# Lignin-Augmented Coal Depolymerization under Mild Reaction Conditions

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Addition of lignin to coal is synergistic in that it significantly improves the quality and yield (by up to 33%) of the liquid products produced from coal under moderate pressure and temperature conditions. For example, the liquids obtained by lignin-assisted depolymerization of coal at 325 °C contain appreciably lower amounts of the undesirable high molecular weight benzene-insoluble compounds, and higher quantities of the desirable lower molecular weight asphaltenes and pentane-soluble fractions over the corresponding fractions in liquids that are obtained by processing either coal or lignin under identical conditions. The experimental data conclusively show that, in addition to the favorable influences of the lignin-assisted depolymerization listed above, lignin also enhances the stability of the coal depolymerization reaction. The liquid product analyses using NMR and size-exclusion chromatography techniques are also presented. The influence of the process variables of temperature and time on lignin-assisted coal depolymerization is investigated thoroughly. Preliminary results seem to be consistent with the original premise of this investigation that phenoxy radicals derived from lignin can enhance the depolymerization of coal.

## Introduction

Lignin, a renewable material, is an inexpensive byproduct of the paper and pulp industry. It is a major component of all vascular plants and has a high content of phenolic components and prevalence of labile methoxy groups, $\alpha$-ether and $\beta$-ether linkages which can readily form phenoxy radicals upon thermal homolytic bond rupture at low temperatures.[1,2] The inherent resonance stabilization of the phenoxy radicals increases the probability of their existence as monomers which may penetrate the coal structure and shuttle hydrogen to hydrogen-poor coal fragments, enhancing coal depolymerization and product stabilization. Coughlin et al.[8] postulated that since coal depolymerization can be promoted by phenols,[3-8] the addition of lignin to coal should promote liquefaction yields.

In a recent paper, Coughlin et al.[8] described coal liquefaction using lignin. They found that, by using lignin, about 43% of the organic portion of Illinois No. 6 coal was liquefied at 300 °C under pressure of 1400 psig ($9.8 \times 10^6$ N m$^{-2}$) of hydrogen in the presence of a hydrocracking catalyst. Most experiments were, however, carried out under higher pressure (1900 psig = $13.3 \times 10^6$ N m$^{-2}$) conditions. They believe that thermal depolymerization of the lignin at relatively low temperatures leads to formation of resonance-stabilized phenoxy radicals, which then attack the coal causing scission of aliphatic carbon–carbon bonds in the coal. Altieri and Coughlin[9] in another study have characterized the products of coliquefaction of lignin and bituminous coal at 400 °C and 1900–2400 psig (($13.3-16.8) \times 10^6$ N m$^{-2}$). The filterable solids from coliquefaction showed increased solubility in benzene. A greater portion of the benzene-soluble material was found to be pentane-soluble oil. In a recent paper, Sato et al.[10] studied coliquefaction of a number of Japanese coals. They have observed that the influence of lignin on coal liquefaction yields is a strong function of temperature. For

**Table I. Analysis of Coal and Lignin**

| | elemental analysis | |
| analysis | coal | lignin[a] |
|---|---|---|
| C | 62.28 | 49.94 |
| H | 4.38 | 5.36 |
| S | 4.40 | 2.96 |
| N | 1.80 | <0.50 |
| O (by diff) | 27.66 | 41.76 |

| Proximate Analysis | | |
|---|---|---|
| | coal | lignin |
| volatiles | 37.51 | 68.05 |
| ash | 18.31 | 11.57 |
| fixed carbon | 44.18 | 20.38 |

[a] Phenolic OH content of 4.25% is reported.[19]

example, at low temperatures (generally below 350 °C) lignin addition retarded the yields obtained from their coal liquefaction experiments, while at high temperatures the lignin addition enhanced the liquid products yield. The reaction pressure given in their paper was very high (300 MPa), although this seems unreasonable.

The objectives of this research were to explore the influence of lignin addition on coal conversion under mild reaction conditions (low pressure) and in the absence of catalysts. A thorough characterization of the products obtained is also reported.

