

BEHAVIOR OF PHENOLICS IN COAL LIQUEFACTION:
SAMPLE CHARACTERIZATION AND EFFECT ON COAL CONVERSION IN A CSTR UNIT

by

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INTRODUCTION

Phenolic components of coal liquefaction solvents have been considered to be beneficial for conversion of coal (1,2). Orchin and Storch (2), for example, reported that the addition of small amounts of cresol to tetralin increased the conversion of coal compared with the yield observed with tetralin alone. Kamiya and co-workers (3) observed a similar effect with phenol or cresol added to a solvent composed of tetralin and 1-methylnaphthalene; the magnitude of the increase was dependent upon the coal used. The reported effect has been ascribed to a variety of factors, one of which is a hydrogen-bonding interaction between the phenolic species and ethers in the coal (2,3), leading to increased cleavage of various ethers.

Awadalla and Smith (4) observed an increase in conversion with p-cresol but suggested that the effect was an artifact of the extraction process, a co-solvent effect arising from lack of prior removal of the phenolic material. Larsen et al. (5), investigating the use of phenol as a solvent for liquefaction of Bruceton Pittsburgh Seam coal, found that a solvent/coal ratio of 1.5 and reaction temperature of 460°C led to a weight increase of the coal of 9% after a 15-min reaction. This large amount of adduction with only a 10% conversion to pyridine-soluble material indicates that phenol is a very poor solvent under these conditions. Runs made at 482°C resulted in an increase in conversion, up to 82% for a 10/1 phenol/coal feed. However, the liquid product contained 14% by weight phenol of which 6% was attached to the coal by other than hydrogen-bonding interactions. An additional 8% was exchangeable with unlabeled material.

Our (6) past work with naphthols, phenol, and cresols using a micro-autoclave unit indicated that phenol and naphthols were poor solvents for coal liquefaction due to high levels of adduction. However, less adduction was observed with the addition of cresols to the solvents. Therefore, a series of runs were made in a CSTR unit to evaluate the effect of adding phenol and cresols to anthracene oil (AO) and SRC-II derived solvents. In addition, an "OH-reduced" solvent and a solvent mixture of AO plus OH-concentrate were tested.

EXPERIMENTAL

The coal was Powhatan No. 5 Mine (Pittsburgh No. 8 Seam) ground to pass at least 98% through 100 mesh screen. Analyses of the coal and solvents are given in Table 1.

The bench-scale liquefaction runs were made in a continuous feed stirred-tank reactor (CSTR) system. A flow diagram of the coal liquefaction unit is shown in Figure 1; its operation has been previously described (7). Samples of the reactor slurry were first stripped with nitrogen, and they were then subjected to sequential Soxhlet extraction using pentane, toluene, and tetrahydrofuran (THF), respectively. Fractions were defined as follows, using as a basis MAF coal feed:

wt% oils = {(MAF coal-pentane insolubles)/MAF coal} x 100
wt% asphaltenes = {pentane insoluble, toluene soluble/MAF coal} x 100
wt% preasphaltenes (PA) = {toluene insoluble, THF soluble/MAF coal} x 100
wt% THF insolubles = {THF insoluble material/MAF coal} x 100

RESULTS AND DISCUSSION

Characterization of the OH-Concentrate: The OH-concentrate (OH-CONC) was isolated by contacting SRC-II solvent with activated Rohm and Haas Co. IRA-904 resin. The OH-CONC was then freed by washes of CO₂/methanol acid and HCO₂H/methanol followed by solvent stripping.

The hydroxyl concentrate of SRC-II solvent was added to a small amount of methylene chloride and analyzed by capillary GC/MS. The greatest portion (56%) of the chromatographic peaks other than solvent was phenol (10%) or alkyl-substituted phenols (46%). Methyl phenols (23%) account for approximately half of the alkyl-substituted phenols with the remainder (23%) being C₂ to C₅ phenols. Other peaks include C₉H₁₀O isomers (10%) and C₁₀H₁₂O isomers (9%) which are probably indanols and methylindanols. Hydroxybiphenyl (1%) and carbazole (3%) were identified. Polynuclear aromatic hydrocarbons accounted for 16% of the peaks. The largest of these was methylphenanthrene (4%). The remainder of the peaks (5%) were small and unidentified.

