Alpha Hydrogen ($H_{\alpha}\%$)	higher 1.7
Beta Hydrogen ($H_{\beta}\%$)	1.6 to 3.55
Gamma Hydrogen ($H_{\gamma}\%$)	0.6 to 1.25
Average Chemical Shift (\bar{H} ppm)	3.15 to 4.55
IR Absorbance Ratios (in CCl_4)	0.27 to 0.36

FIGURE 1
CONVERSION VS. AVERAGE CHEMICAL SHIFT

- CREOSOTE OILS
- RECYCLE SOLVENTS
- △ PETROLEUM OIL

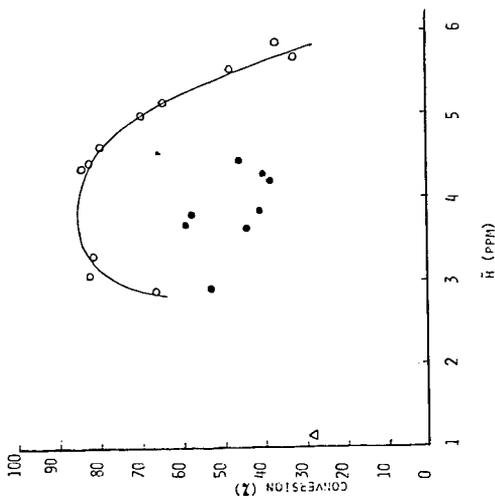


FIGURE 2
CONVERSION VS. HYDROGEN CONTENT

- CREOSOTE OILS WITH WESTERN KENTUCKY COAL
- RECYCLE SOLVENTS WITH WESTERN KENTUCKY COAL
- CREOSOTE OILS WITH AMAX COAL
- RECYCLE SOLVENTS WITH AMAX COAL
- △ PETROLEUM OIL WITH WESTERN KENTUCKY COAL
- ▲ PETROLEUM OIL WITH AMAX COAL

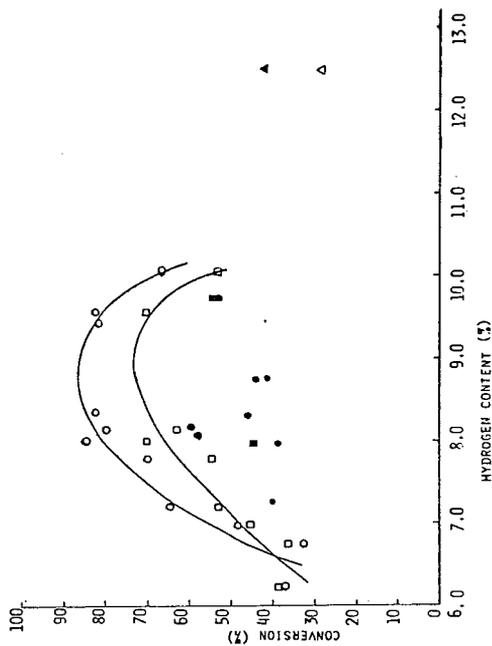
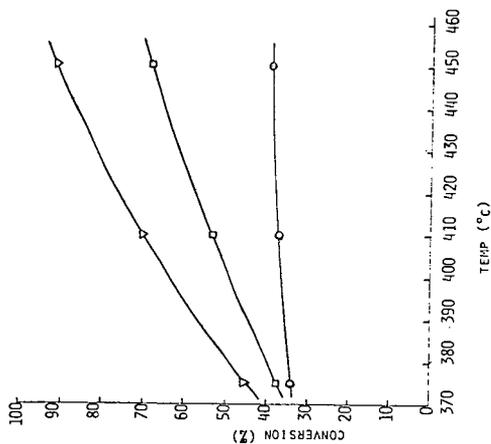


FIGURE 3

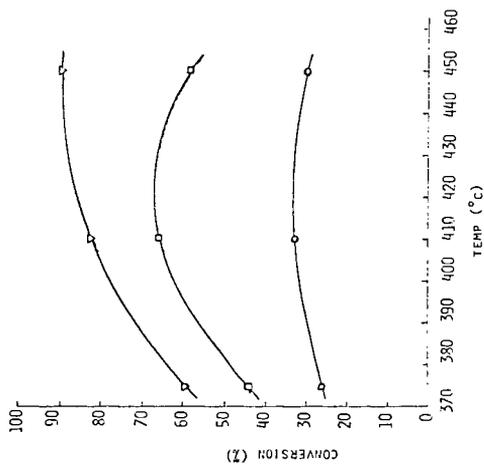
CONVERSION VS. TEMPERATURE

ANVAX COAL
 ○ CREOSOTE OIL
 ▽ HC IX
 □ HC IV



CONVERSION VS. TEMPERATURE

WESTERN KENTUCKY COAL
 ○ CREOSOTE OIL
 ▽ HC IX
 □ HC IV



PRODUCTS OF LIQUEFACTION OF LIGNITE WITH SYNTHESIS GAS BY PRODUCT SLURRY RECYCLE

Bruce W. Farnum, Curtis L. Knudson and Del A. Koch

Grand Forks Energy Technology Center, U. S. Department of Energy
Box 8213 University Station, Grand Forks, ND 58202

Liquefaction of lignite is under study at the Grand Forks Energy Technology Center using a 5 lb coal per hour continuous processing unit (CPU) with various reactor configurations (1). The objectives of the experiment reported in this paper were (a) to test CPU operability under conditions of extensive product slurry recycle with fresh coal addition, (b) to produce a quantity of "lined out" lignite derived liquids for analytical characterization, and (c) to ascertain the function of reaction yields with the degree of line out or number of slurry passes. Objectives (a) and (c) have been discussed at a recent symposium by Willson et al. (2). A one gallon stirred autoclave reactor was operated at 460°C and 4000 psig with an average residence time of about one hour. Redistilled anthracene oil (IBP 296°C at 10 Torr.) was used as a pasting solvent for the initial pass. A 30% slurry of high ash Beulah seam lignite (10.7% ash, 29.6% fixed carbon, 29.5% moisture, 30.2% volatile matter) in pasting solvent was prepared for each pass. The lignite had been pulverized to 100% minus 60 mesh and 90% minus 200 mesh. Batch recycling was carried out through 34 cycles using the unfiltered product as pasting solvent for each subsequent pass. Gases, water and high pressure volatile oils were removed during each cycle. A mixture of equal parts of carbon monoxide and hydrogen was fed through the system at a rate of 1/2 scfm.

Separation of gas and liquid phases at 4000 psig and 300°C was carried out in the unit after the products exited the reactor (Figure 1). The gas phase was then cooled and depressurized producing a water layer, a high pressure volatile oil layer, and tail gases. Yields calculated on a moisture and mineral free coal basis were: C₁-C₄ hydrocarbons 19%, high pressure volatile oils 19%, vacuum distillate 36%, THF soluble vacuum bottoms 9%, and THF insoluble organic polymers 11%.

During Run 27 (64 hours) a slight leak in the autoclave head closure caused loss of the gas head in the reactor with the result that the liquid level rose above the level of the liquid removal tube, and the relatively poorly stirred liquid contacted the overheated wall surfaces. The reactor filled with coked slurry around the space occupied by the stirrer blade and shaft. The suspended solids (minerals and organic polymers) normally present in the product were deposited in the reactor by a process of polymerization of the organic high molecular weight material with inclusion of the mineral particles. Run 27 was terminated after the sixteenth pass. Operation of the CPU was resumed (Run 28) using product from Run 27 as pasting solvent for the first cycle. After the 34th recycle pass, conditions were changed, doubling the slurry feed rate. Coke was found in the reactor at the end of Run 28 and probably occurred for the same reason as in Run 27. However, as indicated in Figure 2 the disproportionate increase in the amount of THF soluble vacuum bottoms was not observed in Run 28, indicating this coking occurred later in the run.

Figure 2 depicts on an MAF coal basis a summation of the yields of the various product fractions obtained. Ash concentration in the product stream paralleled the THF insoluble values showing the same inclusion of inorganic fraction as coke formed in the reactor.

Gas samples were analyzed by on-line gas chromatography. Effluent water samples were characterized by standard analytical methods for waste water and

standard EPA methods (3,4). The average analysis of four samples of condensate water produced under lined out conditions is reported in Table 1.

The aromatic to aliphatic proton ratio of the high pressure volatile oils was monitored as a function of recycle pass number by infrared spectrophotometry and by proton nuclear magnetic resonance spectrometry. 90MHz proton NMR spectra were integrated over the range 9.7 to 6.4 ppm in the aromatic region (Har), 4.2 to 1.7 ppm in the benzylic region (Halp), and 1.7 to 0.25 ppm in the aliphatic methyl and methylene region (Ho). Water and phenolic OH proton signals were omitted, and solvent (deuteropyridine) contributions were subtracted from the total integrated area. Calculation of molecular parameters, f_a , sigma and Haru/Car were carried out as defined by Brown and Ladner (5).

Figure 3 illustrates the approach to constant composition of the high pressure volatile oils collected during each pass. The discontinuity of the curves following the sixteenth pass was caused by the operational problem previously discussed. Agreement of the two methods of analysis was good. A plot of IR ratio versus NMR ratio was linear with a correlation coefficient of 0.96. NMR data is listed in Tables 2 and 3. Gas chromatographic separation indicated about 269 resolved components using a 50 meter OV-101 glass capillary column. There were 30 components present in 1 to 4% concentration, 23 in 0.5 to 1%, 110 in 0.1 to 0.5%, and 106 in 0.01 to 0.1% concentration. Identification of the components of the light oil is in progress and will be reported at a future date.

Low voltage low resolution mass spectrometry provided an indication of the organic oxygen compound type distribution of the high pressure volatile oils (Figure 4). The build up of phenolic oxygen observed by mass spectrometry was also observed by measuring the phenolic OH proton concentration by NMR. The total oxygen content by neutron activation analysis equaled the organic oxygen content from LVMS plus the water oxygen content measured by Karl Fischer titration in the lined out volatile oil. The computer program for analysis of mass data was originally developed for analysis of gasifier tar (6) and accounted for 76% of the total ion current.

Determination of the molecular weight distribution (MWD) of the THF soluble fraction of the product stream was carried out using gel permeation HPLC with uv detection at 365 nm (7). The startup solvent was mostly replaced by lignite derived oil by pass number 5 (Figure 5). The THF soluble fraction of the product stream yields an average MW of 300 relative to Water's polystyrene standards.

Gel permeation chromatography of the non-distillable but THF soluble fraction of the product stream indicated an increase in molecular weight during passes 6-14 which paralleled the trend in percent vacuum bottoms. This is another indication that organic polymerization was the probable cause of coke formation in the reactor. Temperature was held constant during processing. Reactor temperature has been previously observed to be the predominant factor in lowering molecular weight in both batch autoclave studies (8) and stirred autoclave continuous process unit studies (1,2). Figure 6 illustrates the ratio of uv absorbance at 254 nm of high molecular weight to low molecular weight materials versus reactor temperature in studies carried out with the batch autoclave and the continuous stirred autoclave unit. The strong temperature dependence of the MWD between 400 and 500°C is readily observed. That a CPU yielded similar dependence can also be noted.

The ashes obtained from the feed slurry, product slurry and reactor coke material have been examined to determine if the coke contains any enrichment of Ca, Mg, Fe, or Na content. None was observed, supporting the hypothesis that coking was due to polymerization of the organic phase rather than agglomeration and deposition of minerals. Figure 7 depicts the locations where samples were obtained from coke removed from the reactor after Run 28. Three distinct differ-

ently colored regions were observed. The center (B3-1) was softer and slightly sticky, while the other areas were hard and brittle. Ash and sulfur content indicated little variability in composition of the coke from the reactor (Table 4). Analysis of the ashes of feed slurry, product slurry and coke samples with an inductively coupled argon plasma (ICAP) spectrometer after digestion indicates that the Ca, Fe, Mg and Na contents are essentially identical. The data does indicate that no build up of calcium carbonate occurred in the stirred autoclave reactor to cause reactor plugging as has been observed in tubular reactors (9). The presence of 5.7 wt. percent carbonate was observed by TGA analysis indicating carbonates were present. Since much of the sodium and calcium content of low rank coals is dispersed throughout the organic matrix as humate salts, the formation of bicarbonate-carbonate salts is expected from decarboxylation of the humates early in the process. High CO₂ and water concentrations in the reactor may account for not observing carbonate agglomeration.

Acknowledgement: We are indebted to Dr. Warrack Willson (Liquefaction Project Manager), Gene Baker, Raymond Majkrzak and James Tibbetts for operation of the CPU and calculation of yield data. We also thank Dr. Sylvia Farnum, Dr. Warren Reynolds, William Barton, David Miller, Ed Bitzan, Diane Rindt, George Montgomery and Steven Benson for contributions of data and helpful discussions.

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Table 1
Effluent Water Composition^a
(Averages of Recycle Passes 21, 24, 29 and 32)
(Concentrations in ppm)

pH at analysis	8.6
Alkalinity as CaCO ₃	80,400
Ammonia	27,300
Total sulfur	2,380
Total carbon	31,200
Inorganic carbon	12,400
Organic Carbon	18,800
Phenol	6,430
<u>o</u> -cresol	579
<u>m,p</u> -cresols	1,640

a. Analysis carried out under contract by Stearns-Roger, Inc.

Table 2
NMR Analysis of Light Oils^a

Sample	Pass No.	%Har	%H α	%H δ	fa	σ	Haru/Car	%Hphenolic
27L01	0.5	8.0	13.0	79.0	0.167	0.455	1.602	0
L02	4.2	12.7	15.7	71.6	0.264	0.416	1.395	0.79
L03	8.7	19.3	20.1	60.7	0.387	0.364	1.191	1.84
L04	13.6	22.6	20.9	56.4	0.432	0.348	1.182	2.53
28L02	18	21.7	23.2	55.1	0.415	0.393	1.224	2.08
L04	20	17.1	18.3	64.6	0.346	0.404	1.230	1.72
L06	22	19.6	22.0	58.4	0.386	0.413	1.246	2.02
L08	24	19.5	18.8	61.7	0.378	0.380	1.216	2.43
L010	26	21.9	22.8	55.2	0.406	0.392	1.282	2.51
L012	28	20.9	19.5	59.6	0.393	0.370	1.228	2.49
L013	29	21.3	19.7	59.0	0.393	0.373	1.257	2.74
L014	30	22.6	20.7	56.7	0.406	0.383	1.286	2.86
L015	31	21.9	20.7	57.4	0.398	0.376	1.286	2.63
L016	32	22.0	20.4	57.5	0.405	0.384	1.256	2.59
L017A	33	22.5	20.3	57.2	0.410	0.368	1.244	2.74
L018	34	18.6	18.9	62.5	0.351	0.378	1.363	2.07

a. Analyses performed on a Varian EM-390 Spectrometer located at the University of North Dakota Department of Chemistry.