(1) Davoudzadeh, F.; Smith, B.; Avni, E.; Coughlin, R. W. *Holzforschung* **1985**, *39*, 1959.
(2) Glasser, V. W.; Sanderman, W. *Holzforschung* **1970**, *24*, 3, 74.
(3) Sharma, D. K. *Fuel* **1988**, *67*, 186–190.
(4) Heredy, L. A.; Kostyo, A. E.; Neuworth, M. B. *Fuel* **1963**, *42*, 182.
(5) Larsen, J. W.; Sams, T. L.; Rodges, B. R. *Fuel* **1981**, *60*, 333.
(6) Ouchi, K.; Imuta, K.; Yamashita, Y. *Fuel* **1973**, *52*, 156.
(7) Moore, R. H.; Martin, E. C.; Cox, J. L.; Elliot, D. C. *ACS Symp. Ser.* **1977**, 55.
(8) Coughlin, R. W.; Davoudzadeh, F. *Fuel* **1986**, *65*, 95.
(9) Altieri, P.; Coughlin, R. W. *Energy Fuels* **1987**, *1*, 253.
(10) Sato, S.; Murakata, T.; Chiba, T.; Tukakosi, M. S.; Oda, S. *Proc. Int. Conf. Coal Sci., Tokyo, Jpn.* **1989**, 717–720.
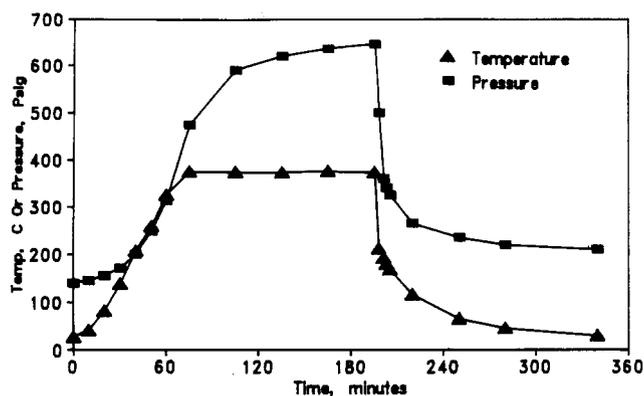
[†] Department of Chemistry.

**Figure 1.** Heating and cooling regimen for coal–lignin (CLT 375-16) conversion. A mixture containing 4 g of coal and 6 g of lignin was reacted in 120 mL of tetralin at 375 °C and 140 psig.

## Experimental Section

The elemental and proximate analyses of the coal and lignin used are provided in Table I. The reactor used is a glass-lined 300-mL autoclave, and it is charged with a mixture of ground (to −200 mesh) Illinois coal (Illinois Basin coal No. 105 obtained from the Argonne Premium Coal Bank), caustic lignin (obtained from steam-exploded aspen, donated by Stake Technology Ltd., Ontario, Canada), and tetralin in the presence of hydrogen gas (∼140 psig = 0.14 × 10⁶ N m⁻²). The mixture is then heated over an 80-min period (approximately) to a desired temperature. The reaction time reported refers to the time after the reactor has attained the desired temperature (Figure 1). A constant temperature is maintained for the duration of the reaction time after which the heat supply to the reactor is shut off and the contents are cooled to below 100 °C over a 30-min period (Figure 1). The reacted coal was then filtered, dried, and weighed.

Several of the liquefaction products were subjected to detailed spectroscopic and chromatographic analyses, and proximate and ultimate analyses were performed on selected solid products. The samples were first vacuum distilled to remove tetralin. The concentrated products were subsequently separated into benzene-soluble and benzene-insoluble fractions; the benzene-soluble fraction was subsequently extracted with pentane to generate a pentane-soluble fraction.[11] To prepare soluble forms of the benzene-insoluble fractions, these samples were first silylated by refluxing with hexamethyldisilazane and trimethylchlorosilane using standard procedures.[12]

NMR spectroscopic data were collected with a Varian VXR300, 300-MHz instrument. All samples were prepared in deuterated chloroform. Proton experiments were done in the conventional manner.[13] In order to obtain accurate quantitative results for ¹³C NMR experiments (i.e., reliable integrations), 100 mg of chromium acetylacetonate was added to shorten the carbon relaxation times and reduce NOE; proton decoupling was also gated to further suppress nuclear overhauser effect (NOE).[14] To obtain reasonable signal-to-noise ratios for ¹³C, total spectral acquisition times of 16 h were required. All NMR spectra were corrected for the contributions of residual tetralin (present at concentration of only a few percent) within the samples.

Size-exclusion chromatography (SEC) was performed using an Altex 110B pump, Rheodyne 7125 injector, and Perkin Elmer Tridet detector operating in the UV absorbance (254 nm) mode. Tetrahydrofuran at 1 mL/min was used as the mobile phase with a Phenomenex Phenogel 100 Å pore size column. The retention of the column was calibrated by using anthracene (MW = 178), chrysene (MW = 228), and a series of five polystyrene standards ranging in molecular weight from 800 to 17 500. In some cases, a column with a wider molecular weight range (100–40 000) was employed. Further, data were collected with an IBM PC with
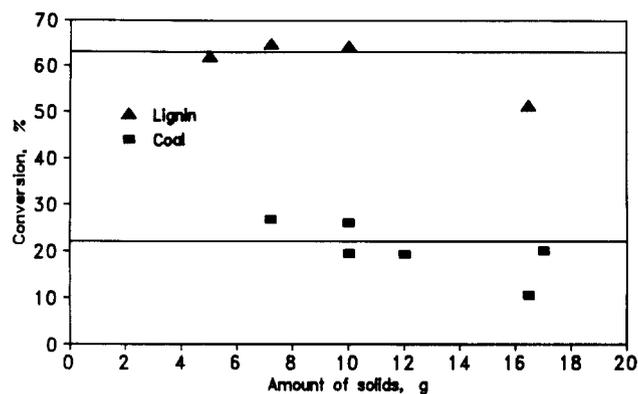
(11) Bartle, K. D. *Fuel* 1979, *58*, 413–422.
(12) Snape, C. E.; Bartle, K. D. *Fuel* 1979, *58*, 898–901.
(13) Snape, C. E.; Jordan, W. R.; Bartle, K. D. In *Coal Liquefication Products: NMR Spectroscopic Characterization and Production Processes*; Schulty, H. D., Ed.; Wiley: New York, 1983.
(14) Ladner, W. R.; Snape, C. E. *Fuel* 1978, *57*, 658–662.



