

COLIQUEFACTION OF COAL AND BLACK LIQUOR

Jong Won Kim[†], Shashi B. Lalvani* and Bilal A. Akash*

Korea Institute of Energy Research, Taejon 305-343, Korea

*Southern Illinois University at Carbondale, IL 62901, U.S.A.

(Received 24 July 1994 • accepted 20 July 1995)

Abstract—Black liquor from the Kraft pulping process to produce cellulose pulp contains lignin and sodium hydroxide, which are known to enhance the dissolution of coal. But no work has so far been done on the depolymerization of coals using black liquor as an additive. The addition of black liquor enhanced the coal conversion yield about 38.6% in this experiment. But the extent of the enhancement was lower than expected values from separate NaOH/coal and lignin/coal experiments.

Key words: Coliquefaction, Coal, Black Liquor, Depolymerization

INTRODUCTION

Coals are still abundant resources, and can be converted into premium liquid fuel by hydrogenation [Berkowitz, 1977]. One method used in hydrogenating coal is to subject the coal to react with a hydrogen donor solvent, such as tetralin [Neavel, 1976]. For an efficient coal depolymerization process, cleavage of selective coal fragments is necessary, and it is normally conducted under high temperature and/or with catalysts.

Effects of aqueous alkali treatment on coal dissolution have been studied [Mirza et al., 1984; Dorland et al., 1992]. Sodium hydroxide is widely used in pretreatment procedures for enhancing coal solubility. Mirza et al. [1984] showed that a dilute alkali (-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 would attack susceptible functional groups or linkages such as -OH, 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. The results indicated that the dissolution of Wyodak subbituminous and North Dakota lignite coals in 50% aqueous sodium hydroxide were enhanced by the addition of the elemental sulfur.

Hessley [1983] observed that phenolic pyrolysis oil obtained from wood is able to convert coal to a coal product which is more soluble. Recent our reports [Lalvani et al., 1991a, b; Muchmore et al., 1991; Akash et al., 1992; Kim et al., 1993] have shown that the addition of lignin to coal during liquefaction significantly enhances the depolymerization rate of coal and the quality of liquid products. Lignin is considered as one of the main precursors of coal and has been studied for over a century and numerous molecular models have been reported [Faulon and Hatcher, 1994], and it was also introduced in the review paper of Kim and Sim [1994].

The extensive work on the composition and characteristics of black liquor from the Kraft pulping process after dissolving the lignin in wood to produce cellulose pulp has been done by Fricke and his colleague [Zaman and Fricke, 1994; Fricke, 1987] and

other investigators [Rydholm, 1965; Sjöström, 1981]. The results showed that black liquor at low solids concentration is a complex solution of organic and inorganic components in water. The non-volatile constituents consist of lignin, low-molecular-weight organic components, sodium hydroxide and sulfur compound such as sulfate and sulfide. Since many components of black liquor are known to exhibit the enhanced dissolution rate of coal, the addition of black liquor is anticipated to give the positive effects on coal liquefaction or catalytic gasification. There are some efforts to produce oil by thermal treatment of black liquors [McKeough and Johansson, 1988], or to use black liquor as a catalyst in the gasification of coal [Valenzuela-Calahorra et al., 1994]. So far, no attempts have been made to depolymerize coals using black liquor as an additive. The present works investigated the possibility of using black liquor for enhancement of coal depolymerization through the analysis of the degree of coal conversion at various reaction conditions. The effects of some model compounds of lignin as additives on coal conversion were also investigated. The model compounds were selected from the reported compounds by Evans and Milne [1987a, b], who studied the elucidation of the molecular pathways in the fast pyrolysis of wood and its principal isolated constituents.

EXPERIMENTAL

Illinois Basin Coal Sample Bank No.105 (bituminous coal) and Westvaco Co. supplied black liquor (Table 1) and tetralin were used in this study. The mixture of NaOH solution and Indulin AT lignin, which is supplied by Westvaco Co. was used as a model black liquor in order to verify the effect of black liquor. Also, some chemicals such as vanillin, o-cresol, resorcinol, 4-hydroxy-3-methoxycinnamic acid, guaiacol, eugenol or phenol were used separately as a model compound for the lignin to check the effect of lignin addition on coal depolymerization.