Table 3
NMR Analysis of Unfiltered Product^a

Sample	Pass No.	%Har	%H α	%H β	f α	σ	Haru/Car
27-Y1	1	33.4	28.6	38.0	0.650	0.296	0.762
27-B2B	3	35.8	28.5	35.7	0.670	0.294	0.774
27-B2D	5	38.0	28.6	33.5	0.693	0.304	0.756
28-2B	18	42.6	28.7	28.7	0.730	0.303	0.750
28-4B	20	43.4	29.3	27.3	0.737	0.284	0.741
28-6B	22	42.7	28.8	28.4	0.734	0.287	0.734
8B	24	43.1	28.3	28.6	0.735	0.286	0.741
10B	26	43.5	27.1	29.5	0.739	0.274	0.723
12B	28	43.0	28.6	28.4	0.741	0.289	0.718
13B	29	43.9	27.7	28.5	0.746	0.278	0.713
14B	30	43.1	28.3	28.6	0.745	0.286	0.701
15B	31	42.5	28.0	29.5	0.737	0.291	0.713
16B	32	44.1	28.2	27.7	0.753	0.289	0.697
17B	33	41.5	30.2	28.3	0.718	0.295	0.770
18B	34	41.1	29.3	29.5	0.735	0.317	0.701
22B	38	41.6	30.8	27.6	0.745	0.326	0.687

a. Analyses performed on a Varian EM-390 Spectrometer located at the University of North Dakota Department of Chemistry.

Table 4
Analyses of the Feed Slurry (FS), Product Stream (PB)^a
and Reactor Coke (CK) by ICAP after High Temperature Ashing^a

Run 28										
Element/ Sample ^b	FS4	FS13	FS15	FS16	FS Ave	PB8	PB13	PB15	PB16	PB Ave
Ca, x10 ⁻³ ppm	83.1	80.3	81.6	83.4	82.1	85.0	78.8	83.2	80.7	81.9
Fe	86.2	84.7	84.5	85.5	85.2	89.0	85.4	89.5	86.2	87.5
Mg	23.4	22.8	23.0	23.6	22.9	24.1	23.0	23.2	23.2	23.4
Mg ₂	22.5	22.6	23.2	22.3		23.6	23.2	23.9	22.9	
Na	28.7	29.4	30.9	27.1		26.9	31.3	29.7	29.7	
Na ₂	27.9	29.4	30.7	27.3	28.9	27.9	31.2	29.7	29.8	29.5
Run 28 Coke										
Element/ Sample ^c	CKB1				CKB3-4					
Ca, x10 ⁻³ ppm	83.9				86.3					
Fe	83.4				87.2					
Mg	23.8				24.2					
Mg ₂	22.9				23.7					
Na	29.4				31.3					
Na ₂	24.9				30.6					

a. Determinations.

b. As an example FS4 = feed slurry on the fourth recycle pass.

c. See Figure 7 for locations where coke samples were obtained.

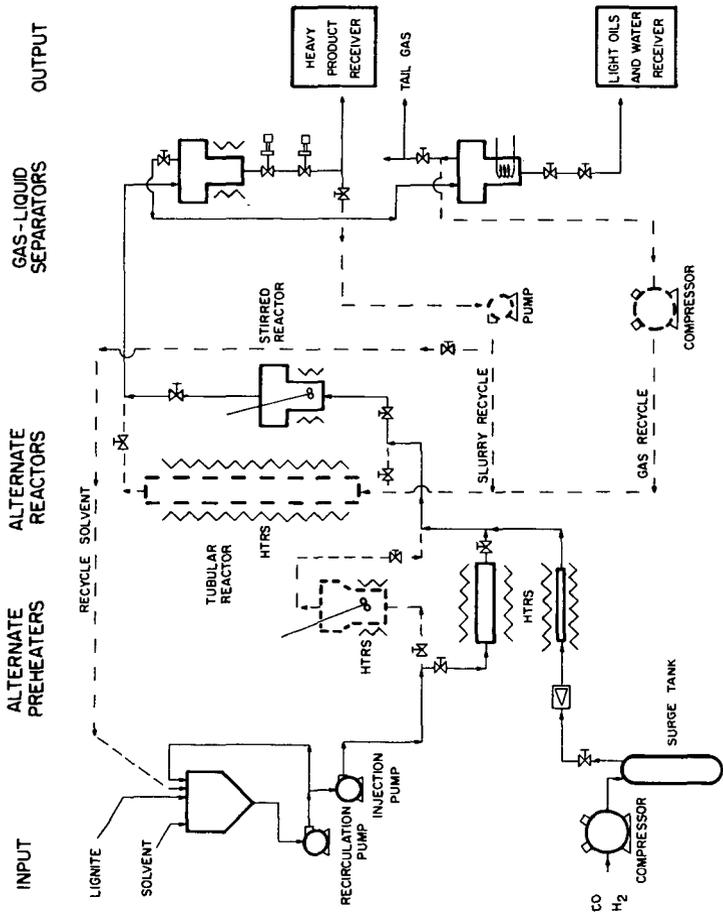


Figure 1. - Schematic diagram of the 6FETC 5-lb coal/hr continuous process unit.

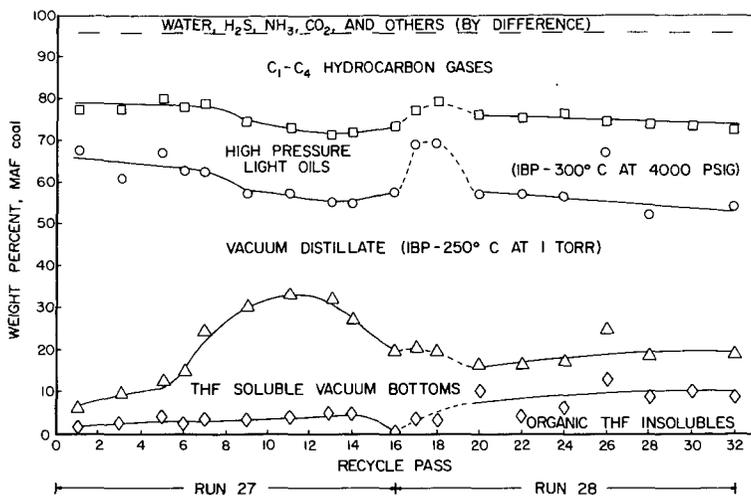


Figure 2. - Runs 27 & 28: Distribution of MAF coal conversion products versus recycle pass.

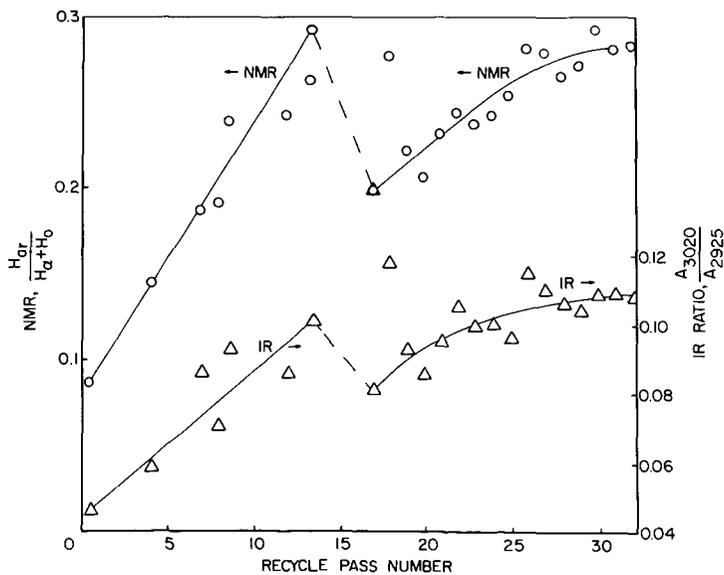


Figure 3. - Aromatic to aliphatic proton ratio by NMR and IR versus recycle pass number.

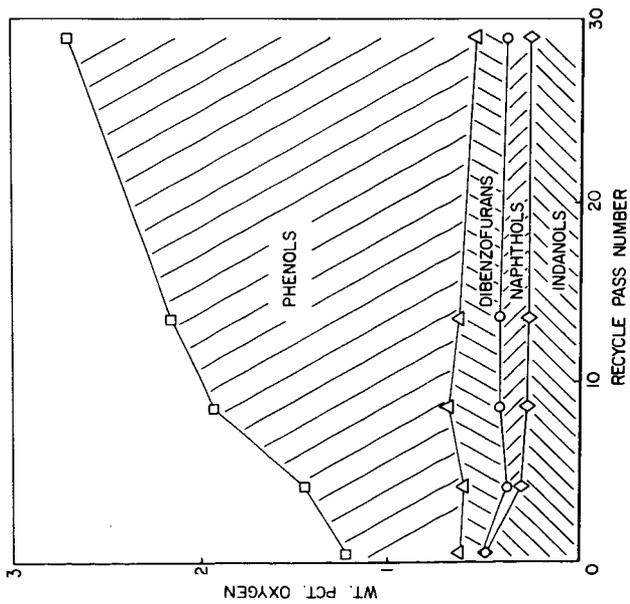


Figure 4. - Oxygen distribution in the high pressure light oils as determined by LVMS.

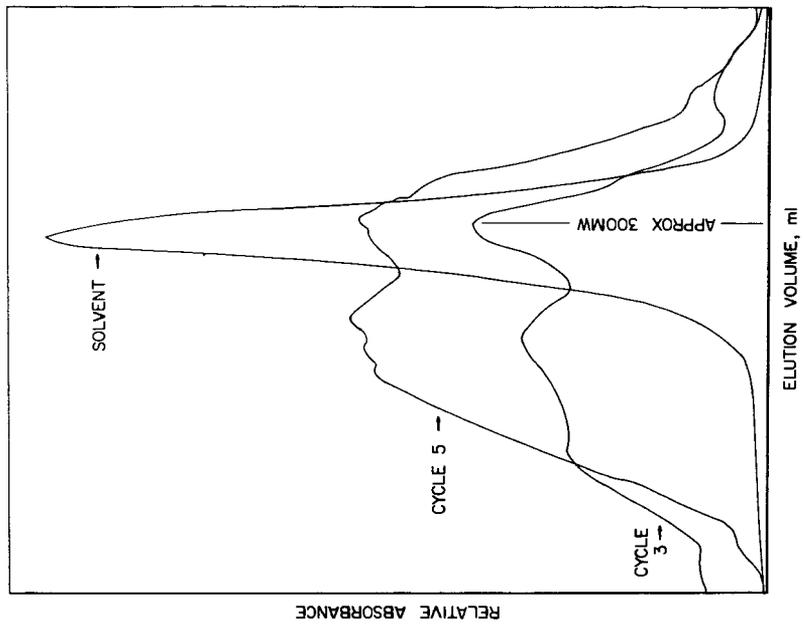


Figure 5. - Changes in the molecular weight distribution with recycle (Run 27). Detection was at 365 nm.

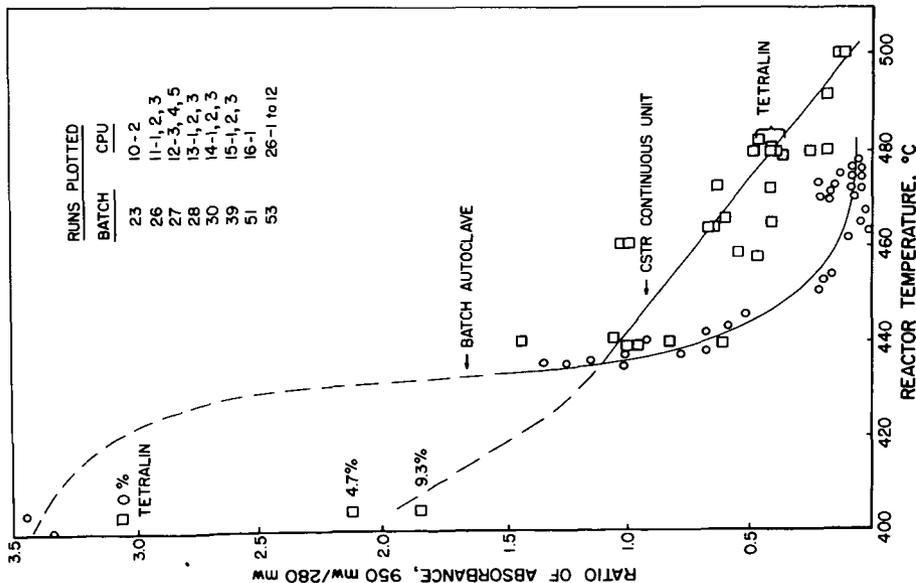


Figure 6. - Ratio of U.V. absorbance at 254 nm of 950 MW to 250 MW material versus reactor temperature for reaction times under 30 minutes.

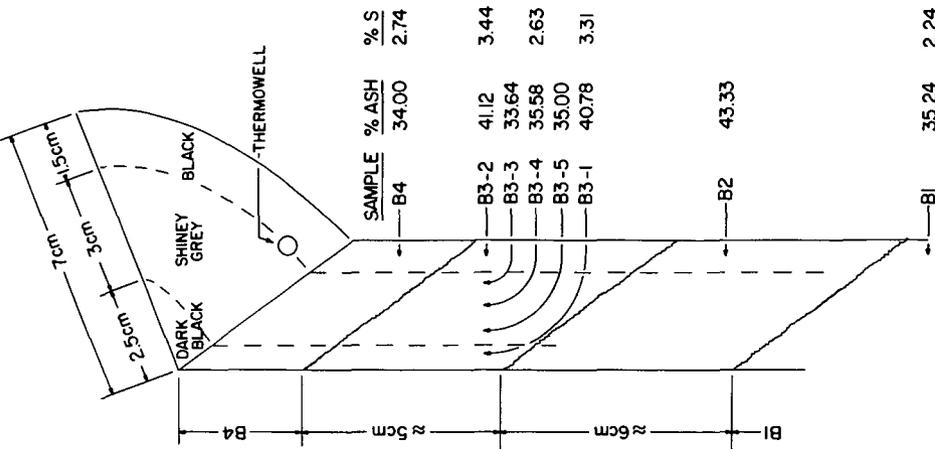


Figure 7. - Location of reactor coke samples from Run 28 and their ash and sulfur contents.