**Figure 2.** Coal and lignin conversion at 325 °C. Experiments were carried out in 120 mL of tetralin.
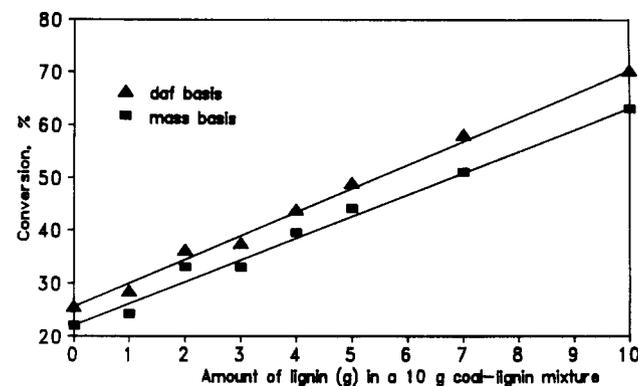


**Figure 3.** Coal–lignin mixture conversion at 325 °C. The straight lines represent the predicted conversions based upon the linear effect of lignin addition to coal under identical reaction conditions. In all the experiments reported, 120 mL of tetralin was used.

ASYSTANT software and subsequently processed by using a spreadsheet program to provide average molecular weight information. These calculations consider the entire chromatogram rather than the peak signals.[15]

The number average molecular weight ($M_n$) and the weight average molecular weight ($M_w$) were calculated respectively by the following formulas:

$$M_n = [\sum_{i=1}^{n}(\text{area})_i][\sum_{i=1}^{n}(\text{area})_i/MW_i]^{-1}$$

$$M_w = [\sum_{i=1}^{n}(\text{area})_i MW_i][\sum_{i=1}^{n}(\text{area})_i]^{-1}$$

and the dispersivity ($D$) is defined as

$$D = M_w M_n^{-1}$$

(Area)$_i$ is the size of a segment with a width of 1 s, under the original distribution curve. $MW_i$ is the corresponding molecular weight. $D$ is an index for the homogeneity of the sample. If $D$ = 1.0 then all molecules of the sample have the same size.

## Results and Discussion

**Influence of Lignin on Coal Conversion.** The results of experiments discussed in this report were carried out at temperatures between 325 and 425 °C and an initial hydrogen gas pressure of 140 psig (0.14 × 10⁶ N m⁻²). The increase in pressure during the course of reaction was observed to be very modest. For example, the pressure rose to only 650 psig (4.55 × 10⁶ N m⁻²) for experiments conducted at 375 °C (Figure 1). In order to determine the maximum amount of coal and lignin that could be charged to the reactor, a number of experiments were conducted

(15) Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size Exclusion Liquid Chromatography*; Wiley: New York, 1989; Chapter 10.

**Table II. Enhancement in Coal Conversion (Mass Basis) due to Lignin Addition[a]**

| temp, °C | coal conversn in absence of lignin (A), % | lignin conversn in absence of coal, % | coal–lignin conversn, % | coal conversn[b] in coal–lignin mix (B), % | enhancmt in[c] coal conversn, % |
|---|---|---|---|---|---|
| 325 | 22.00 | 63.00 | 47.00 | 23.00 | 4.55 |
| 375 | 57.75 | 80.00 | 74.20 | 65.50 | 13.42 |
| 400 | 71.00 | 91.67 | 87.50 | 81.25 | 14.44 |
|  |  | (88.43)[d] |  | (86.11)[d] | (21.28)[d] |
| 425 | 81.00 | 89.83 | 89.80 | 89.75 | 10.80 |
|  |  | (88.43)[d] |  | (91.86)[d] | (13.41)[d] |

[a] Experiments were conducted using a mixture of 4 g of coal and 6 g of lignin for a period of 2 h. [b] Estimate value assuming lignin conversion (%) in the coal–lignin mixture to be the same as for the case when lignin alone is used. [c] Calculated by the formula: [(B − A)/A] × 100. [d] Assumes complete lignin conversion. Note that lignin contains 11.57% ash (Table I).

