

CHARACTERIZATION OF SHORT CONTACT TIME DISSOLUTION PRODUCTS
FROM A SERIES OF VITRINITE-RICH COALS

Randall E. Winans, Hsiang-Hui King, Robert L. McBeth and Robert B. Botto

Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

The objective of this study is to identify the transformations that occur in coal organic structural units during liquefaction. To ensure that mainly primary reactions are being observed, the study has focused on short contact time dissolution in donor solvent media. It has been shown by Neavel that under SCT conditions a significant amount of bituminous coals can be dissolved (1). Whitehurst et al. have reported an in depth study of the SCT reaction on several coals. In our study we have examined the relationship between the compositional parameters of the coals and both their reactivity and product chemical characteristics. Given and his co-workers examined the effects of coal characteristics on longer contact time liquefaction (3-5). This work by Given is one of the first applications of statistical analysis to this type of problem. However, either benzene (3) or ethyl acetate (4,5) was used to extract the products and conversion was calculated from the weight of the insoluble residue. Since the benzene insoluble, pyridine soluble fraction, often called asphaltoids or preasphaltenes, is a key intermediate in the initial stage of coal liquefaction (6,7), we would like to correlate the solubility in hexane, benzene/ethanol, and pyridine with compositional parameters.

We have recently studied the SCT reaction of separated coal macerals (8). In order to separate the macerals by density gradient centrifugation it was necessary to demineralize the coals with HCl and HF and grind them to less than 3 microns. It has been shown that mineral matter exerts a beneficial and possibly unpredictable effect on the coal dissolution (2,9-11). To examine the effects of the demineralization and grinding, a series of 21 of the treated unseparated coals were studied. The original raw coals were obtained from the Penn State Coal Sample Bank. It was observed using multivariate analysis that product solubility, which was used to determine conversion, can be predicted from linear combinations of carbon, hydrogen, density and exinite content.

After considering these results, we felt that in order to make the study more complete, it would be useful to study another set of coals which had not been demineralized. Dr. Richard Neavel consented to supply us with a set of 25 coals from the Exxon Coal Library. These samples are essentially "premium" coals which have been protected from oxidation and are homogeneous. The preparation and some of the properties have been described (12). An advantage of using this set of coals is that other structure studies are in progress in other laboratories and in the Fundamental Chemistry of Coals program at ANL. This information will be useful in interpreting the results from the SCT reaction.

Experimental

SAMPLES Analytical data for the demineralized coals are given in Table 1. The Exxon coals are described in reference 12.

SCT REACTION Typically, 100 mg of coal sample and 300 mg of tetralin were transferred to a thick wall glass tube flushed with nitrogen, sealed, and plunged into a preheated fluidized sand bath at 419°C for 6 minutes. For the demineralized coals 60 mg coal and 240 mg of tetralin were used. After the glass tube was cooled in air and opened, the contents were washed out with hexane, agitated in an

ultrasonic bath, and centrifuged. The supernatant was removed and the insoluble part was washed with three portions of hexane. The hexane insoluble fraction was then extracted successively with portions of benzene/ethanol (1:1) mixture, and pyridine. Each insoluble fraction was dried under vacuum at 60°C (80°C for the pyridine insoluble fraction) and weighed. Conversion was calculated as follows:

$$\text{conversion (\%,daf)} = \frac{\text{wt. of coal} - \text{wt. of insoluble fraction}}{\text{wt. of coal (1-\% ash)}} \times 10^4$$

The benzene solubility was dropped for the Exxon coals when it was found that with the demineralized coals only a few percent more were soluble in benzene compared to hexane.

Approximate molecular weight or size distribution was determined by gel permeation chromatography for the benzene-ethanol soluble products for both the series of demineralized coals and for the Exxon coals. The samples were eluted with THF through a set of three ultra-styragel columns (Waters Associates) having 1,000, 500 and 100 Å nominal pore diameters respectively. The size exclusion limit was approximately 10,000. This set of columns was calibrated using several polymers and large nonpolymeric molecules that could be found in coals. The samples were detected using a UV spectrometer set at 254 nm, and the output digitized and stored using a microcomputer (DEC LSI 11/23). The data was further processed on a DEC VAX 11/780 computer.

Proton NMR data were obtained on the benzene/ethanol soluble product from the reactive Exxon coals. Pyridine-d₅ was used as the solvent and spectra were obtained on a Nicolet 200 MHz instrument. Using the measured areas under the aliphatic and aromatic regions, the fraction of aromatic carbons (*fa*) was determined from the Brown-Ladner equation (11).