The reactor in this experiment was a 300 ml autoclave, and it was charged with ground coal (less than 75 µm), tetralin, and black liquor or model compound. Tetralin purchased from Aldrich Chemical Co. was used after vacuum distillation. The operating method was the same to the procedure described elsewhere [Lalvani et al., 1991a, 1991b]. To describe it briefly, it was heated

[†]To whom all correspondences should be addressed.

Table 1. Characteristics of black liquor, coal and lignin

Black liquor (Westvaco Co.)	pH	13.5	
	% of total solid*	39.8%	
	density	1.54 g/cc	
Coal & Lignin		coal	lignin
Elemental (wt%)	C	63.56	63.83
	H	4.48	5.58
	N	1.30	<0.50
	S	4.54	1.52
Proximate (wt%)	Volatile matter	35.97	60.47
	Fixed carbon	45.34	17.85
	Ash	18.69	1.94

*Analytical method [Libby, 1982]: A 0.5 g sample is added dropwise to a tarred watch glass dish and weighed as quickly as possible. After 4 hr in a 105°C oven, the dish is cooled and weighed. The dry weight divided by the original weight, times 100 is the percentage of the total solids.

at a constant heating rate of 5°C/min to 375°C in the presence of the hydrogen (140 or 200 psig initial pressure) and the temperature was maintained at 375°C for 1 hr, after which the heat supply to the reactor was shut off. The mixture was cooled rapidly by water flowing through an immersed cooling coil. After cooling until the desired temperature of less than 40°C was attained (usually it took 2 hrs), final temperature and pressure were recorded and the produced gas was analyzed by gas chromatography. The reaction mixture was filtered to recover the solid residue, which was washed with dilute hydrochloric acid followed by water, and finally dried under the vacuum at 105°C and weighed. However, in the case of experiments with model compound of lignin, the solid residue was washed by water only before drying. The solid conversion is defined as the mass change per total mass of solids charged to the reactor. The solid residue was weighed after filtering, washing and vacuum drying.

RESULTS AND DISCUSSION

When the black liquor and coal mixture were liquefied in the tetralin, the average of solid recovery was found to be 3.56 g, as shown in Table 2. On the basis of solid recoveries from black liquor and tetralin experiments, the estimated coal conversion was 59.6%, assuming that solidification of black liquor is unaffected

by the presence of coal. This means that black liquor enhances the coal liquefaction yield, about 38.6%, calculated based on 43% yield of coal liquefaction. In all the experiments, liquids were separated into an aqueous phase and organic phase. Final pHs in aqueous phase were in the range 9-10, which are lower than that of original black liquor (pH=13.5). The CO and CO₂ were not detected in the produced gas because those were dissolved in NaOH solution and formed Na₂CO₃. It means that carbon dioxide and carbon monoxide from the liquefaction process lead to a decrease on the black liquor alkalinity, since the gases act as neutralizing agents. In coal or lignin experiments without NaOH or black liquor, C₂H₆ was not appeared. It seemed that NaOH and black liquor promote the breakage of carbon-carbon bonds of coal or lignin.

Some experiments were conducted to determine the effect of black liquor on the coal liquefaction yield. At first, NaOH was used as an additive because it was known to improve coal solubility [Mirza et al., 1984; Dorland et al., 1992]. The solubility of raw coal in the NaOH solution with the pH value 13.5 was calculated based on the weight loss of raw material after drying. The weight loss (solubility) of coal after agitation for 18 hrs at 60°C, atmospheric pressure in NaOH aqueous solution was less than 1.9 wt%. In the case of Indulin at the same condition, weight loss (solubility) was as high as 98.7%. The ethyl and isopropyl esters of lignin were expected to be cleaved at this condition [Kershaw and Bagnell, 1987].

The coal conversion in sodium hydroxide solution with pH 13.5 was 64.5%, which is enhanced about 50% compared to about 43% conversion of coal in tetralin at 375°C for 1hr, as shown in Table 3. The calculated value of coal conversion in coal-lignin-sodium hydroxide solution was 64.6%, which is about the same to the coal conversion in NaOH solution. This means that the NaOH gave most influential effects on coal conversion.

The water in black liquor can be a media of supercritical extraction and would be expected to hydrolyze ester groups at our operating condition [Kershaw and Bagnell, 1987], which is in the range of supercritical condition of water. But the enhancement of the conversion of coal by the addition of water was not observed in this work, as shown in Table 4. The coal conversion at coal/Indulin lignin/water mixture was 42%, which is about the same as that of coal/water experiment based on the assumption that lignin conversion is unaffected by the presence of coal.

