Coliquefaction of Coal and Black Liquor to Environmentally Acceptable Liquid Fuels

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Previous work in our laboratories has demonstrated that addition of lignin to coal during liquefaction significantly increases the depolymerization of coal and enhances the quality of the liquid products. It is believed that thermolysis of the lignin results in the formation of phenoxy and other reactive radicals at temperatures too low for significant thermolysis of the coal matrix; such radicals are effective and active intermediates that depolymerize coal by cleaving methylene bridges. It has been reported that alkali is also effective for extraction of liquids from coal. The work presented here combines these two reactive agents by utilizing the black liquor waste stream from the Kraft pulping process for coal depolymerization. That waste stream contains large amounts of lignin and sodium hydroxide, as well as other components. To permit comparative evaluations of the extent of coal depolymerization by coprocessing coal and black liquor, reference runs were performed with tetralin alone, sodium hydroxide in tetralin, and lignin in tetralin. Results indicated that the sodium hydroxide–tetralin system resulted in almost 67% conversion at 375°C, 1 hour. The black liquor system exhibited a lower conversion of 60%, indicating some inhibition of the depolymerization reactions by components in the black liquor.

Many investigators (Mirza et al., 1984; Dorland et al., 1992) have studied the effects of aqueous alkali treatment on coal dissolution. Sodium hydroxide is widely used in pretreatment procedures for enhancing coal solubility. Mirza et al. (1984) showed that a dilute alkali (about 1.4%) is capable of degrading coal at nearly 100°C and atmospheric pressure, resulting in enhanced extraction in generally available organic solvents. Aqueous NaOH could attack susceptible functional groups or linkages such as ethers, resulting in the formation of alcohols and phenols that are soluble in the aqueous hydrolysis medium. Recently, Dorland et al. (1992) investigated the effect of sulfur on coal treatment in aqueous sodium hydroxide. They reported that the dissolution of Wyodak subbituminous and North

Dakota lignite coals in 50% aqueous sodium hydroxide was enhanced by the addition of elemental sulfur.

Recent work in our laboratories (Lalvani et al., 1991 *a*, *b*; Muchmore et al., 1991; Akash et al., 1992) has shown that the addition of lignin to coal during liquefaction significantly increases the depolymerization of coal and enhances the quality of the liquid products. It is believed that thermolysis of the lignin results in the formation of phenoxy radicals, as well as other reactive radicals at temperatures too low (about 300°C) for significant thermolysis of the coal matrix. It is suggested that such radicals are effective and active intermediates, which depolymerize coal by cleaving methylene bridges.

The chemistry of alkali extraction of coal is similar to the Kraft pulping process for dissolving the lignin from wood to produce cellulose pulp. In the Kraft process, hot caustic is used to dissolve the lignin, and sodium sulfide (or sulfate) is commonly added to improve this removal. The resulting black liquor waste stream consequently contains large amounts of lignin, sodium hydroxide, sodium sulfide, aliphatic acids, saccharinic acids, turpentine, tall oil, etc. Some of these chemicals are recovered at a large energy expense, and the remainder of the liquor is burned as a fuel.

Because of the presence of lignin and NaOH, the addition of black liquor was anticipated to give positive effects on coal liquefaction, but no work has so far been reported on the depolymerization of coals using black liquor. The present work explored the feasibility of using black liquor for enhancement of coal depolymerization through determination of the extent of coal conversion at various conditions.

Experiment

The coal used (IBC no. 105) was obtained from the Illinois Basin Coal Sample Bank. The elemental and proximate analyses of the coal are shown in Table 1. Black liquor and lignin (Indulin AT) were supplied by Westvaco, South Carolina.

Table 1
Analysis of Illinois coal used, IBC no. 105

Component	Percentage
Elemental analysis (maf)	
C	76.24
H	5.36
S	5.39
N	1.57
O [a]	11.44
Proximate analysis	
Volatiles	37.51
Fixed carbon	44.18
Ash	18.31

[a] By difference.

Table 2

Physical characteristics of black liquor

Parameter	Value
pH	13.5
Total solids[a]	39.8%
Density	1.54 g / cm^3

[a]Analytical method (Libby, 1982).

The compositional analyses of black liquor and lignin are provided in Tables 2 and 3, respectively.

A 0.5 g sample was added dropwise to a tarred watch glass dish and weighed as quickly as possible. After 4 hours at 105°C in an oven, the dish was cooled and weighed. The dry weight divided by the original weight, times 100 is the percentage of total solids.

