

## REACTIONS OF LOW-RANK COALS IN SUPERCRITICAL METHANOL

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Supercritical fluid extraction of coals has been investigated as a promising method for the production of liquid fuel products from coal under mild conditions. Studies with alcohols as the supercritical fluid have recently been reported (1, 2, 3, 4). Alcohols would be expected to exhibit greater solubility for polar organic molecules, because of hydrogen bonding or dipole attractive forces; they also provide the opportunity for chemical reactions during the extraction, because of the nucleophilicity of the alcohol oxygen and the tendency to act as a hydrogen donor. Alkylation reactions can also occur. Chen and coworkers have shown that sulfur compounds were removed selectively in supercritical methanol and ethanol extractions (4). This potentially useful application may involve reaction of the alcohol with some of the organosulfur moieties and possibly pyrite in the coal. The exact mechanism of the sulfur removal reaction is unknown. Earlier workers used alcohols at very high temperatures (460-600°C) (5) or in combination with sodium hydroxide (6).

As a part of our study of the interaction of supercritical solvents with low-rank coals, a series of extractions of lignites and subbituminous coals were performed with supercritical methanol in a semicontinuous extraction apparatus. These studies were concerned with establishing yield and conversion data for several coals at various supercritical conditions. Not only can the solvation power of the solvent (which depends on the fluid density) be conveniently controlled over a large range with changes in solvent pressure or temperature, but the rates of chemical reactions occurring in and with the solvent may also be controlled by the wide variation in viscosity and density which are obtained with supercritical fluids.

### Experimental

Supercritical methanol extractions were performed using the semicontinuous processing unit described earlier (7). Methanol solvent was pumped through the fixed coal bed (50 g of dried coal) at 120 ml/hr for 2 hr. The pressure of the supercritical solvent was reduced to atmospheric pressure after passing a back pressure regulator. The extract and solvent were collected in a chilled sample vessel. The noncondensable product gas was measured and collected for subsequent GC analysis. Both the solvent-extract mixture and the extracted coal residue were rotary vacuum distilled to give a moisture and methanol free product. Extracts were analyzed by a number of methods including extraction into base, HPLC and <sup>1</sup>H-NMR of methylated (diazomethane) samples and GC for quantitative determination of individual phenols and carboxylic acids. The phenol analysis involved addition of 2-fluorophenol as an internal standard, extraction into base to remove hydrocarbons and amides, addition of acid and extraction into chloroform, Kuderna-Danish evaporation of the chloroform and GC analysis on a calibrated 60 m DB5 capillary column (FID). Photoacoustic spectra of the coal residues were obtained using a cell obtained from MTEch Photoacoustics with a Nicolet 205XB spectrometer. Thermogravimetric analyses of the coal residues were obtained using a Cahn 2000 thermobalance with an argon atmosphere and a 20°C/min temperature ramp.

## Results and Discussion

### Effects of Temperature and Pressure on Yields

Table 1 summarizes the operating conditions and the experimental results obtained for the supercritical methanol extractions. A series of runs at 250 C using Indian Head lignite was performed at pressures ranging from 1233 psia to 2935 psia ( $P_r = 1.05$  to 2.5). The conversions (weight loss on a maf basis) were found to increase with increasing pressure (i.e. from 4.3 to 6.1 %), while the extract yields (weight of extracted material recovered on an maf basis) increased from 1.8 to 4.4% respectively. This increase in extract yields with pressure can be attributed to change in solvent density. Figure 1 is a plot of the effect of calculated solvent density on the extract yields from Indian Head lignite.

A series of isobaric experiments were performed at 2348 psia ( $P_r = 2.0$ ) with temperatures at 250, 275, 300 and 350°C using several coals. The conversion and extract yields all increased significantly with temperature, however, at the higher temperatures the extract and gas yields become significantly higher than the actual weight loss of the original coal. This net yield of products suggests that the methanol is being incorporated into the products by reacting with various groups in the coal and extract components and also being converted to gas, which contains large amounts of methane.

Table 1. Operating Conditions and Results from the Extraction of Various Coals with Supercritical Methanol. See Table 3 for coal analyses. Reduced temperature ( $T_r$ ) and reduced pressure ( $P_r$ ) are the ratios of temperature and pressure to supercritical temperature and pressure.