In the experiments with the model compounds of lignin, only

Table 2. The effects of black liquor addition on coal liquefaction at 375°C

Run	Pressure (MPa)		Reactants (g)			Solid products (g)	Solid conversion (%)
	Initial	Maximum	Coal	Black liquor	Tetralin		
Black liquor	1.48	17.48	-	40.2	-	2.96	
Black liquor/ distilled tetralin	1.48	18.10	-	41.0	76.0	2.25	
	1.48	18.37	-	41.0	76.0	1.79	
	1.48	19.06	-	41.0	76.0	1.88	
	1.48	17.89	-	41.0	76.0	1.86	
Average						1.95	
Coal/black	1.48	17.68	4.0	41.0	76.1	3.71	
liquor/distilled	1.48	18.03	4.0	41.0	76.0	3.41	
tetralin	1.48	18.37	4.0	41.0	76.0	3.56	
Average						3.56	59.6*

*Conversion % was calculated from the following definition: Average(%)=[initial weight of coal-(weight of solid residue from coal/black liquor/distilled tetralin experiments-solid residue from black liquor/distilled tetralin experiments)]/initial weight of coal×100(%)

Table 3. The effects of sodium hydroxide addition during coal liquefaction at 375°C

Run	Pressure (MPa)		Reactants (g)				Solid conversion (%)
	Initial	Maximum	Coal	NaOH solution	Lignin	Tetralin	
Coal/NaOH/distilled tetralin	1.48	22.23	4.0	40.51		75.4	63.5
	1.48	22.51	4.0	40.21	-	75.5	65.5
Average					-		64.5*
Indulin lignin/NaOH /distilled tetralin	1.48	22.79	-	40.21	4.0	75.5	80.8
Coal/Indulin lignin	1.48	22.16	1.6	40.21	2.4	75.5	75.3
/NaOH/distilled tetralin	1.48	22.16	1.6	40.21	2.4	75.5	75.3
Average							74.3*

*It means 55% enhancement of yield of coal liquefaction, based on the value of 43% coal conversion with coal and tetralin.

**Estimated coal conversion in coal/Indulin/NaOH mixture: $(4 \times 74.3 - 2.4 \times 80.8)/1.6 = 64.6\%$.

Table 4. The effects of water and/or lignin addition during coal liquefaction at 375°C

Run	Pressure (MPa)		Reactants (g)				Solid conversion (%)
	Initial	Maximum	Coal	Water	Lignin	Tetralin	
Coal/water/distilled tetralin	1.48	22.23	4.0	40.21	-	75.5	43
Indulin/water/ distilled tetralin	1.48	22.30	-	40.21	4.0	75.5	81.8
	1.48	23.41	-	40.21	4.0	75.5	83.5
Average							82.5
Coal/Indulin/water/ distilled tetralin	1.48	22.30	1.6	40.21	2.4	75.5	72.5
	1.48	22.85	1.6	40.21	2.4	75.5	66.3*

*Coal conversion in coal/Indulin/water mixture was calculated on the basis of 66.3% conversion $(4 \times 66.3 - 2.4 \times 82.5)/1.6 = 42\%$

Table 5. Experimental data of coal liquefaction with model compounds at 375°C

Additive	Pressure (MPa)	Reactants (g)			Solid conversion (pyridine solubility) (%)
		(Initial H ₂)	coal	additive	
vanillin	1.07	3.6	0.4	120	41.4/(N.A)
o-cresol	1.07	3.6	0.4	120	38.1/(27.5)
4-hydroxy-3-methoxy-cyanamic acid	1.07	3.6	0.4	120	40.2/(N.A)
phenol	1.07	3.6	0.4	120	46.7/(40.4)
guaiacol	1.07	1.6	2.4	120	34.7/(N.A)
resorcinol	1.07	3.6	0.4	120	43.9/(35.9)
eugenol	1.07	3.55	0.45	120	41.7/(30.0)
no additive	1.07	4.0	0	120	43.0

phenol gave positive effects on a coal liquefaction yield, despite that each of them is a kind of monophenols, as shown in Table 5. The pyridine solubilities of the solid residue after the reaction, and the unreacted raw material were compared in order to find extent of conversion of coal to a pyridine soluble form. Extractions were made by the addition of pyridine to a solid sample after filtering and drying. To insure that all extractable materials were removed from the residue, the Soxhlet extraction experiments in this work were run for 24 hrs. Though Miller and Wasden [1984] reported that no effect of sample size in the range of about 0.7-1.5 g on Soxhlet extractions, sample size in each experiment was controlled in the range of 1.0 ± 0.1 g to guarantee consistency of the results.