The ¹H spectrum of the OH-CONC fraction is shown in Figure 2, and the results are summarized in Table 2. This fraction has aromatic, hydroxyl, hydroaromatic, and alkyl substituent functionality. The aromatic region spans from 6 ppm to 8.6 ppm. These aromatic hydrogens represent 39.7% of the total hydrogen. Even though the nitrogen content is relatively low (1.1%), the small amount of intensity between 8.4 ppm and 8.6 ppm in the aromatic region can be assigned to protons ortho to the nitrogen in pyridine-type structures. These protons represent less than 0.3% of the hydrogen. There is a broad resonance at 5.4 ppm which can be assigned to hydroxyl hydrogen. This accounts for 11.3% of the hydrogen in the spectrum. In the region around 3.4 ppm are several smaller signals which can be assigned to methylene bridges between aromatic rings. These methylene bridge hydrogens represent 0.9% of the hydrogen present.

The main type of aliphatic substituent is methyl groups on aromatic rings as evidenced by the sharp signals at 2.2, 2.5, and 2.8 ppm. These signals account for 25.7% of the hydrogen present. There are also some (16.7% of hydrogen) long-chain aliphatic substituents with an average chain length of five carbons. Combining a broad signal at 1.7 ppm, together with an equivalent amount of intensity from the signal at 2.8 ppm, about 5.6% of the hydrogen is hydroaromatic.

The ^{13}C NMR spectrum, given in Figure 3, shows the OH-CONC to have an aromaticity of 77.4%. The ratio of aromatic carbons to hydroxyl-bearing carbons is 8.5:1. The ratio of total carbon to oxygen is 10.9:1, which is reasonably consistent with that of the elemental carbon-to-oxygen analysis of 12.3:1.

The amount of ortho substitution is determined as the difference between the area of the region from 152 ppm to 156 ppm and one-half of the area between 110 ppm and 117 ppm. The amount of meta substitution is determined from the signals at 154-155 ppm, and the difference between the amount of hydroxyl-bearing carbon and the amounts of ortho and meta substitution is para substitution. The results are given in Table 3.

Since the observed ratio of aromatic carbons to hydroxyl-bearing carbons is 8.5:1 and every molecule theoretically has an acidic hydroxyl group, the OH-CONC consists of a mixture of one- and two-ring systems. Because only a small amount of the concentrate has been identified as naphthols, the remainder of two-ring systems should be comprised of single rings joined by short alkyl bridges. There is evidence for both methylene and ethyl bridges in the carbon spectrum. The distribution is shown in Table 3.

The total alkyl-substituted aromatic carbon is 12.8%. This was determined by summing the methylene bridge area times 2, the ethyl bridge area, one half the hydroaromatic area, and the methyl groups on aromatic rings area. The total nonprotonated aromatic carbon is difficult to determine from the normal spectral regions due to the presence of hydroxyl groups which induce an upfield shift to the carbons ortho and para to it. To study this, a NORD-CDRE (noise off-resonance decoupled convolution difference resolution enhancement) experiment was run. The signals upfield of 129.5 ppm are due to bridge carbons in 1- and 2-naphthols. The total bridge carbon is 15.5% as determined from the difference between the total nonprotonated carbon and the alkyl-substituted carbon plus hydroxyl-bearing carbon (11.8%). Therefore, the level of protonated aromatic carbon is 58.5% of the aromatic carbon.

CSTR Experiments: The results of the CSTR runs are summarized in Table 4. As anticipated, SRC-II distillate is a better solvent than A0 at short reaction times (4 min) as indicated by higher overall coal conversion, a lower level of preasphaltenes, and lower hydrogen consumption. With both solvents the yields of oils were negative. With an increase in space time to 15-19 minutes, overall conversions increased to about the same level (72-75%). The recoveries of preasphaltenes were essentially the same at about 5%, and the hydrogen consumptions were equal at 3.5 g/100 g MAF coal. However, a

sizable negative yield of oils was observed in the AO run at 15 minutes. This was apparently due to a high yield of asphaltenes. While this observation appears to be anomalous, the product slurry was extracted a total of five times with essentially the same results.