RESULTS AND DISCUSSION

For both sets of coals the first aspect of the data which we examined was the relationship between composition of the whole coal and the yield of the soluble products. The benzene-ethanol solubility data which was calculated on a wt% of coal (dmmf) is shown in Figure 1 as a function of carbon content. A multivariate analysis was performed on this data using the Statistical Analysis System (SAS) package. The correlations observed for these samples were much poorer than those obtained for the set of demineralized coals. Some representative R² values are given for a selected combination of variables.

	Hexane		Benzene/EtOH		Pyridine	
	DC	Exxon	DC	Exxon	DC	Exxon
C	0.919	0.781	0.843	0.130	0.565	0.027
C,H	0.957	0.841	0.918	0.490	0.781	0.477

DC = demineralized coals.

A plot of predicted and observed benzene-ethanol solubility is shown in Figure 2. This difference found between the two sets of coals may be due to at least two reasons. First, the Exxon coals were not demineralized, and the effects of mineral matter on SCT dissolution may be critical and unpredictable. It should be emphasized that the Exxon coals were processed to give low mineral matter content and in the multivariate analysis, inclusion of the high mineral matter coals did not significantly affect the analysis. Secondly, there is a difference in particle

size, which should influence the variations in yields to a lesser degree. One would expect the smaller particle size samples to give a higher solubility, but it is difficult to deduce why the difference in correlation with composition results. It has been reported by Whitehurst et al. (2) that demineralization increases yields at short contact times especially for lower rank coals.

It is apparent from Figure 1 that for the lower rank coals the demineralized ones are more reactive than the untreated coals. This could account for the more predictable behavior with rank of the demineralized coals. For the Exxon coals in this study and as has been shown in other studies (2) the lower rank coals are less reactive under SCT conditions compared to the high volatile bituminous coals.

Variations observed in molecular size distribution as a function of composition appears to be more similar between the two sets of coals. A relative molecular weight or size distribution was obtained for all the coal products under identical conditions. The absolute values determined for the molecular weights cannot be trusted for coal derived materials. However, comparisons of the results from coal products run under standard conditions can be useful. An example of one of the chromatograms is shown in Figure 3. Most of the chromatograms had inflection points at molecular weights of approximately 300 and 700. All of the chromatograms were divided into three areas at 0-300, 300-700, and 700-10,000, and the relative areas of the three regions determined.

In the initial SCT study of the maceral concentrates, it was observed that the average molecular weight decreased with decreasing conversion (8). In both sets of whole coals this trend is followed. In order to look at the results in a more quantitative way, principal component analysis has been applied to these data. This approach has been eloquently described by Yarzab et al. (4). The objective of this analysis is to identify variables, such as original coal composition and molecular weight distributions, which change in a parallel fashion. The variables that meet this criteria are assigned to a "factor". A coefficient is calculated for each variable in each factor. The closer the coefficient or loading is to ± 1.0 the better the variable correlates with that factor. Loadings with opposite signs indicated that these properties are inversely correlated.

The results of the principal component analysis are shown in Tables 2 and 3 for the demineralized and Exxon coals respectively. Coefficients of less than ± 0.5 have been left out since they are less significant and it makes it easier to see the correlations. In both sets of data the carbon content is directly correlated with the LMW band and inversely with the HMW. The reverse is true for the oxygen content and for the Exxon set, volatile matter, which inversely correlates with LMW and directly with HMW. The MMW band is independent of any of the variables used in this analysis and was assigned the 4th and least significant factor. The values at the bottom of each table indicate the contribution made by each factor in explaining variance observed. It appears that the molecular distribution of the products in SCT dissolution is a function of rank. A plot of the high molecular weight area as a function of carbon content in Figure 4 appears to confirm this observation.

The fa values were determined by NMR for the benzene-ethanol solubles from the Exxon coals. Factor analysis indicated that the fa values inversely correlated with hydrogen content of the coals and with solubilities in both benzene-ethanol and pyridine. A plot of fa's as a function of hydrogen content is shown in Figure 5. These results indicate a problem with using solubility to determine conversion. As expected the more aliphatic products tend to be more soluble. The same amount of bond cleavage in a more aromatic coal could have a lower yield by solubility. From this analysis it could be expected that fa values of the products should approximately follow the solubility. This is what is observed in Figure 6. Although there is significant scatter in the points the trend is apparent.