Separation of Coal-Derived Liquids By Gel Permeation Chromatography

C. V. Philip and Rayford G. Anthony

Department of Chemical Engineering
Texas A&M University
College Station, Texas 77843

INTRODUCTION

Characterization and estimation of components in coal derived products are always time consuming and complex due to the number of various constituents present in them. Most of the people working in this area try to separate coal derived mixtures into four or five fractions and each fraction is enriched with chemically similar species (1 to 7). The fractionation is achieved by either using the difference in the solubility of various components in solvents with different chemical affinities or using absorption chromatography, mainly silica gel columns or various ion exchange and ion-pair columns. The latter achieves a cleaner separation than the former. The major disadvantage of both techniques is the loss of material balance at the end of the separation and the time consuming steps involved. Development of technology on hydro-genation and solvent liquefaction of coal requires analytical techniques for the fast reliable monitoring of coal derived fluids. When solvents like tetralin are used for the liquefaction experiments the analysis of the coal derived products is complex due to the large excess of tetralin and tetralin-derived products in the liquid phase of the system. The removal of the solvent system by conventional separation methods like distillation may result in the partial or complete loss of a number of coal-derived components with boiling points close to that of tetralin. This paper discusses the use of gel permeation chromatography followed by high resolution gas chromatography-mass spectrometry for the separation and characterization of coal derived liquids.

GEL PERMEATION CHROMATOGRAPHY (GPC)

Gel Permeation Chromatography uses columns packed with swelled polymer particles with controlled pore size, formed by the copolymerization of styrene and divinylbenzene. GPC separates molecules according to molecular size based upon a distribution between a stationary phase of controlled pore size distribution and mobile liquid phase. Larger molecules elute faster than smaller molecules since larger molecules are less probable to diffuse into the liquid trapped inside the pore. Selecting the columns with proper pore size which varies from 100Å to 10⁶Å, the technique can be used to separate molecules over a wide range of molecular size, several million to less than 100 molecular weight. The retention volume V_r in a GPC is given by the following equation,

$$V_r = V_i + KV_p$$

where V_i is the column interstitial volume, V_p is the total pore volume and K is the partition coefficient, the ratio of the accessible pore volume to the total pore volume. All solutes elute between V_i and $V_i + V_p$. For Styragel columns the value of the ratio of V_i to V_p is in the order 1-1.3. Consequently the total number of peaks that can be separated on GPC is limited compared to other modes of LC. Relatively larger samples can be separated without sacrificing much of the resolution in about 20

to 40 minutes. Because of its operational simplicity, GPC lends itself as an efficient method for fractionating samples according to molecular size.

EXPERIMENTAL

In the separation of coal derived liquid we used two separate GPC systems. One system consists of four 100 Å μ Styragel columns and THF as the liquid phase, while the other system consists of two 100 Å μ Styragel columns and toluene phase. Two refractometers (Waters Model R 401 and R404) and a UV detector were used for monitoring the effluents from the columns. A flow rate in the range of 0.75 to 1 ml was used for both systems. The samples were injected into the systems as pure liquids or as a concentrated solution. A sample size of about 250 μ l was injected into the column for the separation of coal-derived liquids. Samples from liquefaction experiments using tetralin as hydrogen donor solvent were injected into the columns after filtration using micropore filter without any dilution. Syn-Crude from the Pittsburgh Energy Center pilot plant was obtained as a very viscous material and it was dissolved in THF and injected as a 25% solution after two filtrations using micro-pore filters. Since THF is an excellent solvent for coal-derived liquids, samples were dissolved in THF and used in the GPC system with toluene as the mobile liquid phase. A number of compounds representing various chemical species in coal-derived liquids were obtained from commercial sources and these were used without purification for GPC retention volume studies. When both THF and toluene GPC systems are used for the separation of a coal-derived sample, the fractions from one system were concentrated before injecting into the second system. In certain cases, the samples were completely evaporated and redissolved in the solvent of the second system. Most of these sample manipulations were conducted under dry anaerobic condition. The final characterization of components in various GPC fractions were done using GC and GC-MS. The methodology is expalined in earlier works (8 to 12).

RESULTS AND DISCUSSION

Resolution and percentage of recovery are the two main issues to be solved in order to achieve a successful separation of any complex mixture by chromatographic techniques. The percentage of recovery is very close to 100% for GPC systems using Styragel columns and carrier solvents such as THF and toluene. Figure 1 shows the effect of sample size on peak broadening. Four compounds - octadecane, tetradecane, phenol and tetralin - used in the study represent three major chemical species found in coal-derived products namely straight chain hydrocarbons, phenols and aromatics. The precipitation of octadecane from the mixture was prevented by adding THF (about 15%) to the prepared sample. The use of concentrated or undiluted samples does not affect the specific retention volumes or resolutions. When sample size was increased from a few milligrams to over a hundred milligrams the observed peak broadening was minimal. GPC of a sample with each component over 50 milligram showed unacceptable peak broadening. It was also found that when a sample contained a large amount of one component and other components are not in the over loading range, the resolution of the minor components were unaffected by the overloading effect of the large component.

When THF is used as the mobile liquid phase certain species can hydrogen bond with THF resulting in a larger molecular size and a lower retention volume. When nonpolar solvents like toluene are used the molecular size is more or less unaffected. The retention volume of several compounds in THF and toluene are listed in Tables I and II. The effect of solvent on specific retention volumes of various compounds are illustrated in Figure 2. It is interesting to note that rigid molecules like aromatics have smaller molecular sizes (larger retention volumes) compared to straight chain hydrocarbons of similar molecular weights (8). Phenol hydrogen bonds with THF (1 to 1 complex) resulting in a molecular size larger than a four ring aromatic hydrocarbon. Tetralin, naphthalene and toluene have the same molecular size. It could be inferred that the molecular size in a liquid phase gets a substantial contribution from the

flexible part of the molecules or the bonds with freedom of rotation. No molecular effect resulting from the solute-association with toluene was detected.

The retention volume of known compounds could be used as a guide to fractionate coal-derived liquids. Contrary to the general belief that coal-derived liquids are extremely complex and are formed of several thousands of compounds a simple concept that coal-derived liquids are simple and composed of four or five distinct chemical species such as alkanes, 'asphaltenes', phenols and aromatics was used for GPC separations. By a trial and error method, the technique of fractionating coal-derived liquids by GPC system using THF as the mobile liquid phase was perfected. Figure 3 shows the GPC of a sample from a Texas lignite liquefaction experiment using tetralin as the hydrogen-donor solvent. The sample has about 20% lignite-derived products and the rest composed of tetralin and tetralin-derived products such as naphthalene and decalin. The GPC separates the sample into five fractions. The first fraction is composed of colloidal carbons as well as high molecular weight species. Although the high molecular weight species are not completely characterized, the preliminary test shows that they are mainly of saturated hydrocarbon chains. The second fraction is composed of hydrocarbon chains as well as asphaltenes. Vacuum distillation separates saturated hydrocarbons from the non-volatile asphaltenes. The term asphaltenes is used for a spectra of compounds seen in the GPC with a wide molecular weight distribution but they are relatively non-volatile or decompose at high temperature so that their characterization by GC-MS or MS is so far unsuccessful. Using the elemental analysis of the asphaltene derived from West Virginia sub bituminous coal, can be expressed as $(C_{14}H_{15}O_xN_yS_z)_n$, where values of x, y and z are less than 1. NMR and IR spectra of the asphaltene fraction is similar to those published by other workers (1). The molecular weight distribution, as it is apparent from the GPC pattern resembles to reported values (5).

The aliphatic portion of fraction 2 and fractions 3, 4 and 5 were analyzed by GC-MS and the total ion gas chromatograms of these fractions are shown in figure 4. The peaks are identified in Tables III, IV and V. Since the separation of fractions were made on an arbitrary basis, slight overlapping of some species are expected. The aliphatic fraction is almost free of any phenols and aromatics. A portion of the lower members of alkanes such as dodecane and tridecane are present in the phenolic cut (fraction 3). Although the phenolic cut did not have any aromatics, some of the low molecular weight phenols overlap into the aromatic cut. The cut between the hydrogen donor system namely tetralin and the coal-derived aromatics encounters unavoidable overlapping due to the column overloading effect of the tetralin system, which composes almost 80% of the sample size. Any alkylated aromatic with the exception of toluene (same effective molecular size as naphthalene) has a retention volume lower than that of naphthalene and the overloading causes broadening of the peak resulting from tailing. As a result fairly good separation of aromatics from the tetralin system is obtained. Figure 4e shows the separation of tetralin system. GPC does not separate tetralin from naphthalene or other tetralin-derived products due to their close molecular sizes.

Coal derived liquids from a pilot plant were also separated by GPC followed GC-MS. Since they do not contain a large amount of any hydrogen donor solvent system as in the case of the bench scale experiments, the separation is less complex in appearance. As far as individual components are concerned there is lot of similarity in the general pattern of various coal-derived liquids. Figure 5a shows the GPC of Syn-Crude sample (Pittsburgh Energy Center pilot plant, derived from West Virginia sub-bituminous coal.) Figures 5 b to f show the GPC of the fractions. It could be concluded from these figures that the recovery of the sample injected into the columns is nearly 100%. The components in fraction 1 have a greater tendency for spreading than others.

When the GPC system using THF is used for the separation of coal derived liquids, the GC-MS of various fractions indicate reasonably good separations. But nonvolatile components could still overlap and escape GC-MS detection. If large molecular size aromatics which are nonvolatile are present in the coal-derived liquids, they may be

present in the phenolic fraction. Phenolic fractions of coal-derived liquids from experiments using tetralin contain two isomers of octahydrobinaphthyl (dimeric form of tetralin) as shown in Figure 3b. The phenolic fraction may have overlapping from the low molecular size asphaltenes. Use of a GPC system with toluene as the mobile liquid phase could solve some of these problems. GPC separation of Syn-Crude using toluene is shown in Figure 6a. The fractions were further separated by a GPC system using THF. In the toluene system both phenols and aromatics have more or less similar molecular sizes due to the absence of any hydrogen bonding between the solvent and the coal-derived products. Fraction 3 is composed of phenols and aromatics and Figure 6d shows their separation by the GPC system using THF. It could be assumed that any fraction from the toluene-GPC system should split up in the THF-GPC system if that fraction contains both hydrogen bonding and non-hydrogen bonding species. As expected, all three fractions from Toluene-GPC show signs of spreading due to hydrogen bonding in THF. Ultimately a combined use of two systems using two different solvents such as THF and Toluene can achieve a superior separation for coal derived liquids.

CONCLUSIONS

The analytical techniques have to be developed further for the characterizations of asphaltenes and nitrogen containing species. It is quite likely that the latter could be separated using appropriate solvent manipulations in the GPC systems. It was found that various coal-derived liquids have more or less similar components. Although Texas lignite varies in its BTU value as well as its ash content, a striking similarity in the composition of lignite-derived liquids was observed. Coal-derived liquids from West Virginia sub bituminous coal shows a resemblance to Texas lignite-derived liquids. The amount of aromatic species with three or more rings was detected in relatively small amounts. It could be quite possible that most coal may have a molecular structure made up of loosely bound building blocks such as alkylated phenols and alkylated aromatics (one or two ring-species predominating) and trapped long chain alkanes.

ACKNOWLEDGMENTS

The financial support of the Texas Engineering Experiment Station, the Texas A&M University Center for Energy and Mineral Resources, and Dow Chemical Co., Freeport, Texas, and The Alcoa Foundation, Pittsburgh, PA., is very much appreciated. The lignite was furnished by Alcoa at Rockdale, Texas and by Dow Chemical Co. Collaborative help of Professor Ralph Zingaro of the Chemistry Department is appreciated. Mrs. Argentina Vindiola assisted in collecting some of the data.

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Table I Retention Volume in THF

<u>Compound</u>	<u>Retention Vol.</u>
Pyridine	34.7
Quinoline	33.08
Benzoquinoline	32.00
Acridine	32.00
N-Ethyl Carbazol	30.9
Aniline	30.26
Phenol	30.00
p-Cresol	29.3
Trimethyl phenol	29.0
β -Naphthol	28.64
Octanol	26.8
Tetradecane	25.0

Table II Retention Volume in Toluene

<u>Compound</u>	<u>Retention Vol.</u>
Phenol	21.5
p-Cresol	19.7
Naphthol	19.7
Tetralin	18.97
Indol	17.91
Quinoline	16.66
Octanol	16.28
N-Ethyl Carbazol	14.6
Tetradecane	14.0
Octadecane	11.66

Table III Hydrocarbon Chains Separated from GPC Fraction #2

<u>Aliphatic Fraction</u>		<u>Aliphatic Fraction</u>	
<u>Retention Time</u>	<u>Compound</u>	<u>Retention Time</u>	<u>Compound</u>
<u>(Min.)</u>		<u>(Min.)</u>	
8.0	Dodecane	33.5	Heneicosane
9.7	Tridecane	35.9	Docosane
13.7	Tetradecane	38.2	Tricosane
16.7	Pentadecane	40.4	Tetracosane
19.8	Hexadecane	42.7	Pentacosane
22.9	Heptadecane + Pristine	44.8	Hexacosane
25.7	Octadecane	46.9	Heptacosane
28.3	Nonadecane	48.9	Octacosane
31.0	Eicosane	50.7	Nonacosane

Table IV Phenolic Fraction (GFC Fraction, #3)

Retention Time (min)	Compound	Retention Time (min)	Compound
6.0	Phenol	36.9	n-Tetradecane
7.4	n-Decane	37.3	$C_{14}H_{30}$ + C_1 -Alkylindanol
9.8	o-Cresol	38.1	C_5 -Alkylphenol + C_1 -Alkylindanol
11.2	p-Cresol + m-Cresol	39.3	C_5 -Alkylphenol
12.9	n-Undecane	40.7	C_5 -Alkylphenol
14.9	C_2 -Alkylphenol	42.4	C_2 -Indanol
17.1	C_2 -Alkylphenol	43.2	Dimethyl Benzothiofene
18.2	C_2 -Alkylphenol	43.7	Dimethyl Indanol
19.1	C_2 -Alkylphenol	45.1	n-pentadecane + C_2 -Alkylindanol
20.2	C_3 -Alkylphenol	46.1	C_2 -Alkylindanol
20.8	C_3 -Alkylphenol + n-Dodecane	47.2	C_2 -Alkylindanol
21.9	C_3 -Alkylphenol	48.0	C_3 -Alkylindanol
23.0	C_3 -Alkylphenol	48.9	C_3 -Alkylindanol
23.7	C_3 -Alkylphenol	50.0	C_3 -Alkylindanol + Hexadecane
24.1	C_3 -Alkylphenol	50.9	C_3 -Alkylindanol
24.4	C_3 -Alkylphenol	51.8	C_3 -Alkylindanol
25.8	C_3 -Alkylphenol	53.0	C_1 -Alkylindanol
26.7	C_3 -Alkylphenol	54.1	C_4 -Alkylindanol + C_1 -Alkylindanol
26.9	$C_{13}H_{28}$ n-Tridecane	55.3	C_1 -Alkylindanol
28.1	C_3 -Alkylphenol	56.3	C_1 -Alkylindanol
29.3	n-Tridecane	57.5	C_4 -Alkylindanol
30.0	C_4 -Alkylphenol	59.9	Dimethyl Naphthol
30.5	C_4 -Alkylphenol	61.7	Dimethyl Naphthol
31.3	C_4 -Alkylphenol	62.7	Dimethyl Naphthol
31.5	C_4 -Alkylphenol	63.4	Dimethyl Naphthol
33.5	C_4 -Alkylphenol + Indanol		
33.7	C_4 -Alkylphenol + C_5 Alkylphenol		
34.1	C_4 -Alkylphenol + C_5 Alkylphenol		
35.3	C_5 -Alkylphenol	81.2	Octahydro 2,2 Binaphthyl
36.2	C_5 -Alkylphenol	83.2	Octahydro, Binaphthyl