The direct addition of phenol to AO (4-min space time) was detrimental. While % solvation increased marginally, the yield of asphaltenes increased greatly over that of the run with AO alone. The product slurry was also very sticky and difficult to handle; therefore, pentane may have had some difficulty penetrating into the slurry sample and then extracting the oils. The yields of preasphaltenes were essentially the same for the runs with AO and AO plus phenol.

The addition of OH-concentrate, recovered from an ion exchange resin treatment (Rohm and Haas IRA-904) of SRC-II solvent, to AO had little effect on the distribution of products. Considering the OH-concentrate had a moderate level of hydroaromaticity while that of AO was low, and that the OH-concentrate had already effectively passed through a liquefaction reactor, the OH-concentrate may not react sufficiently with coal radicals to form additional asphaltenes.

The addition of m-cresol appeared to be of particular benefit to the AO runs. This addition resulted in an increase in the yield of oils along with a marginal increase in % solvation. In the case of m-cresol addition to SRC-II solvent at a 15-minute reaction time, there was a small increase in % solvation with nominal increases in each of the product fractions.

Due to a limited amount of available feed sample, only a single CSTR run was made with the solvent recovered after treatment with IRA-904 resin. This solvent contained 1.9% oxygen, while the as-received SRC-II solvent contained 2.8% oxygen. Even this partial removal of hydroxyls appears to be of benefit, as observed by an increase in oil yield, a decrease in asphaltenes yield, and a marginal increase in % solvation (THF solubles).

SUMMARY

Coal liquefaction experiments were carried out at 450°C in a continuous feed stirred-tank reactor (CSTR) to observe the effect of adding phenolics to anthracene oil (AO) and SRC-II recycle solvents. At nominal space times of 4 and 15 minutes, the levels of conversion (THF solubles) were significantly higher with SRC-II recycle solvent than with anthracene oil. The addition of phenol to AO at a ratio of 5/65 resulted in a nominal increase in coal conversion to THF solubles, but the amount of asphaltenes more than doubled resulting in a sizable net loss of solvent. The addition of m-cresol to both AO and SRC-II solvents had a positive effect on coal conversion to both THF and pentane solubles (oils). The partial removal of an OH-concentrate from SRC-II solvent was carried out using Amberlyst IRA-904 ion exchange resin. The "OH-reduced" oil was only marginally better than raw SRC-II recycle solvent for coal liquefaction. A characterization of the OH-concentrate by ^{13}C and ^1H NMR and FTIR indicated a moderate level of aromaticity (77%), a

sizable amount of short-chain aliphatic substitution, and also a sizable amount of hydroaromaticity. GC/MS characterization pointed out a high concentration of one- and two-ring substituted phenolics.

LIST OF REFERENCES

1. A. Pott and H. Broche, U.S. Patent 1,881,927.
2. M. Orchin and H. H. Storch, 1948. Solvation and Hydrogenation of Coal. *Ind. Eng. Chem.*, 40:1385.
3. Y. Kamiya, H. Sato, and T. Yao, 1978. Effect of Phenolic Compounds on Liquefaction of Coal in the Presence of Hydrogen-Donor Solvent. *Fuel*, 57:681.
4. A. A. Awadalla and B. E. Smith, 1982. Apparent Enhancement of Coal Conversions Using Cresol-Tetralin Solvents. *Fuel*, 61:631.
5. J. W. Larsen, T. L. Sams, and B. R. Rodgers, 1981. Internal Rearrangement of Hydrogen During Heating of Coals with Phenol. *Fuel*, 60:335.
6. R. I. McNeil and D. C. Cronauer. Behavior of Phenolics in Coal Liquefaction: Adduction Tendency and Coal Conversion Capability. *Fuel Proc. Tech.* in press.
7. J. S. Abichandani, Y. T. Shah, D. C. Cronauer, and R. G. Ruberto, 1982. *Fuel*, 61:276.