**Table III. Influence of Reaction Time on Coal Conversion[a]**

| time, min | coal conversn in absence of lignin (A), % | lignin conversn, in absence of coal, % (C) | coal–lignin conversn, % | coal conversn[b] in coal–lignin mix (B), % | enhancmt[c] in coal conversn, % |
|---|---|---|---|---|---|
| 0 | 27.75 | 63.30 | 50.10 | 30.30 | 9.19 |
| 30 | 41.75 | 65.83 | 61.00 | 53.76 | 28.77 |
| 60 | 43.38 | 74.67 | 67.97 | 57.91 | 33.50 |
|  | 42.25/44.50 |  | 74.2/64.7/65.0 |  |  |
| 85 | 41.00 | 77.50 | 66.40 | 49.75 | 21.34 |
| 120 | 54.90 | 78.80 | 74.20 | 67.30 | 22.59 |
|  | 52.00/57.80 |  |  |  |  |

[a] Experiments were conducted at 375 °C using a mixture of 4 g of coal, 6 g of lignin and 120 mL of tetralin. Experiments involving coal and lignin alone were carried out using 4 and 6 g of coal and lignin, respectively. [b] Estimated value assuming lignin conversion (%) in the coal–lignin mixture to be the same as for the case when lignin alone is used. [c] Calculated by the formula: [(B − A)/A] × 100.

(Figure 2). The results indicate that about 10 g of solids could be used in 120 mL of tetralin without being limited by availability of hydrogen-transfer solvent. It should be noted that the reproducibility of experiments using coal alone, although satisfactory and in agreement with other studies,[3,8,10] is not nearly as good as that obtained with experiments involving lignin.
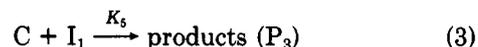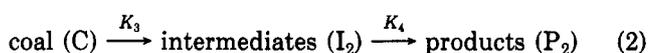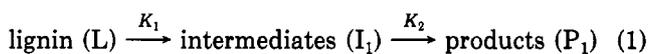
The influence of lignin addition to coal at a temperature of 325 °C as a function of the lignin-to-coal ratio (mass basis) is shown in Figure 3. The straight lines drawn represent the predicted conversions based upon the linear effect of lignin addition to coal under identical reaction conditions. The data obtained indicate that at this low reaction temperature the influence of lignin addition to coal depolymerization was small, in contrast to the significant effect obtained at higher temperatures (reported below). An interesting observation is that even a small amount of lignin addition dramatically (within 2–5%) improve the reproducibility of experiments. Repeated experiments under the same conditions exhibited a standard deviation of 1.9% for experiments conducted with coal–lignin mixtures, compared to 4.2% for coal alone. This observation indicates that lignin addition stabilizes the coal conversion; this information may be of consequence to coal processing.

The influence of the enhancement in coal conversion due to lignin addition is shown in Table II. In these experiments 4 g of coal and 6 g of lignin were used. At 400 °C, coal conversion is 71%, while upon the lignin addition it increases to 86%. The extent of conversion of coal, lignin, and coal–lignin mixture (on mass basis) is observed to be a strong function of temperature. It is observed that the enhancement in coal conversion is as high as 21%. The data show that lignin addition has a favorable influence on coal conversion especially in the temperature range of 375–400 °C. Since at higher temperatures the reaction goes almost to completion (coal and lignin have about 18.3% and 11.6% ash respectively, Table I), the favorable influence of lignin addition to coal conversion may not be discernible and the actual influence may be much greater than reported here. Thus, a number of experiments were

carried out for a shorter period of time.

Runs were performed over different time periods, up to 120 min, for coal, lignin, and coal–lignin mixtures under similar reaction conditions. The results are presented in Table III. Note the significant positive effect of the lignin addition on conversion rate, particularly over the 30–85-min reaction period. The significant conversion that occurs at time zero reflects the reactions that occur during the heat-up period to reaction temperature; times are measured once reaction temperature is attained.

The following reaction mechanism is proposed to explain the enhancement in coal conversion with time data:

$$\text{lignin (L)} \xrightarrow{K_1} \text{intermediates (I}_1\text{)} \xrightarrow{K_2} \text{products (P}_1\text{)} \quad (1)$$

$$\text{coal (C)} \xrightarrow{K_3} \text{intermediates (I}_2\text{)} \xrightarrow{K_4} \text{products (P}_2\text{)} \quad (2)$$

$$\text{C} + \text{I}_1 \xrightarrow{K_5} \text{products (P}_3\text{)} \quad (3)$$

The first two reactions (i.e., (1) and (2)) are hypothesized to occur when lignin and coal alone are depolymerized. When lignin is added to coal, the intermediates from reaction 1 further depolymerize coal via reaction 3. The enhancement in coal conversion obtained is due to reaction 3. The concentration of $I_1$ should be dependent on time, it being zero at the beginning of the experiment, and should increase with time as lignin is depolymerized. At a certain time, $t_m$, $I_1$ should reach a maximum value after which it would decline as it is consumed in reactions 1 and 3. Thus, the enhancement in coal conversion should also increase with an increase in $I_1$ (i.e., with time), and hence it should reach a maximum value and then decline.