Table V Aromatic Fraction (GPC fraction #4)

Retention Time (min)	Compound	Retention Time (min)	Compound
6.1	Phenol	29.6	C ₃ -Alkylindan
6.9	C ₃ -Alkylbenzene + Phenol	30.0	C ₁ -Alkyl-naphthalene
8.9	C ₃ -Alkylbenzene	30.7	C ₃ -Alkylindan
10.1	o-Cresol	31.5	C ₃ -Alkylindan + C ₄ - Alkylindan
11.1	p-Cresol	31.9	C ₄ -Alkylindan
11.9	m-Cresol	32.7	C ₄ -Alkylindan
13.0	m-Cresol + C ₄ - Alkylbenzene	33.7	C ₄ -Alkylindan
13.7	C ₁ -Alkylindan	34.5	C ₂ -Alkyl-naphthalene
14.6	C ₂ -Alkylphenol	35.1	C ₄ -Alkylindane + C ₂ - Alkyl-naphthalene
15.6	C ₂ -Alkylphenol	35.6	C ₄ -Alkylindane
16.2	C ₂ -Alkylphenol	36.2	C ₅ -Alkylindane + C ₂ - Alkyl-naphthalene
17.4	C ₂ -Alkylphenol	37.2	C ₃ -Alkyl-naphthalene
18.5	C ₁ -Alkylindan	37.6	C ₅ -Alkylindan
20.8	Naphthalene	38.2	C ₅ -Alkylindan + C ₃ - Alkyl-naphthalene
21.4	Naphthalene + C ₅ - Alkylbenzene	38.4	C ₃ -Alkyl-naphthalene
21.9	C ₅ -Alkylbenzene	39.5	C ₅ -Alkylindan
22.5	C ₅ -Alkylindan	40.5	C ₃ -Alkyl-naphthalene + C ₅ - Alkylindan
22.9	C ₂ -Alkylindan	40.8	C ₃ -Alkyl-naphthalene
23.7	C ₅ -Alkylbenzene	41.4	C ₃ -Alkyl-naphthalene
25.0	C ₂ -Alkylindan	41.7	C ₃ -Alkyl-naphthalene
25.7	C ₂ -Alkylindan	42.1	C ₃ -Alkyl-naphthalene
26.9	C ₂ -Alkylindan	42.9	C ₄ -Alkyl-naphthalene
27.3	C ₃ -Alkylindan	44.6	C ₅ -Alkyl-naphthalene
28.8	C ₁ -Alkyl-naphthalene		

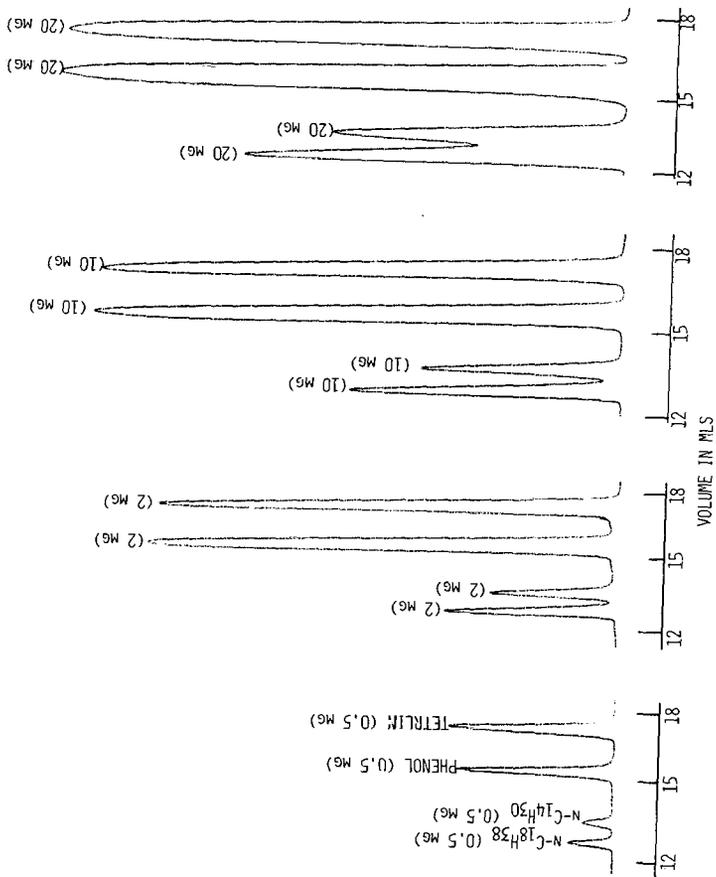


Figure 1. Effect of sample size on retention volume (V_r) and resolution. GPC system used two μ Styragel columns and THF as the liquid phase at a flow rate of 0.75 ml/min.

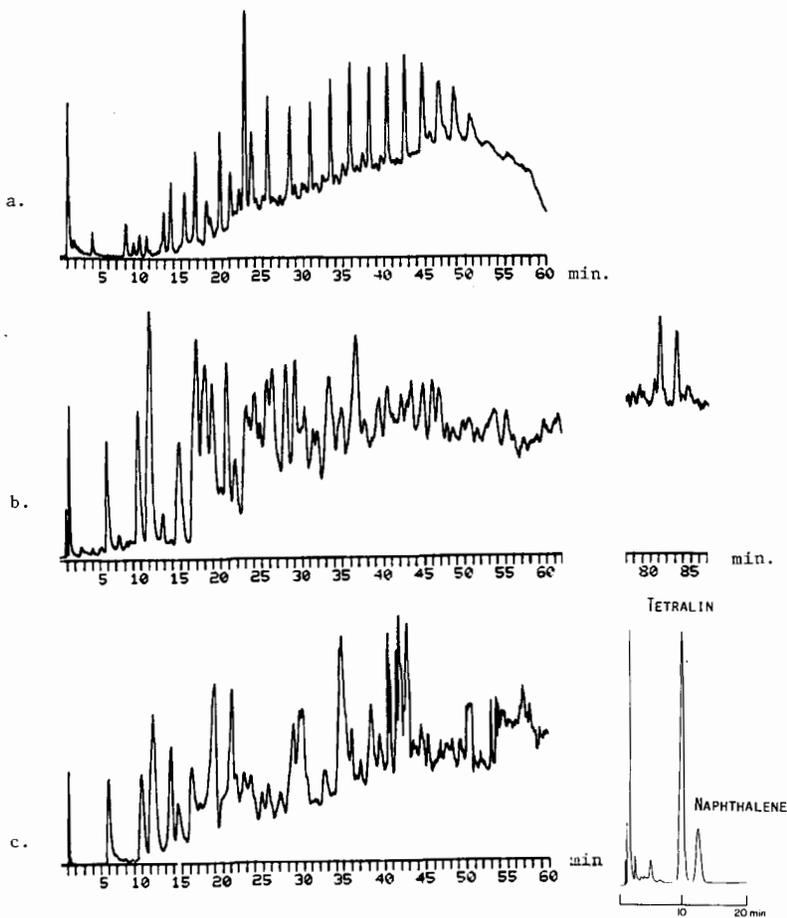


Figure 4. Total ion gas chromatogram of GPC fractions (Figure 3). Column: 5% Dexsil 300 on 100/120 Chromosorb H-WP, 1/8 in. od X 8 ft., carrier gas: 20 ml helium/min., a. Separation of hydrocarbon chains from GPC fraction #2, temperature program 80-270°C at 4 C/min. b. Separation of fraction #3, temperature program: 80-270°C at 2°C/min. for 40 min. followed by 4°C/min., c. Separation of fraction #4, temperature program 50°-270°C at 2°C/min. for 40 min. followed by 4°C/min. d. Fraction #5 was separated on a 10% SP2250 on 100/120 supelcoport 1/4 in. od X 8 ft. SS column at 160°C isothermal. Helium flow rate: 60 ml per min.

Figure 5a. Shows the separation of West Virginia sub bituminous coal-fluid by GPC using four 100 A μ Styragel columns and a flow rate of 1 ml of THF/min. The fraction 1 to 4 reinjected into the same system after concentration and the GPC's of the fractions are shown in Fig. 5b to e in the order.

Figure 6a. Shows the separation of West Virginia sub bituminous coal-derived fluid by GPC using 2 100 A μ Styragel columns and a toluene flow rate of 0.75 ml per min. The fractions were evaporated and redissolved in THF and separated by GPC system using THF solvent (as in Figure 5). The GPC's of the fractions are shown in Fig. b to d in the order. The fractions contained small amounts of toluene.

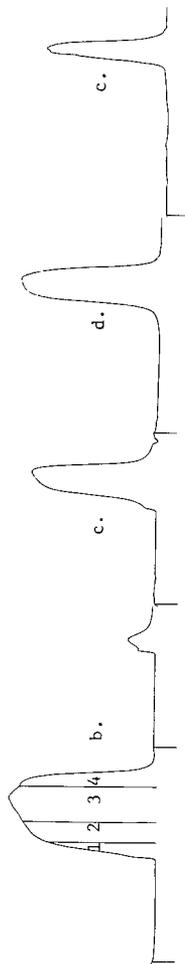


Fig. 5a.

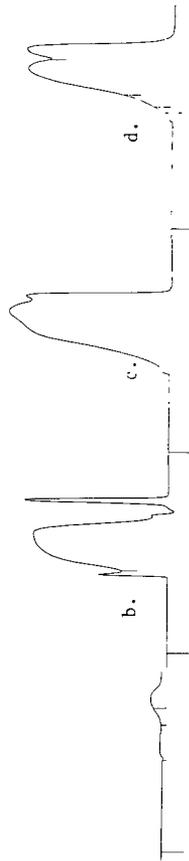


Fig. 6a.

Characterization of Upgraded Coal Liquids
Takao Hara, Krishna C. Tewari, Norman C. Li
Department of Chemistry, Duquesne University, Pittsburgh, PA 15219
Yuan C. Fu
Pittsburgh Energy Technology Center, U.S. Department of Energy
4800 Forbes Avenue, Pittsburgh, PA 15213

INTRODUCTION

The upgrading of coal liquids has become necessary in order to make acceptable fuels for home, transportation and industrial use. Several research groups have stepped up their activities in coal liquid upgrading, as evidenced by a recent symposium (1). However, only a few studies have been reported on characterization and structural analysis of the different fractions obtained in the upgrading of coal-derived liquids.

In this study, upgraded coal liquids from a blend of 30 weight percent of SRC I with 70 weight percent of SRC II, as well as from SRC II, have been studied by IR and NMR techniques. The variation of structural parameters of the upgraded liquids has been determined as a function of reaction temperature and contact time in the catalytic hydroprocessing. The results indicate that along with the decrease in heteroatom contents, asphaltene content, aromatic content and a corresponding increase in aliphatic content, the hydrogen-bonded structure and phenolic OH content of the coal liquids drastically decrease with increase in contact time and temperature. The disappearance of phenolic OH in upgrading process follows a first-order kinetics but no such dependence was observed in case of acidic NH.

EXPERIMENTAL

SRC I and SRC II were made from Kentucky bituminous coal. SRC II was a liquid product with initial boiling point of 453 K and extending into end boiling point of 665K. Elemental analysis of the two products are listed in Table 1, with the results of solvent fractionation based on solubility in toluene and pentane. The blend was prepared by adding 30 parts SRC I to 70 parts SRC II by weight at 413-423 K for 2.5 hrs. under nitrogen pressure.

SRC II and the blend were hydroprocessed over a Ni-Mo catalyst (Nalco NM504) in a trickle bed reactor at hydrogen pressure of 13.8 MPa, liquid hourly space velocities (LHSV) of 0.5, 0.75, and 1.0 hr⁻¹, and temperatures of 672 and 694 K. Prior to the hydroprocessing, the catalyst in the oxide form was presulfided with a H₂/H₂S stream. The hydroprocessing experiments were carried out during a 32-hour continuous operation.

Infrared spectra were recorded on solutions in CS₂ in a 5-mm KBr liquid cell with the solvent in the compensating beam on a Beckman IR-20 infrared spectrometer. The NMR structural parameters (2) were determined before and after hydroprocessing by using a 60-MHz FT NMR spectrometer (Perkin-Elmer R-600).

RESULTS AND DISCUSSION

Several properties, including the results of elemental analysis and solvent analysis for the two kinds of feed materials and their upgraded liquids, are listed in Table 2. The blend and SRC II are sometimes referred as F-1 and F-2, respectively. Hydroprocessed liquids from F-1 are referred as U-1 to U-4, while the upgraded liquid from F-2 is referred as U-5, according to the various hydro-processing reaction conditions as shown in Table 2. With F-1 as feedstock, increase in the H/C ratio is found with increase in contact time at 672 K, but a satisfactory increase in H/C can be obtained at higher temperature of 694 K. Values of H/C and specific gravity of U-5 are comparable to those of light petroleum crude oils such as Kirkuk and Khafji (H/C: 1.68-1.80; specific gravity: 0.85-0.89). Values of U-4 are comparable to heavy petroleum crude oils such as Eocene and Boscan (H/C ratio: 1.51; specific gravity: 0.95 - 0.99 (3). N/C ratio decreases with increase in contact time and temperature.

The IR spectra of F-1 and U-4 are shown in Fig. 1. The decrease of hydrogen-bonded structure after upgrading is seen by the dramatic decrease of broad bands of 3400 cm^{-1} (bonded OH) and 1610 cm^{-1} for U-4. The intense band of 1610 cm^{-1} for F-1 is due to the hydrogen-bonded carbonyl stretching in addition to the skeleton vibration of the aromatic ring (4).