Table 6. Pyridine solubility of raw material and solid residue

Raw material	Pyridine solubility (%)
Parent coal	13.14
Coal/Aspen lignin mixture	27.33 (26.77)*
Aspen lignin	35.86
Solid residue from coal/distilled tetralin***	38.7
Solid residue from coal/lignin/distilled tetralin***	54.7 (51.66)**
Solid residue from lignin/distilled tetralin***	60.3

*The value in parenthesis means the predicted value, which is calculated from pyridine solubility data of parent coal and Aspen lignin.

**Calculated value on the basis of pyridine solubility of solid residue from coal/distilled tetralin experiments and lignin/distilled tetralin experiments.

***Reaction condition: 375°C, 1 hr reaction, 4 g of sample (In the case of coal/lignin mixture, the weight ratio of coal and lignin is 4 : 6 (coal 1.6 g, lignin 2.4 g), and Indulin lignin (Westvaco Co.) was used.

The extraction thimbles containing insoluble portions of a solid sample were dried to constant weight in a vacuum oven at 105°C. The percentage conversion of the organic matter in a solid sample into the soluble products was calculated for pyridine on the dry basis. Pyridine solubility of coal/Aspen lignin mixture before reaction was about the same as the predicted value from the pyridine solubility of coal and Aspen lignin. But the solid residue after reaction contains more pyridine extractable (5.9% increase), as shown in Table 6. The pyridine solubilities of solid residues after reaction with some model compounds are also shown in Table 5. The pyridine solubility of the solid residue was well in accord-

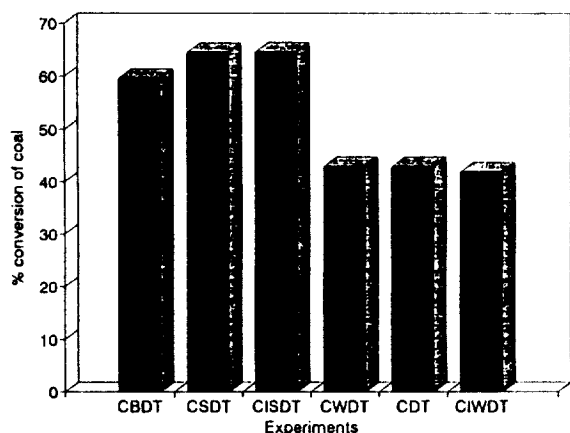


Fig. 1. Comparison of the coal conversion percent in coal liquefaction using additives.

CBDT: coal/black liquor/distilled tetralin, CSDT: coal/NaOH solution/distilled tetralin, CISDT: coal/Indulin lignin/NaOH solution/distilled tetralin, CWDT: coal/water/distilled tetralin, CDT: coal/distilled tetralin, CIWDT: coal/Indulin lignin/water/distilled tetralin

ance with the tendency of the conversion yield. However, It is not clear at the present time why phenol alone gave positive effect on the coal liquefaction yield.

Actually, lignin contains lots of phenolic compounds, and combinations of model compounds can give higher liquefaction yields than each alone. As shown in Table 6, the amount of pyridine extractables of a solid residue from lignin assisting coal depolymerization process were larger than that of coal depolymerization with /or without model compound of lignin. This means that lignin shows some positive effects on coal depolymerization which is not anticipated in this work using model compound separately. The comparison of coal conversion using additives such as black liquor, NaOH is shown in Fig. 1. Generally speaking, black liquor was considered as an additive in coal liquefaction process.

CONCLUSIONS

Black liquor contains alkaline compounds and lignin, which were known to catalyze conversion reactions. The addition of black liquor enhances the coal conversion yield about 38.6%, but the extent of the enhancement is lower than expected values from NaOH/coal and lignin/coal experiments. The NaOH in black liquor seemed to be mostly effective to enhance the conversion of coal. Also, an addition of the lignin in coal liquefaction process increased the yields of the pyridine extractable in a solid residue after the liquefaction and the conversion of coal. This result showed the possibility of using black liquor as the low-cost catalysts during coal liquefaction.