The reactor used was a 300 mL glass-lined autoclave, and it was charged with ground coal ($-$ 200 mesh), black liquor (or NaOH or H$_2$O in the control runs), and tetralin. The reaction mixture was heated to 375°C in the presence of hydrogen (200 psig initial pressure), and the temperature was maintained for 1 hour, after which the heat supply to the reactor was shut off. After cooling, final temperature and pressure values were recorded. The reaction mixture was filtered to recover the solid residue. The solid residue was washed with dilute hydrochloric acid followed by a water wash, and finally, it was dried under vacuum at 105°C and weighed. Solid conversion is defined as percentage, by weight, of the initial charge of solid material that was converted during the liquefaction reaction as determined from the amount of the final solid residue obtained after filtering, washing, and vacuum drying.

Table 3

Analysis of lignin (Indulin AT)

Component	Percentage
Elemental analysis (maf)	
C	63.56
H	5.58
S	1.52
N	< 0.50
O[a]	28.84
Proximate analysis	
Volatiles	60.47
Fixed carbon	37.59
Ash	1.94

[a]By difference.

Results and Discussion

The main objective of this study was to explore whether the addition of black liquor could improve the coal liquefaction yield. Since lignin and sodium hydroxide are known to enhance coal liquefaction yields and are components of the black liquor, control experiments involving lignin and NaOH-assisted coal liquefaction were conducted. Since black liquor is an aqueous solution, control experiments were conducted in which coal was liquefied in a medium of water and tetralin.

NaOH-Catalyzed Coal Liquefaction

Four grams of coal were liquefied for 1 hour in ~ 75 mL of tetralin, to which ~ 40 g of solution of NaOH (pH $\approx$ 13.5, similar to the pH of black liquor) were added (Table 4). The initial pressure of 200 psig of hydrogen rose to about 3200

Table 4
NaOH-catalyzed liquefaction

	Experimental conditions					
	Pressure (psig)		Reactants (g)			
Run no.	Initial H$_2$	Maximum	Coal	Aqueous NaOH	Lignin	Tetralin
CSDT-375-3	200	3210	4.0	40.51	—	75.4
CSDT-375-4	200	3200	4.0	40.21	—	75.5
CSDT-375-5	200	3250	4.0	40.21	—	75.5
ISDT-375-5	200	3290	—	40.21	4.0	75.5
CISDT-375-3	200	3200	1.6	40.21	2.4	75.5
CISDT-375-4	200	3300	1.6	40.21	2.4	75.5

	Results		
Run no.	Solid products (g)	Solid conversion (%)	Coal conversion (%)
CSDT-375-3	1.46	63.5	63.5
CSDT-375-4	1.13	71.8	71.8
CSDT-375-5	1.38	65.5	65.5
Average	1.32	66.9	66.9
ISDT-375-5	0.77	80.8	
CISDT-375-3	0.99	75.3	66.9
CISDT-375-4	1.07	73.3	61.9
Average	1.03	74.3	64.4

psig during the course of the experiments. For these three identical experiments the coal conversion was found to be 63.5–71.8%, averaging 66.9%.

In two identical experiments, in addition to 1.6 g of coal, 2.4 g of lignin with NaOH solution and tetralin were also added (Table 4). The total solid conversion was found to be 75.3% and 73.3% on these runs, averaging 74.3%. When 4 g of lignin alone were liquefied in a solution consisting of 40.2 g of NaOH solution and 75.5 mL of tetralin, the lignin conversion was found to be 80.8%. This enabled us to calculate the coal conversion in coal-lignin mixture (X), assuming that lignin conversion (80.8%) remains unaffected by coal, using the following formula:

$$X = \frac{(\text{total solids})_{\text{coal-lignin}}\ (\%\ \text{solid conversion})_{\text{coal-lignin}} - (\text{lignin in coal-lignin mixture})(\%\ \text{conversion})_{\text{lignin}}}{(\text{Total coal in coal} - \text{lignin mixture})} \quad (1)$$

The average amount of coal conversion was found to be 64.4%, which is slightly lower than the average coal conversion value of 66.9% obtained in the absence of lignin but otherwise under identical experimental conditions. We believe that lignin, which is known to improve the coal conversion yields (Lalvani et al., 1991 a, b; Muchmore et al., 1991), is inhibited from doing so in our experiments because of the presence of NaOH. Lignin is soluble in alkaline solutions, which is an impediment for the transfer of hydrogen from tetralin to the radicals produced from lignin during thermolysis. The lignin radicals could be stabilized by OH− and may not be available for enhancing the rate of coal depolymerization.

The amount of coal conversion in the absence of NaOH was found to be 43.0% (Table 5). However, upon addition of even small amounts of NaOH (0.0656 g/g of coal), coal conversion yield increased to 53.3%. With a further increase in the NaOH concentration, the coal conversion yield continued to increase.