Conclusions

Apparently yields from SCT dissolution of finely ground, demineralized coals can be more accurately predicted than with the dissolution of raw coals. Gross product chemical characteristics do not seem to differ to a large extent. Presently we are examining more detailed chemical characteristics of the various products using pyrolysis mass spectrometry with precise mass measurements.

Acknowledgements

The authors thank the Pennsylvania State University Coal Sample Bank, Professor J.C. Crelling of Southern Illinois University, Professor L. Anderson of the University of Utah, and Dr. R. Neavel of Exxon Research and Engineering Company, for providing the whole coal samples. We are also grateful to Dr. G.R. Dyrkacz and Ms. C.A.A. Bloomquist for demineralizing the coals, Ms. K. Henriksen for obtaining the CPC data, and Mr. A. Kostka for the NMR results. Work performed under the auspices of the U.S. Department of Energy, Fossil Energy program under contract W-31-109-ENG-38.

References

- (1) Neavel, R.C., Fuel 55, 237 (1976).
- (2) Whitehurst, D.D., Mitchell, T.O. and Farcasiu, M., "Coal Liquefaction," Academic Press, NY p. 161 (1980).
- (3) Abdel-Baset, M.B., Yarzab, R.F., and Given, P.H. Fuel 57, 89 (1978).
- (4) Yarzab, R.F., Given, P.H., Spackman, W. and Davis, A. Fuel 59, 81 (1980).
- (5) Given, P.H., Schleppy, R. and Sood, A. Fuel 59, 747 (1980).
- (6) Farcasiu, M., Mitchell, T.O. and Whitehurst, D.D. CHEMTECH 7, 680 (1977).
- (7) Neavel, R.C., "Coal Plasticity Mechanism: Inferences from Liquefaction Studies," in Coal Science, Vol. 1, Ed. M.L. Gorbaty, J.W. Larsen, and I. Wender, Academic Press, NY P. 1 (1982).
- (8) King, H.H., Dyrkacz, G.R. and Winans, R.E. (submitted to Fuel).
- (9) Guin, J.A., Tarrer, A.R., Prather, J.W., Johnson, D.R. and Lee, J.M. Ind. Eng. Chem. Proc. Des. Dev. 17, 118 (1978).
- (10) Guin, J.A., Tarrer, A.R., Lee, J.M., Lo, L., and Curtis, C.W. Ind. Eng. Chem. Proc. Des. Dev. 18, 371 (1979).
- (11) Garg, D. and Givens, E.N. Ind. Eng. Chem. Proc. Des. Dev. 21, 113 (1982).
- (12) Neavel, R.C., Smith, S.E., Hippo, E.J., and Miller, R.N., Preprint, Fuel Division, ACS 25(3), 246 (1980); Proceedings of International Conference on Coal, Dusseldorf, 1981, P. 1 (1981).
- (13) Brown, J.K. and Ladner, W.R. Fuel 39, 87 (1960).

TABLE 1

Analytical Data for Demineralized Coals

Coal	%C ^a	%H ^a	%N ^a	%S ^a	%O ^{a,b}	%Ash	%E ^c	%V ^c	%I ^c	Density
PSOC-106	80.0	4.4	1.3	0.8	13.5	0.4	19.0	35.1	45.9	1.328
PSOC-107	78.7	4.7	1.5	0.4	14.7	0.1	13.1	69.5	17.3	1.301
PSOC-124	82.8	6.9	1.2	1.0	8.1	1.2	56.5	14.6	28.8	1.195
PSOC-151	75.0	4.9	0.8	0.4	18.9	0.3	5.5	83.9	10.5	1.322
PSOC-236	86.9	4.6	1.9	0.5	6.1	0.2	0.2	95.6	4.2	1.280
PSOC-240	67.5	5.0	1.2	1.7	24.6	0.4	4.4	92.1	3.5	1.376
PSOC-268	83.5	4.9	1.4	1.1	9.1	0.4	7.2	82.4	10.4	1.275
PSOC-285	77.5	4.9	1.4	4.4	11.8	3.3	3.0	91.5	5.6	1.276
PSOC-297	79.7	5.6	1.7	1.6	11.4	1.4	19.0	62.8	18.2	1.285
PSOC-380	89.5	3.4	1.1	0.6	5.4	0.2	0	88.6	11.4	1.357
PSOC-403	85.7	4.8	1.8	0.5	7.2	0.2	2.4	91.6	6.0	1.287
PSOC-409	87.1	4.2	1.9	1.5	5.3	1.1	6.5	86.9	6.6	1.317
PSOC-592	77.4	4.9	1.3	2.0	14.4	0.4	12.5	53.0	34.4	1.316
PSOC-594	75.0	4.8	1.2	2.7	16.3	0.5	5.1	88.5	6.6	1.322
PSOC-629	91.0	3.2	0.8	0.7	4.3	0.8	0	90.6	9.4	1.401
PSOC-852	75.3	5.0	1.7	0.4	17.6	0.0	1.9	94.0	4.2	1.309
PSOC-975	69.0	4.6	1.0	0.5	24.9	0.2	4.6	91.6	4.0	1.393
PSOC-1005	69.6	4.5	0.9	0.4	24.6	0.0	1.6	95.5	2.9	1.405
PSOC-1109	70.9	6.6	1.6	1.5	19.4	1.3	70.7	21.4	7.8	1.228
U1	77.3	5.7	1.5	0.7	14.8	1.0	10.2	85.2	4.6	1.244
SIU-744A	81.4	4.7	1.3	0.8	11.8	0.1	4.6	93.8	1.6	1.300
SIU-744B	82.2	5.1	1.4	0.8	10.5	0.3	15.4	71.0	13.6	1.271