Structural parameters were determined from NMR spectra of the coal liquids in CS_2 . There seems to be no significant difference in the parameters of F-1 and F-2. (Table 3). It should be noted, however, that the CS_2 -soluble fraction of the blend (F-1) is 89.5% and that the toluene-insoluble fraction of F-1 could not be dissolved in CS_2 . In using F-1 as feedstock, there is a gradual decrease in f_a accompanied by an increase in the degree of substitution of aromatic nucleus (σ), with increase in contact time of hydroprocessing at 672 K. At the higher temperature of 694 K, f_a of the upgraded oils from F-1 and F-2 were decreased to 0.33 and 0.17, respectively. Table 3 shows that U-5 is mainly composed of aliphatic compounds, and this is supported by the high H/C ratio (Table 2) as well as IR spectra.

Removal of phenolic OH and acidic NH groups in hydroprocessing of SRC liquids was studied kinetically by measuring the intensity of free OH and NH stretching vibrations at 3600 and 3480 cm^{-1} , respectively. The relative decrease of the OH and NH group intensities is summarized in Table 4 in relation to the contact time of hydroprocessing of F-1 at 672 K. The removal of OH group was found to follow first-order kinetics (Fig. 2). However, no such dependence was observed for the NH group. It must be mentioned that the importance of the effect of mass transfer processes or incomplete catalyst wetting has not been considered in this discussion. As shown in Fig. 2, the relative decrease in the N/C ratio also follows a first-order kinetics under the same reaction conditions. The relative reactivity of oxygen removal to nitrogen removal in hydroprocessing of F-1 at 672 K is estimated to be 2:1, from the slopes in Fig. 2.

Fig. 3 shows partial IR spectra of SRC liquids before and after hydroprocessing in rather concentrated CS₂ solutions of the same concentration (19.2 g/l). After hydroprocessing, the intensity of the 3600 cm⁻¹ peak decreases and new absorption at 2670 cm⁻¹ is found in the upgraded oils. The intensity increases with increase in contact time and temperature of hydroprocessing. The absorption in this region can be ascribed to the proton-transfer NH stretching (N⁺ H...O⁻) (5). We have previously found that when an aliphatic amine as triethylamine is added to the acid/neutral fraction of SRC process solvent, new absorptions were found at 2630, 2610 and 2505 cm⁻¹ (6) and we ascribe these to the formation of proton-transfer ionic species, (N⁺ H...O⁻). The spectrum of U-5 shows that it contains a certain amount of such species, even after almost complete disappearance of NH stretching at 3480 cm⁻¹. The implication is that the proton-transfer ionic species are formed under present hydroprocessing conditions.

Table 5 gives the infrared absorbance ratio of CH₃/CH₂ for the hydroprocessed liquids in dilute CS₂ solution. The ratio decreases from 0.87 to 0.56 with increase in contact time of processing at 672 K, using F-1 as feedstock. The result may indicate that the upgraded oils in the hydroprocessing treatment takes on a saturated cyclic structure (7).

Structural parameters in the asphaltene fractions of the upgraded liquids are given in Table 6. It is interesting to note for the asphaltenes that the values of H_{au}/C_a actually decrease with increase in contact time of hydroprocessing, whereas the reverse is true for the unfractionated liquids. There is also an increase in the number-average molecular weight of the asphaltenes which are isolated from liquids which have been hydroprocessed with a longer contact time. The changes in properties of the various asphaltenes are particularly intriguing, and we plan further experiments with the asphaltenes.

Acknowledgments

The authors thank R. F. Batchelder, J. C. Winslow, and Ray Markby for carrying out the hydroprocessing experiments at the Pittsburgh Energy Technology Center. The work at Duquesne University was supported by the U.S. Department of Energy under Contract No. EY-76-S-02.0063.A003.

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Table 1. Elemental and Solvent Analyses of SRC Products

SRC	Elemental Analysis (wt% maf)				atomic H/C ratio	Toluene-insoluble (TI)	Solvent Fractionation Distribution (wt%)		Heavy Oil [†] (HO)
	C	H	O	N			S	Asphaltene** (A)	
SRC I	85.6	6.05	5.6*	2.01	0.84	34.1	48.8	17.1	
SRC II	89.0	8.7	1.16	0.84	0.28	0.0	0.7	99.3	

*by difference, **Toluene-soluble and pentane-insoluble, † pentane-soluble

Table 2. Properties of Hydroprocessed SRC Liquids

Upgrading Conditions Temp. LHSV K hr ⁻¹	Elemental Analysis (wt% maf)				atomic H/C ratio	N/C x10 ²	Solvent Fractionation		Viscosity cp 311 K	Specific Gravity 289/289 K			
	C	H	O*	N			S	TI			HO		
F-1	87.9	7.95	2.5	1.32	0.3	1.3	10.2	18.5	71.3	1.068			
U-1	672	1.0	88.9	9.7	0.7	0.61	<0.1	1.31	10.9	87.5	9.5	0.981	
U-2	672	0.75	89.0	10.1	~0.3	0.50	<0.1	1.36	0.48	92.4	6.1	0.960	
U-3	672	0.50	89.0	10.4	~0.2	0.24	<0.1	1.40	0.23	94.9	5.2	0.942	
U-4	694	0.50	88.5	11.3	~0	0.16	0.017	1.53	0.15	99.5	3.0	0.899	
F-2	694	0.50	89.0	8.7	1.16**	0.84	0.28	1.17	0.81	99.3	5.0	0.999	
U-5	694	0.50	87.3	12.7	~0	0.02	<0.1	1.75	0.02	0.1	99.9	1.5	0.857

*by difference, **by direct method

Table 3. Structural Parameters for Hydroprocessed SRC Liquids

Sample	Proton Distribution (Area %)			Structural Parameters			
	Aromatic H_a	Benzylic H_α	Aliphatic H_o	f_a	σ	$H_o/H_\alpha + 1$	H_{au}/C_a
F-1**	38.9	27.7	33.4	0.66	0.28	2.2	0.93
U-1	21.4	29.7	48.9	0.49	0.42	2.6	0.99
U-2	19.3	28.7	52.0	0.45	0.43	2.8	1.03
U-3	15.7	24.6	59.7	0.41	0.44	3.4	0.97
U-4	12.9	19.6	67.5	0.33	0.43	4.4	1.05
F-2	37.3	29.8	32.9	0.63	0.30	2.1	0.98
U-5	4.6	9.6	85.8	0.17	0.51	9.9	0.98

*Separation point between H_α and H_o chosen at $\delta = 2.1$ ppm

**Elemental analysis of the CS_2 -soluble fraction of F-1: C 88.2, H 8.3, O 2.0, N 1.18, S 0.3. The CS_2 -soluble fractions of F-1 and U-1 are 89.5% and 99.2%, respectively. All other samples are completely soluble in CS_2 .

Table 4. Reduction of Phenolic (OH) and Acidic Nitrogen (NH) Groups in Hydroprocessing of the Blend of SRC I with SRC II

Sample	Unfractionated Liquid	
	% OH*	% NH*
U-1	19	88
U-2	11	82
U-3	4.4	48

*% of original OH and NH groups remaining in the upgraded liquids, determined by IR.

Table 5. Infrared absorbance ratio of CH₃/CH₂ for various hydro-processed SRC liquids.

Sample *	F-1	U-1	U-2	U-3	U-4	F-2	U-5
ACH ₃ /ACH ₂	0.87	0.62	0.59	0.56	0.57	0.83	0.53

*Absorbance of symmetrical stretching vibration of

CH₃ group at 2960 cm⁻¹ : ACH₃
 CH₂ group at 2925 cm⁻¹ : ACH₂

Table 6. Structural parameters of asphaltene fractions isolated from upgraded SRC liquids.

Source of Asphaltene	Proton Distribution (Area%)			Structural Parameters				Mol. Wt.
	Aromatic Ha	Benzyllic H _α	Aliphatic H _β	fa	σ	Ho/H _α +1	Hau/C _α	
F-1	37.9	38.1	24.0	0.76	0.40	1.6	0.64	820
U-1	33.9	36.0	30.1	0.75	0.39	1.8	0.57	1130
U-2	34.0	32.0	34.0	0.75	0.36	2.1	0.54	1180
U-3	34.0	32.5	33.5	0.75	0.36	2.0	0.54	1160

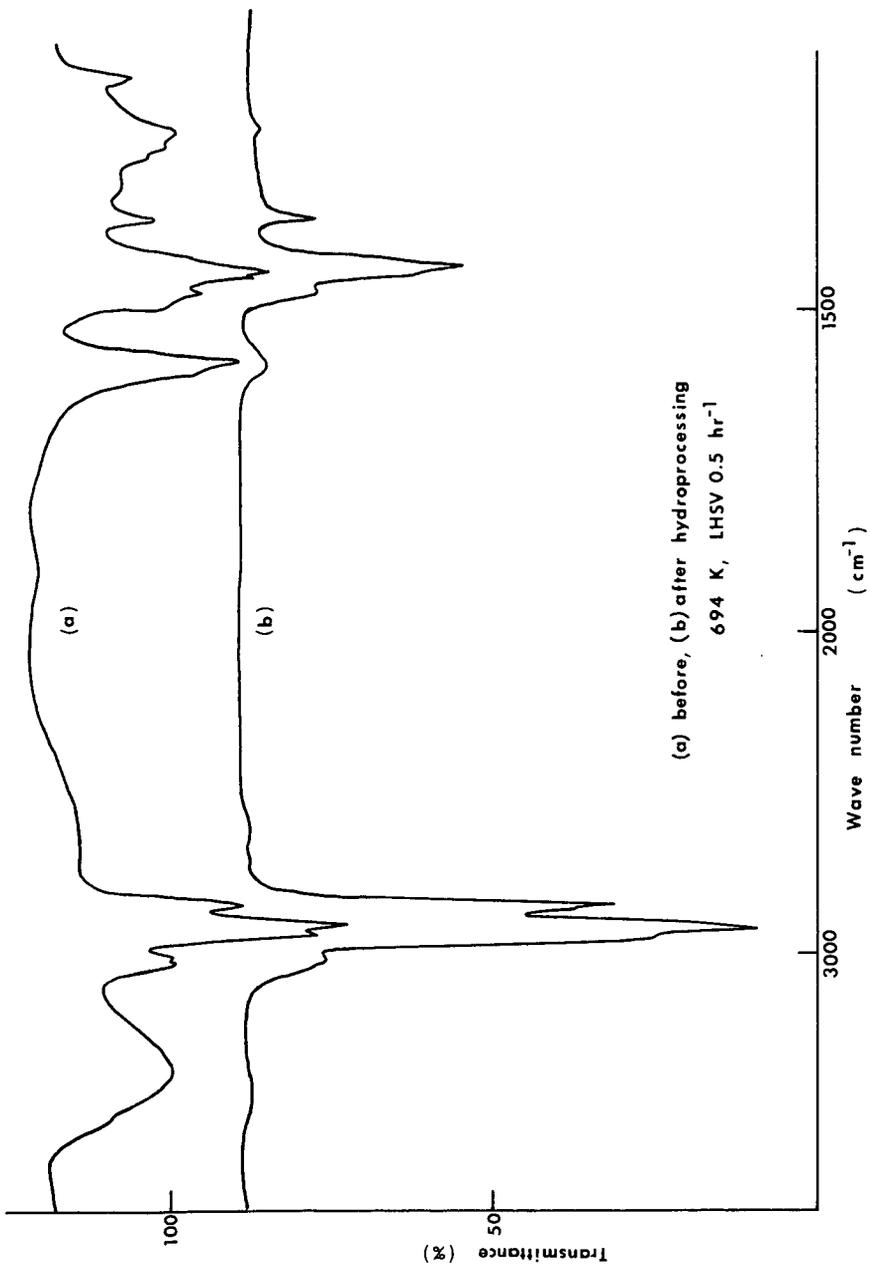


Fig. 1 IR spectra of the blend of SRC I with SRC II before and after upgrading

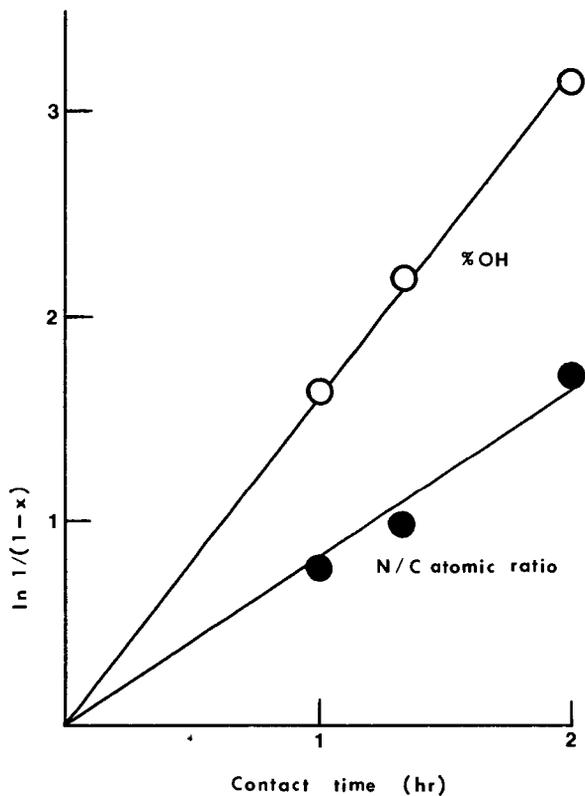


Fig. 2 First-order plot of removal of oxygen and nitrogen

Feed F-1, 672 K

x % conversion

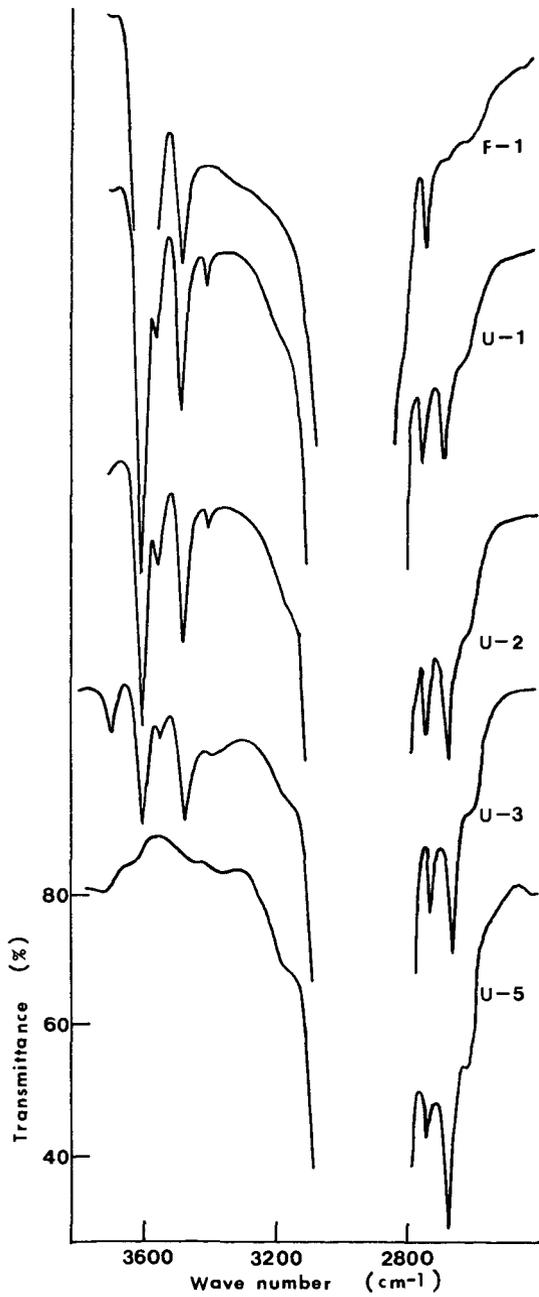


Fig. 3 Formation of proton transfer species (NH⁺) in hydroprocessing
Solvent C₅H₂, 19.2 g/l

A LOW TEMPERATURE REACTION PATH FOR COAL LIQUEFACTION*

M. G. Thomas and R. K. Traeger

Sandia Laboratories, Albuquerque, NM 87185

Introduction

The interaction of coal and solvent to form a gel in the 250-350°C range has significant implications in the efficiency of short residence time or two-stage liquefaction processes and the operation of preheaters in existing coal liquefaction processes. This interaction has been noted (1,2) during the heating of coal slurries in autoclaves where an apparent "endotherm" appears in the time-temperature curve--the "endotherm" is currently believed to be due to a high viscosity gel reducing heat transfer to the thermowell in the autoclave. Evaluation of these transitions leads to the following qualitative results.