Coal	Temp. (°C)	$T_r$	Pressure (psia)	$P_r$	Calc. Solvent Density (g/ml)	Pct. Conv. (maf)	Pct Yield, maf	
							Extract	Gas
Indian Head	250	1.021	1233	1.050	0.134	4.27	1.76	2.25
Indian Head	250	1.021	1468	1.250	0.295	4.98	2.86	2.05
Indian Head	250	1.021	1761	1.500	0.368	4.17	3.05	1.36
Indian Head	250	1.021	2348	2.000	0.412	5.49	3.80	1.66
Indian Head	250	1.021	2935	2.500	0.434	6.13	4.43	2.23
Indian Head	275	1.069	2348	2.000	0.320	8.20	3.88	3.67
Indian Head	300	1.118	2348	2.000	0.224	9.55	4.74	6.91
Indian Head	350	1.216	2348	2.000	0.144	23.30	12.43	22.04
Wyodak	250	1.021	1233	1.050	0.134	1.56	3.08	0.70
Wyodak	250	1.021	2348	2.000	0.412	4.16	6.33	0.65
Wyodak	300	1.118	1233	1.050	0.079	2.73	11.28	3.49
Wyodak	300	1.118	2348	2.000	0.224	6.17	6.59	3.10
Wyodak	350	1.216	1233	1.050	0.063	14.74	12.39	21.60
Wyodak	350	1.216	2348	2.000	0.144	17.55	23.29	22.61
Deer Creek	250	1.021	1233	1.050	0.134	0.20	4.02	0.37
Deer Creek	250	1.021	2348	2.000	0.412	10.11	10.50	0.16
Deer Creek	300	1.118	2348	2.000	0.224	7.99	8.69	0.75
Deer Creek	350	1.216	2348	2.000	0.144	11.79	13.69	5.17
Martin Lake	250	1.021	2348	2.000	0.412	3.95	5.57	0.69
Martin Lake	300	1.118	2348	2.000	0.224	5.60	6.64	1.93
Martin Lake	350	1.216	2348	2.000	0.144	18.24	17.54	19.88

### Composition of the Extracted Material

The composition of the extract obtained from each of the coals varied substantially with the increase in temperature of the extraction with supercritical methanol. The extracts contained the waxy material (alkanes and long chain fatty acids) which were also present in the hydrocarbon extracts of these coals (7). In addition, the methanol extractions contained phenolics, anisoles and methyl esters of mono and dicarboxylic acids. The phenolics and anisoles predominate in the extractions of Indian Head lignite which were carried out at the higher temperatures (Table 2). The methyl esters of dicarboxylic acids, such as dimethyl succinate, predominate at the lower temperature. The anisoles and methyl esters have not been found in any supercritical hydrocarbon solvent or water extraction products from coal nor in any pyrolysis products. The anisoles resulted from methylation of the corresponding phenol hydroxyl groups. The esters have resulted from esterification of carboxylic acids in the supercritical methanol; however, the dicarboxylic acids required for these reactions are produced from the coal by oxidation rather than pyrolysis. Thus the reactions for formation of esters have not been sufficiently elucidated.

Table 2. Yields of Phenols in Supercritical Methanol Extractions as Wt% of Extract Weight.

Phenol	Indian Head Lignite (1)			Wyodak Subbituminous			
	250	300	350	250 (1)	300 (1)	350 (1)	350 (2)
Phenol	.18	.44	.77	.059	.056	.066	.038
o-Cresol	.01	.36	2.02	.007	.065	.149	.132
m-Cresol	.03	.33	1.25	.024	.080	.056	.060
p-Cresol	t	.47	.45	.032	.037	.045	.030
Guaiacol	.42	1.17	1.30	t	t	.003	t
2,6-DiMePhe	t	.19	3.86	.003	.041	.435	.388
2-EtPhe	0	.05	0.43	.003	.014	.019	.022
2,4-DiMePhe	t	.41	5.57	.005	.123	.178	.199
2,5-DiMePhe	t	.04	.97	.002	.020	.041	.055
2,3-DiMePhe	.02	.32	2.37	.006	.045	.117	.116
4-MeGuaiacol	.10	.82	1.98	t	t	.035	.030
2,4,6-TriMePhe	t	.29	13.22	.001	.070	.549	.571
2,3,6-TriMePhe	t	.08	3.61	t	.024	.211	.311
4-MeOPhe	0	.01	.43	t	t	.004	.012
2,4,5-TriMePhe	t	.04	4.42	.007	.040	.092	.114
4,6-DiMeGua	t	.41	1.86	t	t	.045	.004
4-Indanol	t	.24	1.77	.003	.081	.099	.127
3,4,5-TriMePhe	t	t	.84	0	0	.004	.003
5-Indanol	t	.03	.57	.001	.014	.024	.032
2,3,5,6-TMePhe	t	.07	5.59	.003	.016	.147	.252
4-nPrGuaiacol	.02	.22	.58	0	0	.002	.009
1-Naphthol	t	.02	.28	.006	.002	.001	.003
2-Naphthol	t	.05	1.40	t	t	.019	.001

