

The Effect of Solvent Quality on Coal Conversion

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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 magnedrive 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

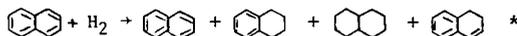
The dissolution behavior of Western Kentucky 9/14 coal was examined in the solvents listed in Table I. The dissolution behavior in each solvent is reported together with the hydrogen content of each solvent. Other conditions were the same for all reactions. Both the creosote oil solvent series and the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

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References

- 1) Guin, J.A., Tarrer, A.R., Lee, J.M., Lo, L., Curtis, C.W., I. & E.C. Proc. Des. and Devel., in press, (1979).
- 2) Brown, J.K. and Ladner, W.R., Fuel, 39, 87 (1960).
- 3) Curtis, C.W., Tarrer, A.R. and Guin, J.A., I. & E.C. Proc. Des., and Devel., in press, (1979).

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

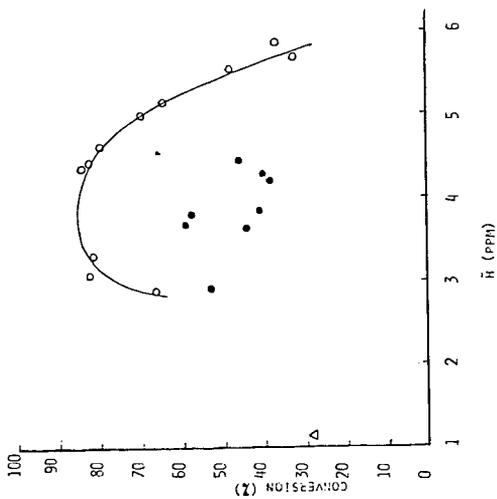


FIGURE 2
CONVERSION VS. HYDROGEN CONTENT

- 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

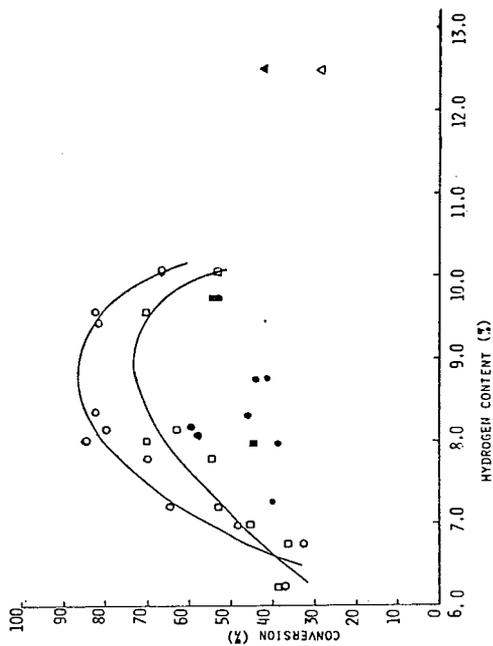


FIGURE 3

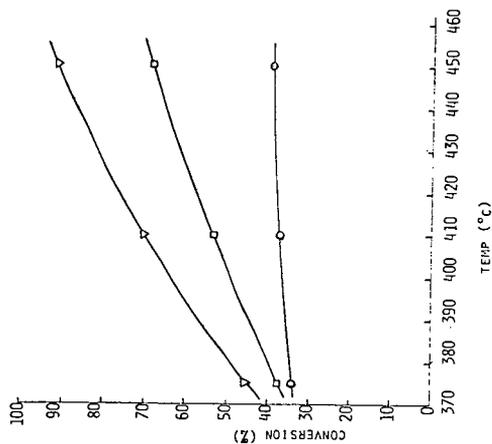
CONVERSION VS. TEMPERATURE

AMVAX COAL

○ CREOSOTE OIL

▽ HC IX

□ HC IV



CONVERSION VS. TEMPERATURE

WESTERN KENTUCKY COAL

○ CREOSOTE OIL

▽ HC IX

□ HC IV