1. Coal Effects - As the reactivity (to benzene solubles) toward liquefaction of the coal increases, the temperature of the transition increases;
 - Lignites do not exhibit a measurable transition.
2. Solvent - Transitions are not noted with pure hydrogen donor solvents as tetralin;
 - Magnitude of the transition increases as dissolving ability of the solvent increases.

Work by Cronauer (3) and Whitehurst (4) suggests initial solvent coal reactions which form adducts.

This paper summarizes the results of initial experiments on coal-solvent interactions. Results of low temperature (300°C) batch studies are compared to results obtained from 400-450°C, short residence time continuous reactor studies.

Materials

Three coals of varying reactivity were reacted with pure and coal-derived solvents; analyses are shown in Table 1 (5).

Table 1. Analyses of Coals and Solvents

Ultimate	Illinois #6 Burning Star	West Va. Ireland	Bruceton	SRC II Heavy Distillate	Creosote #4 Cut
Carbon	71.5	73.0	81.3	89.9	90.8
Hydrogen	4.8	5.2	5.3	7.6	5.8
Nitrogen	1.5	1.2	1.6	1.4	1.1
Sulfur	3.3	4.5	1.2	0.4	0.4
Ash	10.0	10.0	3.7	.05	< .05

Three non-coal-derived solvents used were hexadecane, phenanthrene--both C.P. grade--and tetralin, technical grade.

Table 2 summarized results of autoclave liquefaction studies on the three coals.

* This work supported by the U.S. Department of Energy.

Table 2. Coals

Coal	Autoclave Results(5)			Transition Temp.(2) in Creosote Oil, #4 Cut (°C)
	Time	Temp (°C)	% Conv to ØH Sol	
Illinois #6 Burning Star	30	430	-	300
West Virginia Ireland Mine	30	430	64	240
Bruceton	30	430	44	200

Experimental

Two systems were used. The first was a glass system constructed with Schlenk apparatus. A 100 ml flask was topped with an adiabatic (silvered) reflux column. A thermocouple was inserted directly into the slurry and the system was continuously flushed with argon at 1 atmosphere. Slurries contained approximately 9g coal and 22g solvent. The system was stirred with a teflon-coated stir bar in the slurry. (When high viscosities were reached, this method was ineffective.) This apparatus was also employed for heating the dry coals to 300°C. In these cases, a thin layer of coal covered the bottom of the flask and the thermocouple was in direct contact with the flask.

The second system was a four-stage continuous flow reactor. Slurries of 30% coal/70% solvent were employed. Procedures and results are given in reference 6.

Analysis

Products have been analyzed by exhaustive Soxhlet extraction with benzene, followed by a THF extraction of the benzene insols (7) and a separation of benzene sols into pentane sols and insols (7). Some samples were filtered using a pressure filter fitted with #50 Waltman filter paper. Viscosities were measured with a Brookfield LVT viscometer.

Stability of Coal and Solvents

Experiments on the coal and solvent individually were carried out to determine if reactions observed were due to the individual components. Results shown in Table 3 indicate no significant chemical reaction occurs below 370°C and heating to 300°C does not result in THF solubility. However, softening is noted in the 300-330°C range.

Table 3. Thermal Response of Coals and Solvent

Coal	DSC (Broad Endotherm)	Maximum Rate of Wt Loss TGA	Temperature of Maximum Expansion by Dilatometry	Changes in Solubility Observed After Heating to 300°C
Ill #6 BS	~ 370°C	~ 450°C	300°C	None
W. Va.	~ 370°C	~ 450°C	-	None
Bruceton	~ 370°C	~ 450°C	330°C	None
SRC II Heating Dist	Boiling heating to 450°C	Boiling Range heating to 450°C	290-550°C; no change noted in	

Solvent-Coal Studies at Low Pressures

Results of studies made under inert gas at one atmosphere are shown in Table 4.

Table 4. Low Temperature Liquefaction Results

Coal	Solvent	Temp °C	Time Min.	% Soluble Based on MAF Coal	
				% Benzene	% THF
Solvent Effects					
Bruceton	Hexadecane	200	15	0	0
	Tetralin/ Phenanthrene	200	15	-0.4	11
	SRC II H.D.	200	15	-6.0	25
Coal Effects					
Bruceton	SRC II	200	15	-6	25
W. Va.		260	15	-12	22
Ill #6		300	15	-4	19
Ill #6		300	300	-6	23
Temperature Effects					
Bruceton	SRC II	25	0	0	0
		25	15	4	12
		50	15	8	13
		93	15	7	12
		120	15	6	13
		130	15	4	11
		170	15	3	13
200	15	-6	25		

The data from the low temperature experiments show the following:

- Solvent: (a) A non-reactive solvent as hexadecane does not dissolve the coal. Tetralin/phenanthrene mix is a good hydrogen donor but does not give as large a THF conversion as the SRC II heavy distillate.
(b) Increased THF conversion is accompanied by increasing solvent loss (benzene solubles).
- Coal: The least reactive coal (Bruceton) toward liquefaction at higher temperatures is dissolved more readily at lower temperatures. This agrees with the transition temperatures noted in autoclave heatup curves.
- Temperature: Approximately 13% of the coal can be extracted in 15 minutes with THF and this solubility does not increase with temperature until the autoclave transition temperature is reached; THF solubility increases and solvent is lost.

High viscosity products were noted when the THF solubility exceeded 20%; the products contain a high preasphaltene/oil ratio. This condition was only observed when the temperatures equaled or surpassed temperatures where endotherms had been observed in autoclave experiments with the respective coal/solvent systems.

Continuous Reactor Data

If the reactions are thermally activated and no significant mechanism changes occur between 300 and 400°C, short time 400°C effects should be similar to the 15 minute low temperature data just described. Product distributions from the reactor runs with Ill. #6 coal, Figure 1, show that preasphaltenes are produced at short times, apparently at the expense of solvent. These distributions result in high viscosities.

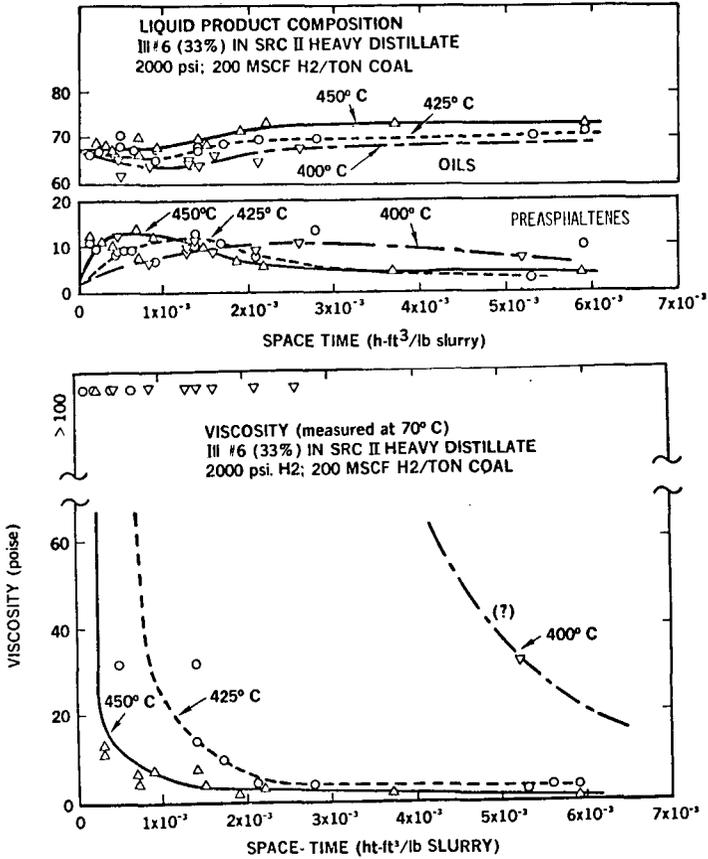


Figure 1

Thus, these continuous reactor data, at short reaction times, agree qualitatively with the low temperature, batch data. Initial regressive reactions have been noted in solvent imbalance during pilot plant short residence time preheater studies (8).

Evaluation of conversion data from the continuous reactor indicate the asphaltene concentration in the slurry product is independent of temperature and dependent on conversion at short times (benzene conversions of 0-55%). These data (Figure 2) suggest a series reaction sequence from coal to asphaltenes.

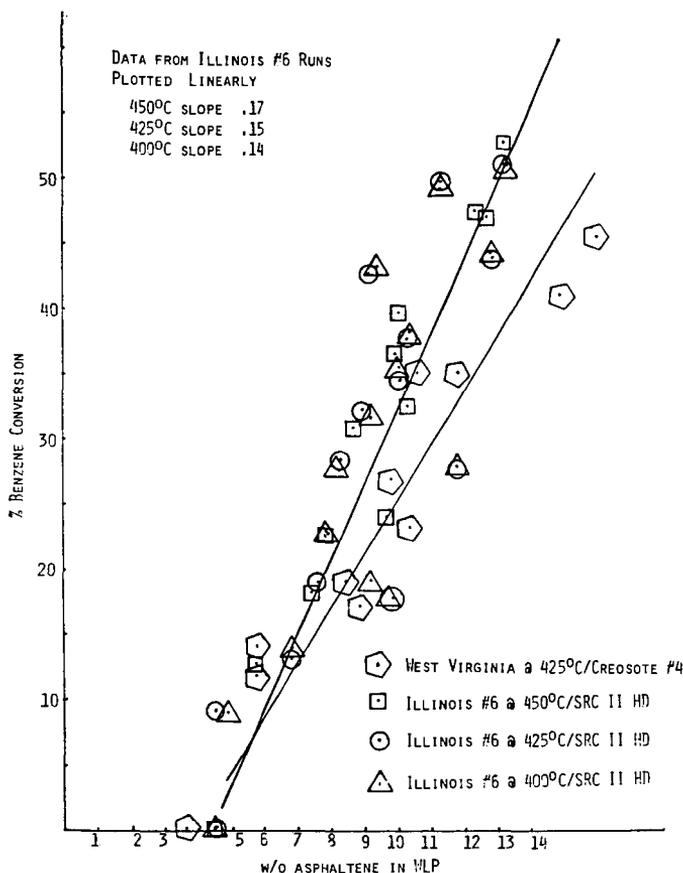
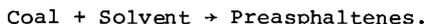


Figure 2

Discussion

Onset of a solvent-coal reaction occurs in the 200-300°C temperature range. The temperature and extent of this reaction are dependent on the coal and solvent. In this initial reaction, THF soluble products increase but solvent is lost indicating formation of a THF soluble, coal-solvent reaction product. This reaction product, defined in the preasphaltene or asphaltol compounds, results in high viscosity products--possibly gels.

A number of kinetic studies of coal liquefaction (Cronauer) processes made at long reaction times (< 10 min) show the liquefaction mechanisms can be represented by parallel reactions of coal to pre-asphaltenes, asphaltenes, oils and gases. However, these data show coal itself does not undergo thermosolvolytic at temperatures to 300°C and free radical processes need not be invoked to explain the reactions observed in the 200-300°C range. The data do suggest an initial series reaction of



The hydrogen donating capability of the solvent does not appear to be critical at this stage, but functional groups that can interact with the coal and cause swelling are important.

This initial series reaction is also indicated in the short time, continuous reactor results, Figure 2, where the preasphaltene content rises along with a solvent loss early in the reaction; subsequent decrease in preasphaltene content is accompanied by an increase in oil and asphaltene concentrations. The asphaltene content (and similarly the oil) is defined by the benzene conversion at 400, 425, and 450°C. The dependence of asphaltene and oil on conversion and not on temperature further suggests that the reaction of coal to preasphaltene goes to completion. Product distributions derived from two sources--coal and preasphaltene--would almost certainly be dependent upon temperature.

Preasphaltene chemistry needs further clarification. The extent, and possibly type, of coal-solvent interaction changes with temperature. Only about 30% THF conversion occurs at low temperatures with 80-95% conversion occurring over 400°C.

Conclusions

Coal liquefaction is initiated at 200-300°C by the reaction of solvent and coal to form preasphaltenes. The temperature of the reaction is a function of the coal type and the solvent. This reaction product imparts high viscosity to the slurry and its chemistry may influence subsequent liquefaction reactions. Understanding of this initial reaction is important to evaluate the applicability of advanced, two-stage liquefaction processes and could lead to the development of new, low temperature and pressure liquefaction schemes.