REFERENCES

Akash, B. A., Muchmore, C. B., Koropchak, J. A., Kim, J. W. and Lalvani, S. B., "Investigations of Simultaneous Coal and Lignin Liquefaction: Kinetic Studies", *Energy & Fuels*, **6**, 629 (1992).
 Berkowitz, N., "An Introduction to Coal Technology", Academic Press, Inc., New York (1977).
 Dorland, D., Stiller, A. H. and Mintz, E. A., "Effect of Sulfur on Coal Treatment in Aqueous Sodium Hydroxide", *Fuel Process-*

ing Technology, **30**, 195 (1992).
 Evans, R. J. and Milne, T. A., "Molecular Characterization of the Pyrolysis of Biomass: 1. Fundamentals", *Energy & Fuels*, **1**, 123 (1987a).
 Evans, R. J. and Milne, T. A., "Molecular Characterization of the Pyrolysis of Biomass: 2. Applications", *Energy & Fuels*, **1**, 311 (1987b).
 Faulon, J. and Hatcher, P. G., "Is There Any Order in the Structure of Lignin", *Energy & Fuels*, **8**, 402 (1994).
 Fricke, A. L., "Physical Properties of Kraft Black Liquor: Summary Report-Phase I and II", DOE report Nos. AC02-82CE40606 and FG02-85CE40740 (1987).
 Hessley, R. H., "The Solubilization of Coal with Wood Pyrolysis Oil: The Roll of Phenolic Components", *Fuel Processing Technology*, **8**, 33 (1983).
 Kershaw, J. R. and Bagnell, L. J., "Extraction of Brown Coals with Supercritical Fluid Mixtures: Implications for Coal Structure", *Fuel*, **66**, 1739 (1987).
 Kim, J. W., Akash, B. A., Muchmore, C. B., Koropchak, J. A. and Lalvani, S. B., "Stability of Liquids Derived from Reaction of Coal and Lignin", *Fuel Processing Technology*, **33**, 175 (1993).
 Kim, J. W. and Sim, K. S., "Lignin Assisted Coal Depolymerization", *Korean J. of Chemical Industry and Technology*, **12**, 543 (1994).
 Lalvani, S. B., Muchmore, C. B., Koropchak, J. A., Akash, B., Chavez, C. and Rajagopal, P., "Coal Liquefaction in Lignin-Derived Liquids under Low Severity Conditions", *Fuel*, **70**, 1433 (1991a).
 Lalvani, S. B., Muchmore, C. B., Koropchak, J. A., Akash, B., Chivate, P. and Chavez, C., "Lignin-Augmented Coal Depolymerization", *Energy & Fuels*, **5**, 347 (1991b).
 Libby, C. E., "Pulp and Paper Science and Technology, Vol. 1. Pulp", McGraw-Hill, New York (1982).
 McKeough, P. J. and Johansson, A. A., "Oil Production by High-Pressure Thermal Treatment of Black Liquors-Process Development Studies", in "Pyrolysis Oils from Biomass", ACS Symposium Series, No. 376, p. 104, American Chemical Society, Washington, D. C. (1988).
 Miller, R. L. and Wasden, F. K., "Comparison of Experimental Solvent Extraction Techniques to Determine the Apparent Composition of Solvent Refined Coal", *Fuel Processing Technology*, **9**, 117 (1984).
 Mirza, Z. B., Sarkar, M. K. and Sharma, D. K., "Extraction of Coals through Dilute Alkaline Hydrolytic Treatment at Low Temperature and Ambient Pressure", *Fuel Processing Technology*, **9**, 149 (1984).
 Muchmore, C. B., Lalvani, S. B., Koropchak, J. A. and Akash, B., "Lignin-Assisted Coal Depolymerization", Proceedings of International Conference on Coal Science, p. 718 (1991).
 Neavel, R. C., "Liquefaction of Coal in Hydrogen-Donor and Non-donor Vehicles", *Fuel*, **55**, 237 (1976).
 Rydholm, S. A., "Pulping Processes", Interscience Publishers, New York, 576 (1965).
 Sjöström, E., Chap. 7, "Wood Chemistry-Fundamentals and Applications", Academic Press, New York (1981).
 Valenzuela-Calahorra, C., Pan, Y. G., Bernalte-García, A. and Gómez-Serrano, V., "Thermogravimetric Study of Anthracite Gasification in CO₂ Catalyzed by Black Liquor", *Energy & Fuels*, **8**, 348 (1994).
 Zaman, A. A. and Fricke, A. L., "Correlations for Viscosity of Kraft Black Liquors at Low Solids Concentrations", *AIChE J.*, **40**, 187 (1994).