Pressures: (1) = 2348 psia; (2) = 1233 psia

Abbreviations: Phe = phenol; Me = methyl; Et = ethyl; Pr = propyl; Gua = guaiacol; MeO = methoxy; T = tetra; t = trace

Other phenols identified by GC/MS and retention time but not quantitatively determined: 6-MeGuaiacol, 3,4-DiMePhe, 3,5-DiMePhe, 4-EtPhe, 4-EtGuaiacol, 2,3,5-TriMePhe, 2,3,4,6-TMePhe, EtMePhe (5).

The distribution of phenol types found in the extracts of Indian Head lignite carried out at 250° (Table 2) was similar to that found in pyrolysis products (8); that is, large amounts of phenol and cresols, smaller amounts of virtually every type of alkyl phenol isomer, a limited series of mainly 4-substituted guaiacols and catechols (these were not quantitatively analyzed). Since the Wyodak subbituminous coal has a very small methoxy group content, corresponding to a low concentration of guaiacol groups in the coal, only traces of guaiacols were found in the low-temperature extracts. The yields of phenols from the Indian Head extractions were much higher than those from the Wyodak coal at all temperatures.

With both coals the higher temperature extractions yielded a distribution of phenols distinctly different from that obtained in the low-temperature extractions. Large increases in the yields of 2,6-dimethylphenol and 2,4,6-trimethyl phenol were especially noticeable. This is evidence for methylation of the ring carbons of the phenols which occurs mainly at the positions ortho to the hydroxyl group of the phenol. In addition to the quantities reported in Table 2 for the phenols which were included in our calibration, numerous other C<sub>4</sub>-, C<sub>5</sub>- and C<sub>6</sub>-substituted phenols were identified in the 350° extracts by GC/MS. Methylation of the aromatic rings of the guaiacols and catechols was also observed to have occurred during the extraction at high temperatures; large amounts of 4,6-dimethylguaiacol, 3,4-dimethylguaiacol, 3,6-dimethylguaiacol, C<sub>3</sub>-guaiacols, C<sub>4</sub>-guaiacols and C<sub>5</sub>-guaiacols were found by GC/MS. Most of the components of the product from extraction of Indian Head lignite at 250°C and most of the low molecular weight products from extraction at higher temperatures have been identified; however, many of the Wyodak extraction products are still under investigation.

The effects of pressure on the yields of phenols was investigated at two pressures, 2348 psia and 1233 psia. The data for extraction of Wyodak subbituminous coal at 350°C at these two pressures are presented in Table 2. Similar yields for each of the individual phenols are observed. The phenol yield structure is therefore dominated by temperature rather than pressure effects, consistent with the hypothesis that release of phenols from the coal matrix is controlled by activation energies for bond cleavage rather than diffusion. Density and viscosity effects on the phenol reaction products are negligible.

#### Comparison of residue surface groups

The residues from the supercritical methanol extraction of Indian Head lignite at three temperatures were examined using photoacoustic spectroscopy to determine the changes in functional groups on the surface which result from extraction and reactions of the lignite with the solvent. The spectra for the original dried lignite and three residues are shown in Figure 2. The broad carboxyl OH stretching band extending from 3500 to 2000 cm<sup>-1</sup> progressively decreases with samples of increasing extraction temperatures, corresponding to conversion of the carboxylic acids to methyl esters or to decarboxylation. The carbonyl stretching band in the original lignite at 1695 cm<sup>-1</sup> is changed to 1717 cm<sup>-1</sup> (with shoulder at higher wave number) in the 250° and 300°C extracts, also indicating the conversion to the ester. The carbonyl band decreases somewhat and exhibits a peak at 1730 cm<sup>-1</sup> in the 350°C extract, which indicates further conversions. The intensities of the methyl absorptions at 2960 and 1455 cm<sup>-1</sup> increase significantly with the extraction temperature. These changes in vibrational bands of the surface groups are consistent with the alkylation which has occurred during the extraction with supercritical methanol.