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THE SELECTIVITY OF COAL MINERALS AND SRC RESIDUE
ASHES FOR HYDRODESULFURIZATION IN THE SRC PROCESS

D. Garg, A. R. Tarrer, C. W. Curtis,
J. M. Lloyd, and J. A. Guin

Chemical Engineering Department
Auburn University
Auburn, Alabama 36830

INTRODUCTION

Many improvements have been made in the Solvent Refined Coal (SRC) process over the past year. During this time period, several solid/liquid separation techniques have evolved that offer promise for cost reduction in ash removal. Concurrently, technical feasibility for the Kerr-McGee's process for critical solvent deashing has been demonstrated on a pilot scale at the Wilsonville SRC facility. Since this separation process can be used to fractionate liquified coal as well as for deashing, a fraction of the liquefied coal could be used as make-up process solvent. As a result, process solvent regeneration appears no longer to be a limiting operational factor for the dissolver stage (1). Now the dissolver performs three basic functions: liquefaction of coal, regeneration of the process solvent and desulfurization of coal liquids. Several studies have shown that liquefaction occurs very rapidly while desulfurization occurs slowly. Thus, now that the Kerr-McGee's process can be used to offset solvent deficiencies, desulfurization may limit dissolver operations, particularly when a solid SRC is produced.

Hydrogen generation for SRC processing is a major operational cost, making short reaction times with minimum hydrogenation severity desirable. The overall objective of this study is to develop a methodology for using mineral additives to increase the rate of desulfurization during coal liquefaction. Some iron containing minerals, including the ash of SRC residue, have been shown to act as in situ sulfur scavengers (2). The addition of such minerals to the dissolver feed may allow sulfur removal requirements to be met with shorter reaction times and consequent lower hydrogen consumption.

The role of mineral additives in coal liquefaction processing is to increase desulfurization with minimal but sufficient hydrogenation. Selectivity is a measure used to rate the effectiveness of the different mineral additives studied. By definition, selectivity is the ratio of the amount of sulfur removal to the amount of hydrogen consumed for a given reaction time.

In previous studies, the effects of relatively large amounts of mineral additives on reaction rates have been examined (3) in order to clearly delineate the effects of the additives. However, in actual application, such large amounts would be prohibitive due to the associated material handling difficulties. Therefore, one of the major objectives of this work is to demonstrate that only small, easily processed, amounts of mineral additives are required for effective sulfur scavenging, provided that the iron contained in the additives is in a form available for reaction and is present in stoichiometric amounts.

EXPERIMENTAL

Reagents and Materials

Light recycle oil (LRO) and Western Kentucky 9/14 coal were obtained from the Wilsonville SRC Pilot Plant, operated by Southern Services, Inc. The LRO contains

0.2 % sulfur and the Western Kentucky coal is analyzed to be 67.8% C, 4.9% H, 3.10% S and 12% mineral matter. The coal was dried overnight at 100°C and 25 inches Hg vacuum before use.

Coal minerals, SRC residue ash; magnetite; pyrite; hematite; reagent grade Fe_2O_3 ; commercial Fe_2O_3 catalyst; and reagent-grade reduced iron, were used as mineral additives for hydrogenation and hydrodesulfurization reactions. Commercial grade Fe_2O_3 (Fe-0301T, 20% Fe_2O_3 mounted on activated alumina) was obtained from the Harshaw Chemical Company. This catalyst was ground to various particle sizes to study the effect of mass transfer on the reactions. Hematite was obtained from Cities Services and magnetite, from Chemalloy Chemical Company. SRC residue obtained from the Wilsonville SRC Pilot Plant was oxidized before use. Hydrogen gas of 99.995% purity was obtained from Union Carbide. All other chemicals were reagent grade.

Equipment

A small tubing bomb reactor and a commercial 300 cc magnedrive autoclave (Autoclave Engineers) were used for all reaction studies and have been previously described (2-4). Varian gas chromatographs (Models 1800 and 920) were used for analysis of liquid and gas liquefaction products. The sulfur content of coal and liquefaction products was determined by using a Leco Sulfur Analyzer (Model 532). Elemental analyses of various mineral additives were determined by energy dispersive X-ray fluorescence analysis (EDXRF). The surface area of the mineral additives was determined by the nitrogen adsorption technique.

Reaction Conditions:

Coal liquefaction reactions were performed for time periods ranging from 15 to 120 minutes, at 410°C and with stirring rates of 1000 rpm except during mass transfer studies when the reactions were stirred at different rates ranging from 600 to 1400 rpm. The autoclaves were charged with 40g of coal, 80g of LRO, and 10g of additive. Benzothiophene desulfurization was studied in a small tubing bomb reactor (12ml capacity). The benzothiophene reaction, 10% benzothiophene in dodecane with appropriate amounts of mineral additives, was performed at 1250 psi hydrogen pressure (at room temperature) and 410°C for 30 minutes.

RESULTS AND DISCUSSION

Effect of the Amount of Additive

Elemental iron has been shown to act as an effective *in situ* sulfur scavenger (2-4). The effect of different amounts of iron on the sulfur content of the total liquid products from coal liquefaction reactions is shown in Figure 1 where the ratio S/S_B is plotted versus Fe/Fe_S . These ratio terms are defined as: S is the weight percent of the residual sulfur; S_B , residual sulfur for the baseline case, i.e. no iron present for the same reaction conditions; Fe, the weight percent of iron added; Fe_S , the stoichiometric amount of iron required to react with the sulfur to be removed. Fe_S is computed on the following basis: 1) the organic sulfur content of the coal is 1.23%; 2) pyritic sulfur of the coal, 0.79%, is reduced to the FeS form; and 3) the sulfur content of the solvent is 0.27%. The residual sulfur (S/S_B) decreased significantly (from 0.79 to 0.53) with increasing amounts of iron ($\text{Fe}/\text{Fe}_S = 1.3$ to 20). The decrease in residual sulfur content is most significant when Fe/Fe_S is less than 10. When Fe/Fe_S is increased from 10 to 20, a decrease of only 0.07 occurred in S/S_B which is just slightly more than the standard deviation of S/S_B (± 0.02). Therefore, in this range, additional amounts of iron appear to have little effect on sulfur removal.

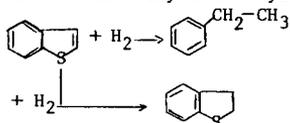
The effect of different amounts of Fe_2O_3 on residual sulfur is also shown in Figure 1. No significant decrease in residual sulfur occurs, when 71% of the stoichiometric required amount of iron is present as Fe_2O_3 (i.e. $\text{Fe}/\text{Fe}_S = 0.71$).

It should be noted that the surface area of the Fe_2O_3 used in this study is $8.9 \text{ m}^2/\text{gm}$. (Table I) Apparently, since no hydrogen sulfide (H_2S) is present in the product gases when stoichiometric amounts of iron are present, all of the iron present in the form of relatively high surface Fe_2O_3 reacts with any H_2S formed. Furthermore, essentially the same degree of desulfurization occurs with a stoichiometric excess of Harshaw iron catalyst, which has a surface area of $60 \text{ m}^2/\text{gm}$, as that obtained with an equivalent amount of Fe_2O_3 . Therefore, the greater surface area of the Harshaw catalyst does not appear to have any significant effect on desulfurization, because equivalent amounts of iron are available in both cases to react with the H_2S produced in the reactor.

The effect of different amounts of iron and Fe_2O_3 on the final hydrogen partial pressure and, consequently, on total hydrogen consumption is shown in Figure 2. The same amount of hydrogen is consumed in either the presence or absence of iron: $H_f/H_o = 0.58 \pm 0.02$, where H_f and H_o are the final and initial hydrogen partial pressures, respectively. Under the same reaction conditions, more hydrogen is consumed when Fe_2O_3 is present: $H_f/H_o = 0.45 \pm 0.01$; however, approximately the same amount of hydrogen is consumed irrespective of the amount of Fe_2O_3 present. Since hydrogen consumption does not depend on the quantity of Fe_2O_3 present, Fe_2O_3 is not significantly reduced at the reaction conditions used. Since more hydrogen is consumed with Fe_2O_3 , the selectivity of iron (sulfur removal per hydrogen consumption) is higher than that of Fe_2O_3 , provided that sufficient iron, i.e. $\text{Fe}/\text{Fe}_S=10$, is present (Fig. 3).

Model Compound Studies

The hydrogenation of benzothiophene under different reaction conditions and with different catalysts produces a variety of products including ethylbenzene, dihydrobenzothiophene, styrene and phenylethanethiols (5,6). Using the iron additives listed in Table I and the reaction conditions stated, the major products observed in this study are ethylbenzene and dihydrobenzothiophene.



The conversion of benzothiophene to these reaction products as catalyzed by the different mineral additives is given in Table I. The mineral additives, Fe_2O_3 and Co-Mo-Al, promoted complete conversion of benzothiophene to ethylbenzene. However, complete conversion to ethylbenzene does not result when iron is the mineral additive; in fact, only 45% of the benzothiophene is converted to ethylbenzene with no significant dihydrobenzothiophene formation. In the benzothiophene reaction, the amount of iron used is considerably less than the amount found necessary for maximum desulfurization of coal/oil reaction mixtures. The Fe/Fe_S for the benzothiophene reaction is 2.7 compared to the optimum Fe/Fe_S of 10 observed for the coal/oil slurries. While in the range of $\text{Fe}/\text{Fe}_S < 10$, desulfurization has been shown in the coal/oil reactions to depend on the amount of iron present. This result is verified in the benzothiophene reaction as given in Table II, where the conversion of benzothiophene is shown to vary significantly with the amount of iron present during the reaction. The conversion of the benzothiophene increases from 23% to 54% with a corresponding increase of Fe/Fe_S from 0.72 to 2.7. Furthermore, when a Harshaw catalyst is used and iron is present in the amount of $\text{Fe}/\text{Fe}_S = 0.37$, a low conversion of benzothiophene is observed; whereas, complete conversion to ethylbenzene occurs when approximately twice the required stoichiometric amount, $\text{Fe}/\text{Fe}_S = 1.9$, is used. As observed in the coal/oil reactions discussed previously, the higher surface area Harshaw Fe_2O_3 catalyst does not result in any significant increases in the desulfurization of the benzothiophene system.

Iron sulfide additives, pyrite and FeS_{1+x} , do not react with the H_2S product, and, as previously reported (3,4), are not as effective in increasing desulfurization

rates as iron and Fe_2O_3 . The results given in Table II concur with these conclusions. In the presence of the iron sulfide additives, the benzothiophene is converted primarily to dihydrobenzothiophene -- a product of hydrogenation -- instead of ethylbenzene -- a product of hydrodesulfurization. In contrast, when iron or Fe_2O_3 is present during reaction, the primary product is ethylbenzene.

Effect of Reaction Time

The rate of hydrodesulfurization of coal liquids is generally consistent with that of petroleum feedstocks: both substances are considered mixtures of sulfur-containing compounds, each of which reacts at a rate proportional to its concentration. The rate of the total sulfur removal can be approximated as if there are only two reactive components.

$$r_{\text{HDS}} = \alpha_1 K_1 C_S + \alpha_2 K_2 C_S$$

where C_S is the total concentration of the sulfur-containing compounds; α_1 and α_2 are the fractions of reactive and unreactive components, respectively; K_1 and K_2 are the rate constants of the reactive and unreactive components (7).

The parameters, α_1 , α_2 and K_1 , K_2 , vary according to the additive present during reaction as shown in Figure 4. When Fe_2O_3 is added, more sulfur is removed in the first 15 minutes of reaction than in two hours when no additive is present. In addition, considerably less hydrogen is consumed when Fe_2O_3 is present in a 15 minute reaction than after two hours without any additives (See Figure 5). The hydrogen consumption with Fe_2O_3 is 20% as opposed to 44% for no additive. The use of mineral additives such as Fe_2O_3 is beneficial, in that shorter reaction times are needed for desulfurization with less total hydrogen consumption. Furthermore, these minerals can be added without any sacrifice in coal conversion as shown in Figure 6.

Influence of Mass Transfer

The three phase reaction system present in coal liquefaction may be influenced by mass transfer effects. To determine whether mass transfer regulation is occurring, experiments were performed using different stirring rates and different particle sizes.

A direct test to determine the importance of gas/liquid transport was performed by varying the stirring rates while holding all other variables constant. As can be seen in Table 5, for stirring rates between 600 and 1400 rpm, neither the rate of desulfurization nor hydrogen consumption is very sensitive to and, consequently, is not affected by agitation rate. Therefore, gas/liquid mass transport has no apparent influence on either hydrogenation or desulfurization.

Generally, decreasing the catalyst particle size increases the effectiveness factor and the liquid/solid mass transfer coefficient. Reducing the particle size will increase the observed reaction rate when the reaction is controlled either by liquid/solid mass transport or by pore diffusion. However, reducing the particle size is not a definitive test for pore diffusion. Although the behavior of Fe_2O_3 is more like a reactant than a catalyst, the absence of particle size effects should be indicative of the absence of liquid/solid mass transfer control.

A series of experiments were performed with different Fe_2O_3 particle sizes to determine the effect of particle size on desulfurization. The rate of desulfurization is observed to be essentially independent of particle size as shown in Table IV. The rate of hydrogen consumption does vary slightly with different particle sizes.

Since the observed desulfurization rate is independent of both the Fe_2O_3 particle size and the stirring rate (within experimental error), it appears that

desulfurization is neither pore diffusion nor liquid/solid mass transfer controlled, implying then that the reaction is kinetically controlled. The rate of hydrogen consumption may be somewhat limited by mass transfer since it is influenced by particle size. An indication of the importance of particle size on hydrogen consumption rate is demonstrated in Table V. The rate of hydrogenation increases with decreasing particle size.

Comparison of Activities of Different Coal Mineral Additives

Coal mineral residues from the SRC process and ashes from the residues and Western Kentucky 9/14 coal were added to the coal liquefaction reactions to determine their effect on desulfurization and hydrogen consumption. An elemental analysis of the additives is given in Table VI. The iron content of these additives ranges from a low of 3.37% in SRC residue to a high of 26.92% in Western Kentucky ash while the sulfur content ranges from 0.47% in SRC ash to 3.81% in Kerr-McGee residue. The apparent differences in the elemental composition of SRC residue and Kerr-McGee residue observed in Table VI may be accounted for when the source of each is considered: SRC residue is obtained from filtration and Kerr-McGee residue is obtained through solvent deashing. In both cases, the residues were ashed to eliminate the carbonaceous coating and to convert the minerals to an oxide form for sulfur scavenging.