Coal Liquefaction in Aqueous Solutions

When 4 g of coal were liquefied in a mixture of 40.2 g of water and 75.5 g of tetralin, the solid conversion yield was found to be equal to 43.0% (Table 6). We find that addition of water under our experimental conditions has no influence on coal conversion. Although it has been reported in the literature that water addition

Table 5
Effect of NaOH content on coal conversion yield

Amount of NaOH (g NaOH /g coal)	Solid or coal conversion (%)
0	43.0
0.0656	53.3
0.225	63.5
0.25	68.6

Run condition: 4 g coal; 40.2 g aqueous NaOH, with indicated amounts of NaOH; 75 mL tetralin; 200 psig H_2 initial hydrogen pressure; and final pressure 3000 psig. No water in the system.

Table 6
Effect of water addition on coal and lignin conversion

| | Experimental conditions | | | | | |
| | Pressure (psig) | | Reactants (g) | | | |
Run no.	Initial H_2	Maximum	Coal	Water	Lignin	Tetralin
CWADT-375-1	200	3210	4.0	40.2	—	75.5
IWADT-375-1	200	3220	—	40.2	4.0	75.5
IWADT-375-2	200	3380	—	40.2	4.0	75.5
CIWADT-375-1	200	3220	1.6	40.2	2.4	75.5
CIWADT-375-2	200	3300	1.6	40.2	2.4	75.5

| | Results | | |
Run no.	Solid products (g)	Solid conversion (%)	Coal conversion (%)
CWADT-375-1	2.28	43.0	43.0
IWADT-375-1	0.73	81.8	
IWADT-375-2	0.66	83.5	
Average	0.70	82.6	
CIWADT-375-1	1.10	72.5	57.35
CIWADT-375-2	1.35	66.3	42.0
Average	1.23	69.4	49.7

does enhance coal liquefaction yields, we believe that the relatively low pressures (~ 3200 psig) in our experiments are not sufficient for the creation of the supercritical state of water. Coal conversion increases dramatically under supercritical conditions because of the enhanced transport properties of the solvent used. Water can also serve as a source of hydrogen necessary for the reduction of coal if it is used in combination with carbon monoxide and a suitable catalyst (Bockrath et al., 1988). However, under our operating conditions, water would be expected to hydrolyze ester groups (Kershaw & Bagnell, 1987). We believe the above two reasons are responsible for our observation that water addition did not improve the coal conversion yield.

Two identical experiments were conducted to liquefy lignin (alone) in a mixture of water and tetralin. Lignin conversion was found to be ~ 82.5% (mass basis). When coal (1.6 g) was added to lignin (2.4 g) and the mixture was liquefied in water and tetralin, the average solid conversion for two experiments was found to be 69.4%. The coal conversion in the coal-lignin mixture was calculated using

Eq. (1) and was found to be equal to 49.75%, which is about 15.7% greater than the corresponding coal conversion (43%) in the absence of lignin but otherwise identical experiments. This enhancement in coal conversion due to lignin addition was also reported in our previous papers (Lalvani et al., 1991 *a*, *b*; Muchmore et al., 1991; Akash et al., 1992); however, in the earlier work, liquefaction was carried out in tetralin alone (i.e., in the absence of water). Our results further confirm our belief that under the experimental conditions used in our experiments (i.e., low pressure and no catalyst) the addition of water has no positive influence on coal conversion yields.

Black Liquor Liquefaction

In the experiments described below, about 40–41 g of black liquor (solid content ~ 16 g) were liquefied. When no hydrogen donor solvent (i.e., tetralin) was used, the solid conversion yield was about 81.5%; however, upon the addition of tetralin, the average solid conversion rose to 88.1% (Table 7). When 4 g of coal were added to the black liquor in the presence of tetralin, the average solid conversion yield was found to be equal to 82.5%.

Coal conversion in black liquor (Y) was calculated and found to be equal to 59.8% by the following formula, assuming that the addition of coal does not affect the black liquor liquefaction yield:

$$Y = \frac{(\text{coal used}) - (\text{solid recovered})_{\text{coal-black liquor}} + (\text{solid recovered})_{\text{black liquor}}}{(\text{coal used})} \qquad (2)$$