**Product Characterization.** Solubility of coal in benzene according to Pelipetz[16] was used as a measure of the extent of coal hydrogenation. Solubility in benzene and pentane is a measure of the "oil" produced. The pentane-insoluble but benzene-soluble fraction is called asphaltenes. Asphaltenes are high molecular weight in-

(16) Pelipetz, *J. Ind. Eng. Chem.* **1948**, *40*, 1259–1264.

**Table IV. Fractionation of Liquefied Products[a] Obtained at 325 °C**

|  | pentane solubles, % | asphaltenes, % | benzene insolubles, % |
|---|---|---|---|
| CT5 | 46.56 | 21.60 | 31.84 |
| CLT6 | 59.10 | 26.32 | 7.84 |
| LT3 | 46.16 | 19.88 | 25.60 |

[a] Percentages based on mass of starting aliquot. CT5: 10 g of coal reacted in 120 mL of tetralin at 325 °C for 2 h. CLT6: 3 g of coal and 7 g of lignin mixture reacted in 120 mL of tetralin at 325 °C for 2 h. LT3: 10 g of lignin reacted in 120 mL of tetralin at 325 °C for 2 h.

**Table V. NMR Shift Classification[13]**

| hydrogen type | symbol | chem shift, ppm |
|---|---|---|
| aromatic | $H_A$ | 6.0–9.0 |
| phenolic | $H_{OH}$ | 5.0–9.0 |
| ring-joining methylene | $H_F$ | 3.4–5.0 |
| $CH_3$, $CH_2$, and CH ($\alpha$ to an arom ring) | $H_a$ | 1.9–3.4 |
| $CH_3$, $CH_2$, and CH ($\beta$ or farther from arom ring + paraff $CH_2$ + CH) | $H_b$ | 1.0–1.9 |
| $CH_3$ ($\gamma$ or farther from arom ring + paraff $CH_3$) | $H_c$ | 0.5–1.0 |

termediate products in coal liquefication. The presence of asphaltenes in coal-derived liquids has been also discussed by Weller et al.[17] The viscosity of the coal-derived liquids is affected by the amount and the molecular weight of the asphaltenes as reported by Sternberg.[18]

Table IV lists the mass distribution of three liquefied products fractionated into pentane solubles, asphaltenes, and benzene insolubles. The products represent a liquefied coal (CT5), a liquefied lignin (LT3), and a liquefied mixture containing 30% coal and 70% lignin (CLT6). The primary observation from this data is that the mixture of coal and lignin produced a liquefied product containing substantially larger amounts of the more desirable pentane-soluble and asphaltene fractions. Altieri and Coughlin[9] also observed enhanced formation of asphaltenes for coal–lignin liquids obtained with their process conditions.

Proton NMR spectra were obtained for all of the fractions and classified by using the system described in Table V. The results of this classification are listed in Table VI. The pentane-soluble fraction of the CLT liquid generally exhibited H levels which were intermediate between those of the coal or lignin alone and approximately what might be expected for a mixture of pentane-soluble fractions from the liquefaction of coal and lignin independently. The exceptions were a reduced level of $H_\gamma$, which was a minor portion of the H within the fraction, and an elevated level of $H_\alpha$. For the coal–lignin asphaltenes, higher $H_\alpha$ and $H_A + H_{OH}$, and lower $H_\beta$ were measured. For the coal–lignin benzene insolubles, which represented a very small fraction of the CLT liquids, higher $H_A + H_{OH}$, and lower $H_\gamma$ and $H_\alpha$ were measured. Overall, the coal–lignin liquids exhibited higher $H_\alpha$ and lower $H_\gamma$ (once again, a small fraction). The elevated $H_\alpha$ levels may indicate enhanced hydrocracking, as described by Coughlin's research group.[9]

Since the proton NMR data suggested more significant chemical differences for the asphaltenes, ^{13}C NMR data were also obtained for these fractions. Table VII sum-

(17) Weller, S.; Pelipetz, J. *Fuel* 1951, 29, 208–211.
(18) Sternberg, W. *ACS Symp. Ser.* 1975, No. 20, 111–122.
(19) Glasser, W. G.; Barnett, C. A.; Muller, P. C.; Sarkanen, K. V. *J. Agric. Food Chem.* 1983, 31, 921–930.