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Table 1
Analyses of Solvents and Coal

<u>Chemical Analysis (wt%)</u>	<u>Raw A0</u>	<u>Raw SRC-II</u>	<u>OH-CONC</u>	<u>OH Reduced</u>	<u>Coal*</u>
Carbon	91.2	87.2	82.0	88.4	72.3
Hydrogen	5.9	8.7	7.8	8.5	5.1
Nitrogen	1.0	0.9	1.1	0.9	1.5
Oxygen	1.3	2.8	8.9	1.9	7.9
Sulfur	0.6	0.4	0.2	0.3	0.6
Ash	-	-	-	-	9.7
	100.0	100.0	100.0	100.0	100.0

*Powhatan No. 5 Mine (Pittsburgh Seam) coal.

Table 2
¹H NMR Analysis of SRC-II Hydroxyl Concentrate

Aliphatic Hydrogens

Methylene bridge	0.9%
Methyl	25.6
Hydroaromatic	5.6
Long alkyl chain (i.e., C ₅)	<u>16.7</u>
Total aliphatic	48.7

Hydroxyl Hydrogens

11.3

Aromatic Hydrogens

Aromatic hydrogen ortho to N	0.3
Others	<u>39.7</u>
Total aromatic	<u>40.0</u>

Total 100.0%

Table 3

¹³C NMR Analysis of SRC-II Hydroxyl Concentrate

Aliphatic Carbons

Methylene bridges between rings	1.4%
Other carbons α to aromatic rings	2.0
Methyl groups attached to rings	5.7
Hydroaromatic carbons	7.3
Long-chain alkyls (from ¹ H) (est.)	<u>6.2</u>
Total aliphatic carbons	22.6%

Aromatic Carbons (Ar-C)

Ortho methyl groups (to OH)	3.0
Naphthols	1.0
Unknown ortho substituents	<u>0.9</u>
Total substituted Ar-C's ortho to OH groups	4.9
Substituted Ar-C's meta to OH groups	9.9
Substituted Ar-C's para to OH groups	<u>7.4</u>
	22.2*
Hydroxyl substituted Ar-C	9.3
Protonated Ar-C	<u>45.9</u>
Total	100.0

*This is also subdivided as follows:

Alkyl-substituted Ar-C	10.0
Aromatic bridge carbons	<u>12.2</u>
Total	22.2

Table 4
Summary of CSTR Runs with Phenolic Additives

Solvent/Additive	Space Time (min)	% Solvation ⁽¹⁾ (g/100 g)	Hydrogen Consumption ⁽²⁾ (g/100 g)	Yields ⁽²⁾ (g/100 g)		
				Oils	Asphaltenes	Preasphaltenes
Anthracene Oil	4.2	55.4	3.0	-7.0	29.9	19.9
+m-Cresol	4.3	58.3	2.4	9.6	30.2	27.0
+Phenol	4.4	58.5	2.1	-46.5	71.3	22.1
+OH-CONC	4.1	56.7	2.5	-9.9	33.5	23.6
Anthracene Oil	15.2	74.7	3.4	-35.5	82.9	6.7
+m-Cresol	19.1	80.2	4.3	-2.1	55.3	3.7
SRC-II Solvent	4.7	61.3	1.8	-5.3	41.8	14.0
OH-Reduced SRC-II	4.6	63.9	2.7	2.1	34.5	17.8
SRC-II Solvent	19.0	71.7	3.6	12.3	33.2	4.7
+m-Cresol	15.0	76.6	3.6	14.5	34.9	7.5

Notes: (1) Solvation is given as grams of tetrahydrofuran solubles/100 grams MAF coal.
(2) Yields are given as grams/100 grams MAF coal.