Although coal conversion yield of 59.8% in black liquor is significantly greater than the corresponding 43% yield in the absence of black liquor and represents 28% enhancement in coal liquefaction, it is still lower than the conversion yield (64.6%) for coal in lignin and NaOH − catalyzed experiments conducted under identical experimental conditions. However, the coal conversion yield in black liquor is greater by 16.8% than the yield obtained when coal was liquefied in a mixture of lignin, water, and tetralin. The data (Table 5) also show that the addition of only NaOH affects the coal conversion yields much more positively than does the addition of lignin or black liquor. Although black liquor does contain NaOH and lignin, it is possible that other chemical species such as sulfates or sulfides may impart a slightly deleterious effect on the coal conversion yields. In our study, no analysis of solid or liquid samples was carried out, and the influence of sulfur compounds in black liquor on coal conversion was not investigated either. It is also possible that lignin present in black liquor may not catalyze coal depolymerization because, as we suggested earlier, that solubility of lignin in NaOH may render the radicals produced from lignin ineffective, possibly due to stabilization by OH − . Future work will involve studies of the above-stated effects on black-liquor-assisted coal liquefaction and a thorough product characterization.

Conclusions

The addition of NaOH to coal (0.25 g NaOH /g coal) increased the coal conversion yield by almost 55% under liquefaction conditions described in this paper (375°C, 1

Table 7
Effect of black liquor addition on coal liquefaction

| | Experimental conditions | | | | |
| | Pressure (psig) | | Reactants (g) | | |
Run no.	Initial H$_2$	Maximum	Coal	Black liquor	Tetralin
BK-375-1	200	2520	—	40.2	—
BKDT-375-2	200	2610	—	41.0	76.0
BKDT-375-4	200	2650	—	41.0	76.0
BKDT-375-5	200	2750	—	41.0	76.0
BKDT-375-6	200	2580	—	41.0	76.0
CBLDT-375-2	200	2550	4.0	41.0	76.1
CBLDT-375-4	200	2600	4.0	41.0	76.0
CBLDT-375-5	200	2650	4.0	41.0	76.0

| | Results | | |
Run no.	Solid products (g)	Solid conversion (%)	Coal conversion (%)
BK-375-1	2.96	81.5	
BKDT-375-2	2.25	86.2	
BKDT-375-4	1.79	89.0	
BKDT-375-5	1.88	88.5	
BKDT-375-6	1.86	88.6	
Average	1.95	88.1	
CBLDT-375-2	3.71	81.7	56.0
CBLDT-375-4	3.41	83.2	63.5
CBLDT-375-5	3.56	82.5	59.8
Average	3.56	82.5	59.8

hour). Lignin addition to coal liquefaction experiments in a mixture of water and tetralin also resulted in about a 15.7% increase in the yield over that obtained in tetralin alone. The addition of black liquor resulted in an enhancement in coal conversion yields; however, the observed increase is lower than that obtained in the presence of NaOH because lignin present in the black liquor is not very effective due to the OH$^-$ presence.

References

Akash, B. A., C. B. Muchmore, J. A. Koropchak, J. W. Kim, and S. B. Lalvani. 1992. Investigations of simultaneous coal and lignin liquefaction: Kinetic studies. *Energy and Fuels* 6:629–34.

Bockrath, B. C., H. M. Davis, S. Friedman, and E. G. Illig. 1988. Water and nondonor-vehicle-assisted liquefaction of Illinois bituminous coal. *Energy and Fuels* 2:534–38.

Dorland, D., A. H. Stiller, and E. A. Mintz. 1992. Effects of sulfur on coal treatment in aqueous sodium hydroxide. *Fuel Processing Technology* 30:195–204.

Kershaw, J. R., and L. J. Bagnell. 1987. Extraction of brown coals with supercritical fluid mixtures: Implications for coal structure. *Fuel* 66:1739–41.

Lalvani, S. B., C. B. Muchmore, J. A. Koropchak, B. Akash, P. Chivate, and C. Chavez, 1991*a*. Lignin-augmented coal depolymerization under mild reaction conditions, *Energy and Fuels* 5:347–52.

Lalvani, S. B., C. B. Muchmore, J. A. Koropchak, B. Akash, C. Chavez, and P. Rajagopal. 1991*b*. Coal liquefaction in lignin-derived liquids under low severity conditions. *Fuel* 70:1433–38.

Libby C. E., (ed.). 1982. *Pulp and paper science and technology*, vol. 1. *Pulp*, New York: McGraw-Hill.

Mirza, Z. B., M. K. Sarkar, and D. K. Sharma. 1984. Extraction of coals through dilute alkaline hydrolytic treatment at low temperature and ambient pressure. *Fuel processing Technology*. 9:149–62.

Muchmore, C. B., S. B. Lalvani, J. A. Koropchak, and B. Akash. 1991. Lignin-assisted coal depolymerization. *Proceedings of International Conference on Coal Science*, 717–20.