**Table VI. Proton Distribution via NMR[a] (%) of Products Obtained at 325 °C**

|  | CT5 | CLT6 | LT3 |
|---|---|---|---|
| **Pentane Solubles** | | | |
| $H_c$ | 9.1 | 1.2 | 3.1 |
| $H_b$ | 44.2 | 33.7 | 30.7 |
| $H_a$ | 28.1 | 36.9 | 29.8 |
| $H_F$ | 3.4 | 3.6 | 3.4 |
| $H_A + H_{OH}$ | 15.3 | 24.5 | 33.1 |
| **Asphaltenes** | | | |
| $H_c$ | 8.3 | 4.2 | 2.5 |
| $H_b$ | 25.4 | 11.4 | 23.5 |
| $H_a$ | 28.9 | 33.3 | 21.1 |
| $H_F$ | 8.6 | 21.4 | 26.3 |
| $H_A + H_{OH}$ | 28.9 | 29.7 | 26.6 |
| **Benzene Insolubles (Silylated)** | | | |
| $H_c$ | 9.3 | 3.9 | 7.5 |
| $H_b$ | 48.5 | 39.9 | 16.5 |
| $H_a$ | 22.5 | 7.3 | 30.1 |
| $H_F$ | 0.0 | 1.5 | 23.1 |
| $H_A + H_{OH}$ | 19.7 | 47.4 | 22.7 |
| **Overall Mass-Averaged Values[b]** | | | |
| $H_c$ | 9.0 | 2.12 | 3.8 |
| $H_b$ | 41.5 | 26.0 | 23.1 |
| $H_a$ | 26.5 | 31.2 | 25.7 |
| $H_F$ | 3.5 | 7.8 | 12.7 |
| $H_A + H_{OH}$ | 19.6 | 26.0 | 26.4 |

[a] Obtained by using Varian VXR 300-MHz NMR spectrometer with $CDCl_3$ as solvent. [b] Determined from data for the individual fractions and the mass fraction data of Table IV.

**Table VII. Carbon Distribution via ^{13}C NMR (%) of Liquefied Product Obtained at 325 °C[a]**

|  |  | asphaltenes | | |
|---|---|---|---|---|
|  | ppm | CT5 | CLT6 | LT3 |
| carbonyl | 170–210 | 4.98 | 8.42 | 8.50 |
| aromatic C–O | 148–168 | 8.20 | 13.80 | 6.32 |
| aromatic C–C, C–H, C–N | 100–148 | 55.63 | 47.31 | 64.70 |
| methylene, methine | 22.5–60 | 24.28 | 23.48 | 20.04 |
| methyl | 11–22.5 | 6.59 | 6.99 | 0.44 |
| | | ratio of aliph/arom C | | |
| CT5 | | 0.5549 | | |
| CLT6 | | 0.6440 | | |
| LT3 | | 0.3165 | | |

[a] CT5: 10 g of coal reacted in 120 ml of tetraline at 325 °C for 2 h. CLT6: 3 g of coal and 7 g of lignin mixture reacted in 120 mL of tetralin at 325 °C for 2 h. LT3: 10 g of lignin reacted in 120 mL of tetralin at 325 °C for 2 h.

marizes the data derived from these spectra. The primary differences indicated for the CLT liquid are a higher level of aromatic C–O, a higher level of methyl C, and lower levels of aromatic C–C, C–H, and C–N. The addition of oxygen indicated by the elevated levels of aromatic C–O in the presence of lignin suggests that phenoxy radicals, postulated to be important products of lignin thermolysis during coliquefaction with coal,[8,9] may be involved in substitution reactions with the coal solids. Further, the asphaltene fraction from the coal-lignin product mixture exhibited a higher aliphatic-to-aromatic carbon ratio than did the asphaltenes from either coal or lignin alone.

Material balance on a number of experiments is repoted in Table VIII. The liquid product yields were calculated by subtracting the mass of solid residue and the gases produced from the initial solid mass charged to the reactor. The enhancement in liquid products obtained due to the lignin addition is found to be 48.6%, which compares very favorably with the corresponding enhancement of 13.4%, calculated on the solid mass basis (Table I). Thus, the data show that, due to lignin addition, the increase in liquid

**Table VIII. Mass Measurements for Liquefaction and C/H and O/H (Atomic) Ratios of Products Obtained[a]**

| | (A) initial mass charged, g | | (B) solid | (C) gases | liq produced, g | enhancmt in liq |
| sample | coal | lignin | residue mass, g | produced, g | (by diff)[b] | prod obtained,[c] % |
| --- | --- | --- | --- | --- | --- | --- |
| coal (4 g) | 4 | 0 | 2.31 | 0.25 | 1.44 (D) | |
| lignin (6 g) | 0 | 6 | 1.50 | 0.50 | 4.00 (E) | |
| lignin/coal (6 g/4 g) | 4 | 6 | 3.22 | 0.64 | 6.14 (F) | 48.6 |

| liquid sample | C/H | O/H |
| --- | --- | --- |
| coal (4 g) | 0.93 | 0.05 |
| lignin (6 g) | 0.85 | 0.11 |
| coal/lignin (4 g/6 g) | 0.89 | 0.09 |

[a] Reaction was carried out for 1 h at 375 °C. Experimental conditions as in Table III. [b] A − (B + C). [c] [F − (D + E)/D] × 100.