Thermogravimetric data obtained with the extracted coal residues indicate that the supercritical methanol extracts a significant portion of the compounds which would have normally volatilized in the 200° to 400°C range. These curves also exhibit the effect of methylation of oxygen groups which thermally decompose at temperatures above 400° resulting in release of additional products.

Table 3. Proximate and Ultimate Analyses of Coal Samples Used in Experiments.

	<u>Wyodak</u>	<u>Deer Creek</u>	<u>Gascoyne</u>	<u>Indian Head</u>	<u>Martin Lake</u>
<u>Proximate Analysis</u>					
Volatile Matter	43.5	42.0	40.1	43.8	42.2
Fixed Carbon (by diff)	50.0	47.2	41.2	48.0	42.8
Ash	6.5	10.8	18.6	8.5	15.0
<u>Ultimate Analysis</u>					
Hydrogen	4.26	5.66	3.93	4.74	0.32
Carbon	64.62	71.21	57.56	66.20	61.88
Nitrogen	1.01	1.27	.87	.96	1.23
Sulfur	.58	.36	1.76	.72	1.17
Oxygen (by diff)	23.04	10.70	17.28	19.19	20.40
Ash	6.5	10.8	18.6	8.2	15.0

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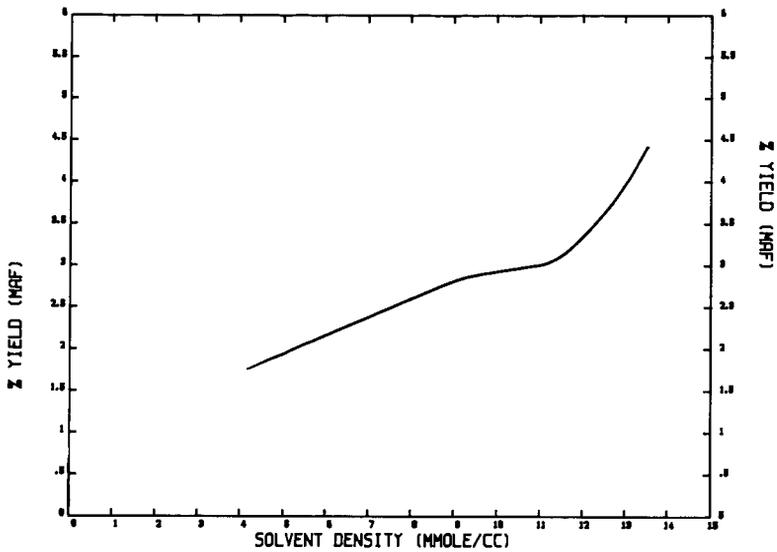


Figure 1. Plot of extraction yields from Indian Head lignite versus solvent density of methanol at 250°C.

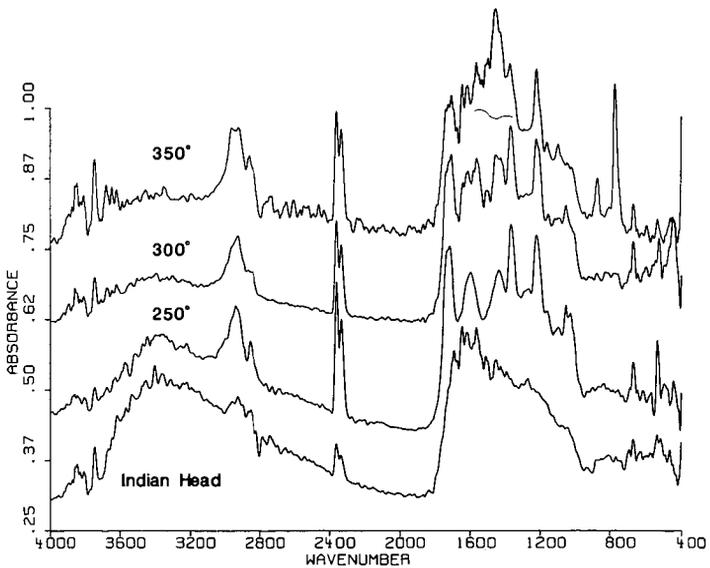


Figure 2. Photoacoustic spectra of dried Indian Head coal and residues from supercritical methanol extraction.