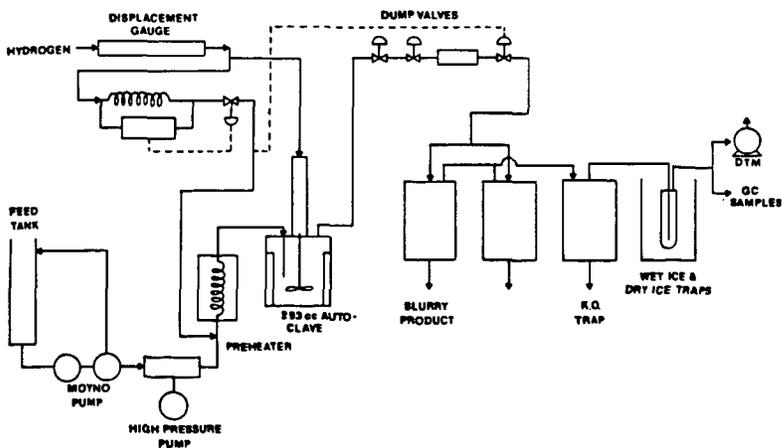


FIGURE 1 SCHEMATIC OF THE BENCH-SCALE CSTR UNIT

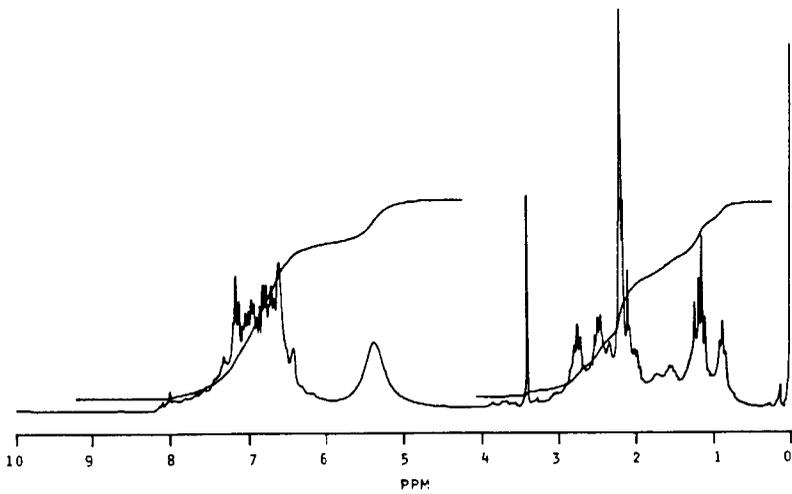


FIGURE 2 ^1H -NMR SPECTRUM OF SRC-II DERIVED HYDROXYL-CONCENTRATE

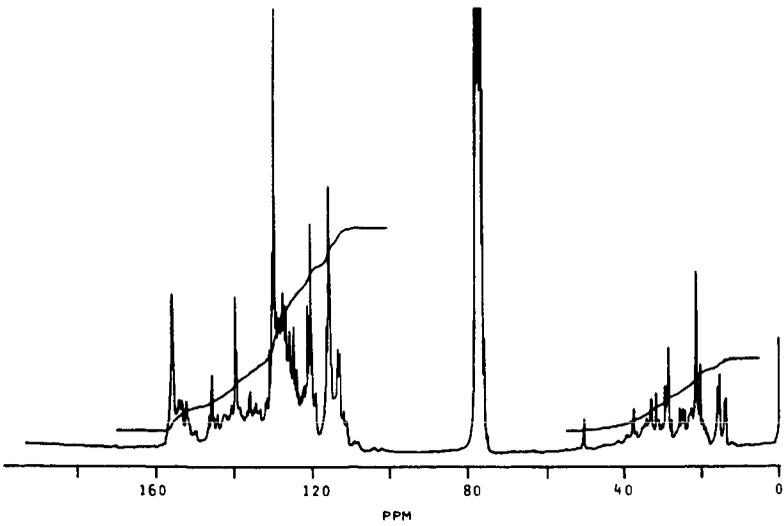


FIGURE 3 ^{13}C -NMR SPECTRUM OF SRC-II DERIVED HYDROXYL-CONCENTRATE