**Table IX. Molecular Weight Data for Liquid Products Obtained at 325 °C[a]**

| | $M_n$ | $M_w$ | dispersivity |
| --- | --- | --- | --- |
| pentane solubles | | | |
| CT5 | 236 | 319 | 1.35 |
| CLT6 | 97 | 305 | 3.14 |
| LT3 | 184 | 334 | 1.81 |
| asphaltenes | | | |
| CT5 | 336 | 1244 | 3.70 |
| CLT6 | 282 | 1426 | 5.06 |
| LT3 | 287 | 1095 | 3.81 |
| benzene insolubles[b] | | | |
| CT5 | 392 | 6849 | 17.5 |
| CLT6 | 3223 | 11099 | 3.44 |
| LT3 | | | |
| silylated benzene insolubles[b] | | | |
| CT5 | 3176 | 9446 | 2.98 |
| CLT6 | | | |
| LT3 | | | |

[a] Data obtained by using Phenomenex 100-Å pore column (molecular weight range 100–10000); THF mobile phase at 1 mL/min; calibration using polyaromatic and polystyrene standards. Experimental conditions as in Table IV. [b] Data for some benzene-insoluble fractions are omitted due to retention times being outside the linear for the column.

products obtained is very significant. The liquid product from the coal–lignin mixture also has a lower C/H atomic ratio than that from the coal alone (Table VIII). The liquid product from the coal–lignin mixture has also a fairly low O/H atomic ratio of 0.09.

Data for size-exclusion chromatography of the various fractions are listed in Table IX. Included are values for dispersivity, given as the ratios of $M_w$ to $M_n$. One notable observation from this data is that, for the pentane-soluble and asphaltene fractions, the dispersivities of the coal–lignin liquids are higher than those for other samples, suggesting that coal–lignin liquids for these fractions consist of a wider range of chemical compounds. However, these differences in dispersivity result from small increases in the concentrations of low molecular weight species, which have a dominating influence upon $M_n$ determinations.

Table X lists the distribution of fractions for products obtained at higher temperatures (375 °C) than the previously characterized products. As before, the coal–lignin mixtures (CLT-375-3 and CLT-375-2) produced a lower fraction of the less desirable benzene insolubles than that obtained by processing the coal alone (CT-375-3). The difference between the coal–lignin and coal alone products is not as large as that obtained for the lower temperature products, however. Table XI lists the proton distribution data for the various fractions; once again, the differences between the products are smaller than before. Comparison of these data to those in Table VI indicates that these higher temperature products have greater aromatic character than those obtained at low temperature.

**Table X. Fractionation of Liquefied Products Obtained at 375 °C[a]**

| | pentane solubles, % | asphaltenes, % | benzene insolubles, % |
| --- | --- | --- | --- |
| CT-375-3 | 36.10 | 50.84 | 13.06 |
| CLT-375-3 | 41.52 | 50.04 | 8.44 |
| CLT-375-2 | 33.25 | 60.50 | 6.06 |

[a] CLT-375-3: mixture of 4.0 g of coal and 6.0 g of lignin reacted in 120 mL of tetralin at 375 °C for 1 h. CLT-375-2: same as CLT-37-3 but 2 h reaction time. CT-375-3: 4.0 g of coal in 120 mL of tetralin at 375 °C for 1 h.

**Table XI. Proton NMR Distribution (%) of Products Obtained at 375 °C[a]**

| | CT-375-3 | CLT-375-3 | CLT-375-2 |
| --- | --- | --- | --- |
| | Pentane Solubles | | |
| $H_c$ | 8.86 | 9.15 | 5.65 |
| $H_b$ | 31.22 | 35.45 | 28.83 |
| $H_a$ | 29.68 | 23.83 | 26.15 |
| $H_F$ | 2.39 | 4.81 | 5.79 |
| $H_A + H_{OH}$ | 27.85 | 32.04 | 33.58 |
| | Asphaltenes | | |
| $H_c$ | 5.68 | 3.84 | 5.24 |
| $H_b$ | 21.08 | 18.66 | 25.17 |
| $H_a$ | 32.07 | 29.71 | 31.73 |
| $H_F$ | 9.46 | 14.59 | 8.93 |
| $H_A + H_{OH}$ | 31.71 | 33.19 | 28.93 |
| | Benzene Insolubles (Silylated) | | |
| $H_c$ | 8.06 | 7.70 | 8.39 |
| $H_b$ | 25.22 | 28.50 | 30.47 |
| $H_a$ | 22.89 | 23.57 | 27.93 |
| $H_F$ | 13.78 | 12.48 | 3.32 |
| $H_A + H_{OH}$ | 30.04 | 27.73 | 29.88 |
| | Overall Values for Coal Liquids[b] | | |
| $H_c$ | 7.20 | 6.40 | 5.60 |
| $H_b$ | 25.30 | 24.40 | 26.60 |
| $H_a$ | 30.00 | 26.80 | 29.60 |
| $H_F$ | 7.50 | 10.40 | 7.50 |
| $H_A + H_{OH}$ | 30.10 | 32.20 | 30.50 |

[a] Experimental conditions as in Table IX. [b] Determined from data for individual fractions and the mass fraction data of Table X.