^adry and ash free basis.

^bby difference.

^cE=exinite, V=vitritinite, I=inertinite.

TABLE 2. DEMINERALIZED COALS, VARIMAX ROTATED FACTOR PATTERN FOR PRODUCT MOLECULAR WEIGHT DISTRIBUTION

	<u>Factor 1</u>	<u>Factor 2</u>	<u>Factor 3</u>	<u>Factor 4</u>
Carbon	-0.80550			
Hydrogen		0.89706		
Sulfur		0.73940		
Oxygen	0.85843			
Nitrogen	-0.81678			
HMW	0.90740			
MMW			0.94011	
LMW	-0.96976			
Density		-0.91986		
Exinite		0.85784		
Vitritinite		-0.72136		
Inertinite		0.86206		
Pyridine Sol.	0.89258			

Variance explained by each factor:

Factor 1, 4.836022; Factor 2, 3.347514; Factor 3, 1.793194; Factor 4, 1.681776

TABLE 3. EXXON COAL VARIMAX ROTATED FACTOR PATTERN FOR PRODUCT MOLECULAR WEIGHT DISTRIBUTION

	<u>Factor 1</u>	<u>Factor 2</u>	<u>Factor 3</u>	<u>Factor 4</u>
Carbon	-0.85545			
Hydrogen		0.91672		
Sulfur		0.65336	0.53082	
Oxygen	0.79685			
VM	0.89172			
MM		0.93145		
Inert		0.70451		
HMW	0.91429			
MMW			0.96824	
LMW	-0.88076			

Variance Explained by Each Factor:

Factor 1, 3.980301; Factor 2, 2.006584; Factor 3, 1.756227; Factor 4, 1.258782

Figure 1. Product solubility in benzene-ethanol as a function of carbon content.

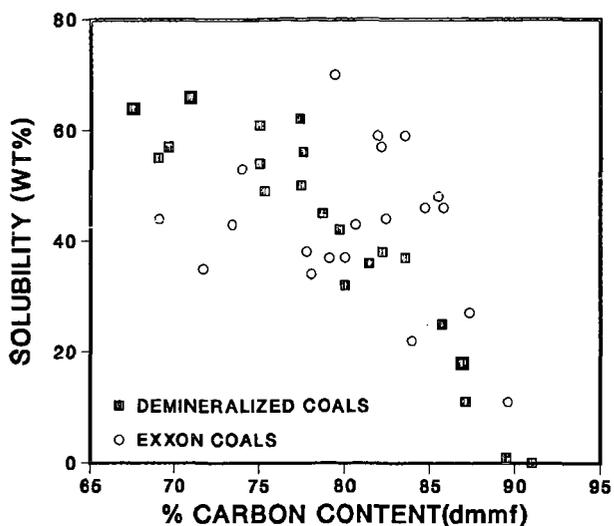


Figure 2. Predicted benzene-ethanol solubilities from multivariate least squares analysis using C and H content.