A comparison of the activity of different coal mineral additives is given in Table VII. In the cases of no additive, SRC residue, and Kerr-McGee residue, the organic sulfur removed from the system is essentially identical. The same is true for hydrogen consumption. After ashing, both the Kerr-McGee and SRC residue ashes show increased activity for sulfur removal; from ~ 23% for the residue to 43% for the ashes. Two possible reasons for these differences are: 1) the carbonaceous coating may not completely dissolve under reaction conditions, in effect, inhibiting sulfur scavenging or 2) the change in mineral form upon oxidation may provide the correct form for sulfur scavenging. Although the iron concentration in the Kerr-McGee residue ash is approximately three times higher than that of the SRC residue ash, the sulfur removal is essentially the same. This fact may be due to the difference in coal type, the mineral forms in the coal feedstock and the mineral forms present after processing and ashing. Mineral inhibitors may also be present in the Kerr-McGee residue ash that limit sulfur removal. Another possible reason for the same sulfur removal even with different iron contents for the two ashes is that the sulfur content of the Kerr-McGee residue ash is greater than that of the SRC residue ash.

The activity of iron, magnetite (Fe_3O_4) and Fe_2O_3 is compared in Table VIII. Fe_2O_3 and Fe show essentially the same amount of sulfur removal although their surface areas differ by more than an order of magnitude. In contrast, magnetite has a surface area between that of Fe and Fe_2O_3 but does not have the ability to remove sulfur like Fe_2O_3 . It appears from Table VIII that magnetite is not as effective as a sulfur scavenger as Fe; however, since equivalent amounts of iron, Fe/Fe_S , are not used and sulfur removal is sensitive to the amount of iron present when $\text{Fe}/\text{Fe}_S < 10$, more experimental data is needed to compare their relative activities. Both magnetite and Fe have a low surface area and low hydrogen consumption while Fe_2O_3 has a relatively high surface area and a much higher hydrogen consumption. Since hydrogenation appears to be somewhat limited by mass transfer, the differences in selectivity among Fe, magnetite and Fe_2O_3 may be due to the effects of mass transfer.

ACKNOWLEDGMENTS

This work was supported by the Department of Energy. The authors wish to acknowledge the technical assistances of Don Colgrove and David Watson of the Auburn University Chemical Engineering Department.

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Table I: EFFECT OF MINERAL ADDITIVES ON THE HYDRODESULFURIZATION OF BENZOTHIOPHENE

ADDITIVE	Fe/Fe _s	BENZOTHIOPHENE CONVERSION,%	PRODUCT DISTRIBUTION OF CONVERTED BENZOTHIOPHENE,%		
			DIHYDROBEN- ZOTHIOPHENE	ETHYL- BENZENE	HYDRODESULFUR- IZATION,%
NONE	-	0.0	0.0	0.0	0.0
CO-MO-AL	-	100.0	0.0	100.0	100.0
Fe ₂ O ₃ (Reagent grade)	1.9	100.0	0.0	100.0	100.0
Fe	2.7	45.0	5.0	95.0	43.0
Reduced Pyrite,	-	42.0	65.0	35.0	15.0
FeS _{1+X} Pyrite, FeS ₂	1.2	40.0	90.0	10.0	8.0

Benzothiophene: 0.45g
Additive: 0.5g

Table II: EFFECT OF Fe AND Fe₂O₃ ON HYDRODESULFURIZATION OF BENZOTHIOPHENE

ADDITIVE	Fe/Fe _s	BENZOTHIOPHENE CONVERSION,%	PRODUCT DISTRIBUTION OF CONVERTED BENZOTHIOPHENE,%		
			DIHYDROBEN- ZOTHIOPHENE	ETHYL- BENZENE	HYDRODESULFUR- IZATION,%
NONE	-	0.0	0.0	0.0	0.0
Fe(3%)	0.72	23.0	39.0	61.0	14.0
Fe(6%)	1.4	35.0	26.0	74.0	26.0
Fe(10%)	2.7	54±2.0	0.0	100.0	54±2.0
HARSHAW Fe ₂ O ₃ (10%)	0.37	24.0	40.0	60.0	13.0
POWDER Fe ₂ O ₃ (10%)	1.9	100.0	0.0	100.0	100.0

Benzothiophene: 0.45g
Additive: 0.5g

Table III: EFFECT OF AGITATION RATE ON COAL LIQUEFACTION USING A HARSHAW IRON CATALYST

RPM	H ₂ S PARTIAL PRESSURE, psig	SULFUR DISTRIBUTION, %		YIELD ^b H _f /H _o %	HYDROGEN ^c CONSUMPTION, %	SULFUR ^d REMOVAL, %	DESULFURIZATION RATE, %	HYDROGEN CONSUMPTION RATE, %	HYDROGEN CONSUMPTION RATE, %
		LIQUID	SRC						
600 ^e	0.0	0.26	0.58	87.0	0.38	56.0	0.467	0.517	0.517
800	0.0	0.25	0.56	87.0	0.37	58.7	0.489	0.525	0.525
1000	0.0	0.29	0.65	90.0	0.34	51.7	0.431	0.55	0.55
1400	0.0	0.28	0.57	90.0	0.42	53.3	0.444	0.483	0.483

Reaction Time: 120 minutes Initial Hydrogen Pressure: 2000 psi Additive: 10g

^aSo = 0.60% Organic Sulfur Content of the Coal Oil Slurry $\text{byield, \%} = \frac{\text{Ash}_f - \text{Ash}_i}{\text{Ash}_f(1 - \text{Ash}_i)} \times 100$

HYDROGEN CONSUMPTION, % = $1 - \frac{H_f}{H_o} \times 100$ (This is % of hydrogen charged initially into the reactor.)

^dSULFUR REMOVAL, % = $\frac{\text{So} - \text{Total Liquid Sulfur}}{\text{So}} \times 100$ ^eStirring rates below 600 are impractical due to solid settling problems.

Table IV: EFFECT OF Fe₂O₃ PARTICLE SIZE ON COAL LIQUEFACTION

PARTICLE SIZE, MESH	H ₂ S PARTIAL PRESSURE, psig	SULFUR DISTRIBUTION, %		YIELD, H _f /H _o %	HYDROGEN CONSUMPTION, %	SULFUR REMOVAL, %	DESULFURIZATION RATE, %	HYDROGEN CONSUMPTION RATE, %	HYDROGEN CONSUMPTION RATE, %
		LIQUID	SRC						
-35+ 60	0.0	0.26	0.56	73.0	0.53	56.7	0.472	0.392*	0.392*
-60+ 80	0.0	0.30	0.64	90.0	0.43	50.0	0.417	0.475	0.475
-80+150	0.0	0.26	0.54	89.0	0.50	56.7	0.472	0.417	0.417
-80+150	0.0	0.26	0.59	90.0	0.46	56.7	0.472	0.45	0.45
-200	0.0	0.29	0.65	90.0	0.34	51.7	0.431	0.55	0.55

*Lower hydrogen consumption because of incomplete coal dissolution (73.0% as opposed to 90.0%).

Reaction Time: 120 minutes
Fe₂O₃: 10g

Table V: PORE-DIFFUSION STUDY

PARTICLE SIZE, MESH	AVERAGE SIZE, mm.	HYDROGEN CONSUMPTION RATE, %/MIN.
-35+ 60	0.335	0.392
-60+ 80	0.214	0.475
-80+150	0.141	0.417
-80+150	0.141	0.45
-200	0.0895	0.55

Table VI: X-RAY ANALYSES OF DIFFERENT COAL LIQUEFACTION RESIDUES AND THEIR ASHES

ELEMENT	SRC RESIDUE (KY 9/14 COAL)	SRC ASH (KY 9/14 COAL)	WEIGHT	PERCENT	KY 9/14 COAL ASH
			K-M RESIDUE (KY 6 COAL)	K-M-ASH (KY 6 COAL)	
Si	13.54	27.86	6.97	23.86	18.02
Fe	3.37	6.80	5.66	18.49	26.92
Ca	1.30	3.03	0.31	1.16	1.55
K	0.43	1.01	0.67	2.02	1.75
Cl	0.22	0.37	0.62	0.26	0.46
Ti	0.14	0.34	0.19	0.61	0.66
Mn	0.02	0.05	0.03	0.09	0.09
Sr	0.04	0.09	-	-	0.07
Zn	-	0.02	0.02	0.06	0.03
V	-	0.04	0.02	-	0.09
Cu	-	0.02	0.02	0.14	0.10
Br	-	-	-	-	-
Rb	-	-	-	-	0.01
Pb	-	-	-	-	-
Al	3.86	9.20	3.29	10.51	11.11
Mg	-	2.10	2.20	-	-
S	2.14	0.47	3.81	0.58	0.86
C	54.02	-	59.33	-	-
H	2.67	-	3.44	-	-
N	1.35	-	1.56	-	-
O(by difference)	16.90	51.40	11.86	42.22	38.28
	100.00	100.00	100.00	100.00	100.00
Surface Area m ² /gm.	-	4.78±0.03	-	8.8±0.14	4.6±0.045

Table VII: COMPARISON OF ACTIVITY OF DIFFERENT COAL MINERAL ADDITIVES

ADDITIVE	PARTIAL PRESSURE OF H ₂ S, ps±g	HYDROGEN CONSUMPTION, %	TOTAL LIQUID SULFUR, %	ORGANIC SULFUR REMOVAL %	Fe/Fe _s	Se	SURFACE AREA m ² /g
None	16.0	41.0	0.46	23	-	0.57	
SRC Residue	58.0	42.0	0.46	23	0.56	0.56	
SRC Ash	3.0	51.0	0.34	43	0.81	0.85	0.85
Kerr McGee Residue	14.0	46.3	0.47	22	0.98	0.47	
Kee McGee Ash	1.0	49.0	0.35	42	2.25	0.85	0.85
Western Ken. 9/14 Coal Ash	1.8	52.0	0.34	43	3.21	0.83	0.83

Average Coal Dissolution is 90.0% in all cases.
Reaction Time: 120 minutes
Additive: 10g

Table VIII: COMPARISON OF ACTIVITY OF Fe, MAGNETITE AND Fe₂O₃ (REAGENT GRADE)

ADDITIVE	PARTIAL PRESSURE OF H ₂ S, ps±g	HYDROGEN CONSUMPTION, %	TOTAL LIQUID SULFUR, %	ORGANIC SULFUR REMOVAL, %	Fe/Fe _s	Se	SURFACE AREA m ² /gm.
Fe ₂ O ₃ (Reagent Grade)	0.0	55.0	0.25	55	6.86	8.9±0.04	1.0
Magnetite	0.0	43.6	0.35	41	8.83	0.75±0.02	0.94
Fe	0.0	41.5	0.28	53	10.42	0.25±0.01	1.3

Figure 1
 THE EFFECT OF Fe AND Fe₂O₃ ON THE
 SULFUR CONTENT OF THE
 TOTAL LIQUID PRODUCTS

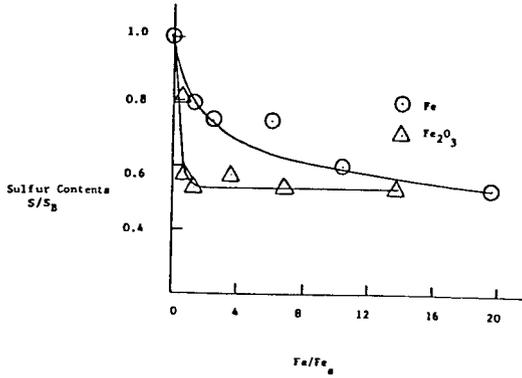


Figure 2
 THE SELECTIVITY OF Fe AND Fe₂O₃
 FOR SULFUR REMOVAL ON THE BASIS OF EQUIVALENT AMOUNTS OF Fe

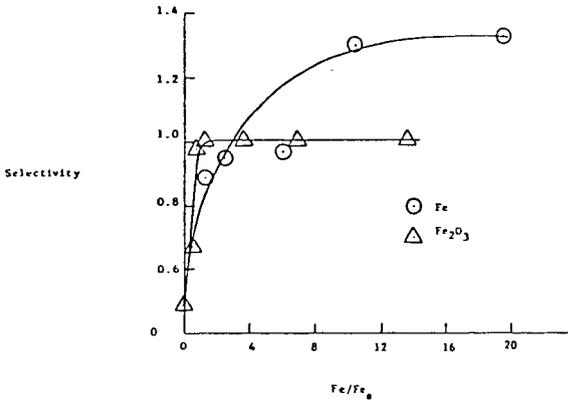


Figure 3
 THE EFFECT OF Fe AND Fe₂O₃ ON HYDROGEN
 CONSUMPTION AS A FUNCTION OF Fe CONCENTRATION

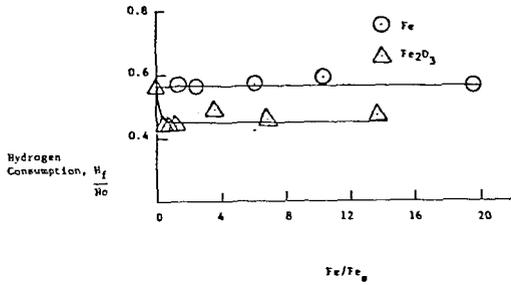


Figure 4
 THE EFFECT OF ADDITIVE TYPE
 ON SULFUR REMOVAL

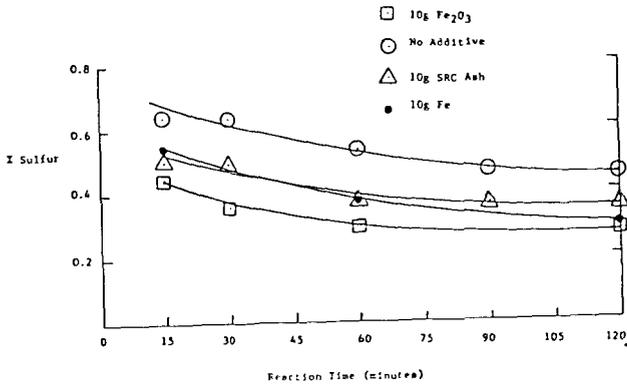


Figure 5
THE EFFECT OF ADDITIVE TYPE
ON HYDROGEN CONSUMPTION

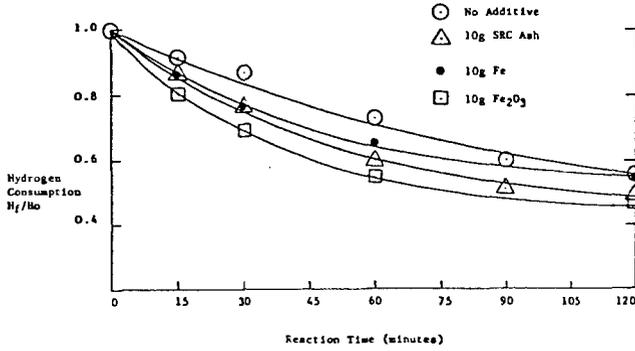


Figure 6
THE EFFECT OF ADDITIVE TYPE
ON COAL CONVERSION