Size-exclusion chromatography data for the higher temperature products are compiled in Table XII. In general, the data for the coal alone are lower than those for the coal–lignin mixtures (CLT's). However, since the CLT's consist of a greater abundance of the lower MW pentane-soluble and asphaltene fractions (Table X), the overall average MW's for the products (Table XII) are very similar. The dispersivity index (D) for most liquid fractions is observed to be much greater than 1, which indicates that in a given sample molecules are not of the same size. The dispersivity indexes of the pentane-soluble fractions for the coal (CT) and CLT samples are approximately equal to one another. However, a great variation in the indexes is seen in benzene-insoluble and asphaltene fractions for

**Table XII. SEC Data for Coal Liquid Fractions Obtained at 375 °C[a]**

| samples | $M_n$ | $M_w$ | dispersivity |
|---|---|---|---|
| pentane solubles | | | |
| CLT-375-2 | 382.47 | 987.96 | 2.58 |
| CT-375-3 | 224.25 | 575.62 | 2.57 |
| CLT-375-3 | 400.49 | 1072.46 | 2.68 |
| asphaltenes | | | |
| CLT-375-2 | 597.24 | 1318.47 | 2.21 |
| CT-375-3 | 647.66 | 891.94 | 1.38 |
| CLT-375-3 | 623.46 | 1005.54 | 1.61 |
| benzene insolubles | | | |
| CLT-375-2 | 1109.25 | 6852.35 | 6.18 |
| CT-375-3 | 881.77 | 3268.31 | 3.71 |
| CLT-375-3 | 1164.48 | 9867.98 | 8.47 |
| silylated benzene insolubles | | | |
| CLT-375-2 | 569.70 | 1706.34 | 3.00 |
| CT-375-3 | 371.31 | 2691.30 | 7.25 |
| CLt-375-3 | 314.38 | 2656.76 | 8.45 |

**Overall Molecular Weight Data for Coal Liquids Produced at 375 °C**

| samples | $M_n$ | $M_w$ | dispersivity |
|---|---|---|---|
| CLT-375-2 | 523.02 | 1229.57 | 2.35 |
| CT-375-3 | 458.72 | 1012.74 | 2.21 |
| CLT-375-3 | 504.79 | 1172.69 | 2.32 |

[a] Experimental conditions as in Table IX.

various samples (CT and CLTs) as shown in Table XII.

## Conclusions

Lignin and lignin-derived liquids improve (by up to 33%) the overall coal conversion under mild reaction conditions (pressure ~650 psig = 4.55 × 10⁶ N m⁻²).

Liquids produced from coal–lignin mixtures at 325 °C contain appreciably lower amounts of the undesirable high molecular weight benzene-insoluble compounds and higher quantities of the desirable lower molecular weight asphaltenes and pentane-soluble fractions over the corresponding fractions in liquids obtained by processing the coal or lignin alone.

Addition of lignin to coal results in the lowering of C/H and O/H ratios of the liquids obtained.

[13]C data for coal–lignin products obtained at 325 °C indicate the addition of oxygen to the liquid products, as would be expected based on the interaction of phenoxy radical species with the liquefaction process. For reactions conducted at higher temperature (375 °C), NMR and SEC data indicate a greater similarity between the liquid products derived from coal–lignin and those derived from coal alone. The data show that enhancement in coal conversion is maximum at 1 h reaction time. SEC data also show that the coal–lignin mixture derived liquids after 1 h reaction time have lower molecular weight than the corresponding liquids produced at 2 h reaction time.

**Registry No.** Lignin, 9005-53-2; tetralin, 119-64-2.

# Communications

## Size Exclusion Chromatography of Alkali-Solubilized Coal

*Sir:* Recently, there has been an increasing interest in finding microorganisms that are able to degrade coal. An easy method that can be used to screen for such organisms is to grow them on water-solubilized coals and, using size exclusion chromatography (SEC), determine if resulting coals have a reduced molecular weight (MW). [SEC only yields information concerning the shape and size (hydrodynamic volume) of a molecule as compared to a set of standards. For simplicity, the term molecular weight is used instead of stating that a molecule has the same hydrodynamic volume as a globular protein of a given molecular weight.] Unfortunately, there are many difficulties associated with the SEC of biologically treated, solubilized coal molecules. These difficulties are similar to those observed for the SEC of humic acids[1,2] and other coal-derived materials[3–6] and include the binding of coal molecules to SEC matrices. These interactions may be minimized by eluting samples in alkaline solutions containing amines[2] or by using either high-performance liquid chromatography (HPLC) or conventional liquid chromatography (LC) SEC media with aqueous buffers containing Tween 80.[7,8] Unfortunately, these studies have not eliminated the possibility of reversible binding occurring nor have they determined if solubilized coals are able to interact with growth medium components or microbial metabolites thereby altering the coal's apparent molecular size and shape. In this paper, we report optimal conditions for performing SEC of solubilized coal (e.g., SynChropak GPC 300 HPLC column using aqueous buffers at neutral pH's) and that few constituents present in microbial growth media affect these determinations.

A stock coal solution of 0.2% Mississippi Wilcox[9,10] in 0.1 N NaOH was made and stored anaerobically. Under these conditions, greater than 90% of the organic carbon was solubilized (data not shown). Aliquots were eluted through SEC media (standardized by using nine different

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