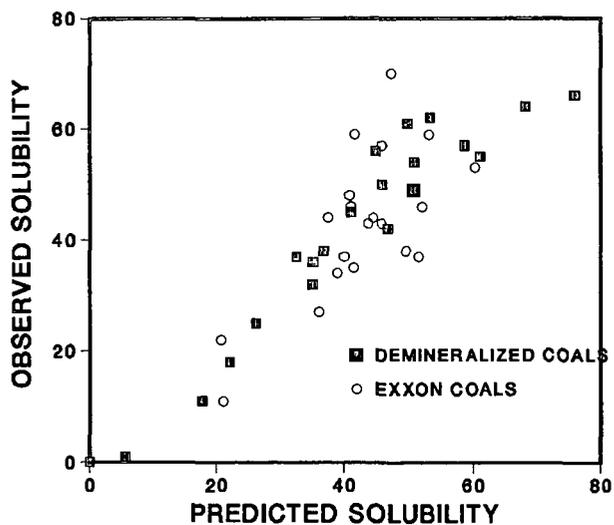


Figure 3. GPC of the benzene-ethanol soluble portion from a demineralized coal(psoc 107).

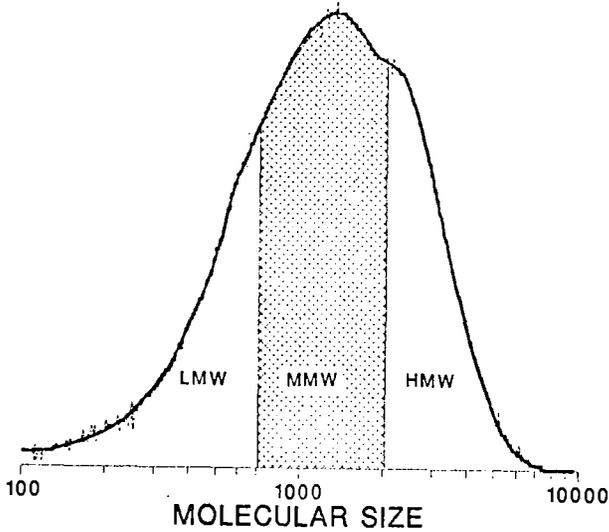


Figure 4. The change in relative amounts of high molecular species with carbon content of the coals.

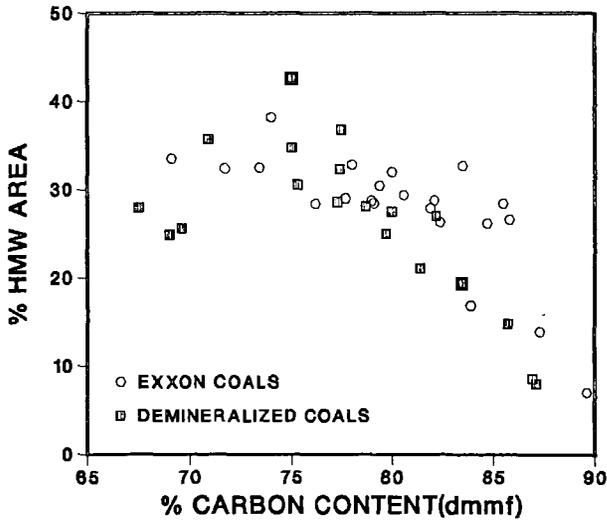


Figure 5. Variation of the f_a of benzene-ethanol solubles with hydrogen content for Exxon coals.

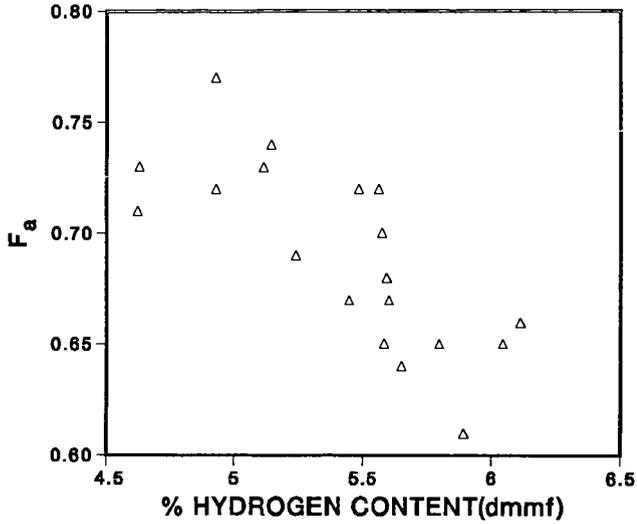


Figure 6. Variation of f_a with benzene-ethanol solubility for the Exxon coals.

