

Effect of Peroxides during Pretreatment for Coal Liquefaction

Masaharu Nishioka

19069 McFarlin Drive, Germantown, Maryland 20874

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Soaking coal in a coal liquid at a temperature between 350 and 400 °C prior to coal liquefaction is a very effective conversion method, which does not make use of hydrogen.^{1–3} It has been found that the addition of small amounts of peroxides for this procedure provides further conversion. This communication reports results which may be useful in the development of an economical liquefaction process.

Coal molecules are strongly associated with each other, resulting in difficult solubilization.^{1,4} This in turn produces only a portion of coal that is extracted with good solvents.⁵ Since intra- and intermolecular interactions stronger than hydrogen bonds and dispersion forces are significant in coal, higher temperatures are necessary to overcome these interactions.¹ Temperatures above 300 °C may be required to provide the sufficient solvation of coal.² If temperatures are lower than 300 °C, coal may associate more at higher temperatures because coal tends to reach a stable conformation due to molecular mobility at such temperatures.^{1,6,7}

Solvation will result in more swelling, dissolution, and reduction in particle sizes as schematically shown in Figure 1. A better reactivity is expected for more dissociated coal (Figure 1c) during coal liquefaction. From a structure point of view, the following suggestions are made to solvate coal before liquefaction:

- (1) coal should be treated at as low concentrations as possible,^{4,8}
- (2) coal should be treated at temperatures higher than 300 °C,²
- (3) raw coal should be used rather than dried coal,⁹
- (4) demineralized coal should be used if a catalytic effect of mineral is negligible.⁹

These optimal conditions must be determined from a processing point of view. As for observations regarding the effect of temperature, higher temperature soaking at between 350 and 400 °C led to significantly effective conversion.² Coal liquefaction that followed generated a 30% increase in the oil yield and a 15–20% decrease in the gas yield compared with results obtained using conventional methods.³ Additionally, it is helpful to develop economical liquefaction if a further step is available for dissociated coal before liquefaction. It was reported that light fractions were formed from coal and petroleum-derived heavy ends by reactions using radical initiators such as hydrogen peroxide (H₂O₂)¹⁰ and cumene hydroperoxide (CHP)¹¹ at temperatures of 120–350 °C. A coal-derived sample was heated in cyclohexane at 350 °C in

Table 1. Elemental Analyses of Coal and a Coal Liquid (wt %)

sample	H ₂ O	Ash	element (daf)			
			C	H	N	S
Illinois No. 6	10.4	14.5	78.1	5.4	1.3	5.4
Coal liquid			88.4	11.4	0.2	<0.1

Table 2. Run Numbers and Experimental Conditions for High-Temperature Soaking by the Addition of Radical Initiators Using Illinois No. 6 Coal

run no.	temp. (°C)	time (h)	solvent (50 mL)	atmosphere (0.7 MPa) ^a	additive	amount (mL)
1	350	0.5	tetralin	nitrogen		
2	350	0.5	tetralin	nitrogen	CHP ^c	1
3	350	0.5	tetralin	nitrogen	CHP ^c	5
4	350	0.5	tetralin	nitrogen	H ₂ O ₂ ^b	5
5	350	2.0	tetralin	nitrogen		
6	350	2.0	tetralin	nitrogen	H ₂ O ₂ ^b	5
7	350	0.5	coal liq.	nitrogen		
8	350	0.5	coal liq.	nitrogen	H ₂ O ₂ ^b	5

^a Pressure: at 25 °C. ^b 3% in water. ^c CHP: cumene hydroperoxide.

the presence of H₂O₂ (0.3%).¹⁰ The sample before and after heating was analyzed by gas chromatography, and it was found that *n*-alkanes and polycyclic aromatic hydrocarbons were newly produced in quantities 10–20 times more than the abundance in the original sample. The atmospheric residue of crude oil was heated at 120 and 300 °C in the presence of CHP (2%).¹¹ The heating caused a ~16% increase in the fraction boiling in the range 100–540 °C. For the above reasons, the effect of these additives at a pretreatment stage of coal liquefaction was studied in this communication.

Illinois No. 6 coal was obtained from the DOE Coal Bank at Pennsylvania State University. A coal liquid derived from Illinois No. 6 coal was obtained from the Wilsonville pilot plant.¹² The elemental analyses of this coal and coal liquid are shown in Table 1. All the reagents and solvents were obtained from Aldrich Chemical Co. (Milwaukee, WI) and Fisher Scientific (Pittsburgh, PA), and HPLC-grade solvents were used without further purification. H₂O₂ (3% in water) and cumene hydroperoxide (CHP) (80% in cumene) were used.

Coal samples (5 g) were then charged into a 250 mL autoclave (model 4576; Parr Instrer ument Co., Moline, IL). After adding tetralin or the coal liquid (50 mL) and additives, we evacuated and purged the system with nitrogen five times. Next, the autoclave was heated at ~5 °C min⁻¹ to the required temperatures under nitrogen (initial pressures: 0.7 MPa), and the mixtures were heated at 350 ± 5 °C min⁻¹ for 0.5–2 h agitating with the autoclave stirrer (500 rev min⁻¹). After treatments, the autoclave was cooled with water in the cooling line up to 200 °C and then in an air atmosphere to room tempera-

* Corresponding author. E-mail: m.nishioka@att.net.

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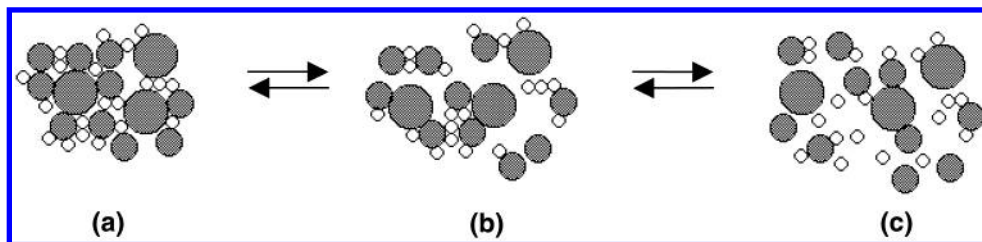


Figure 1. Associative equilibrium change of coal in solvents at high temperature.

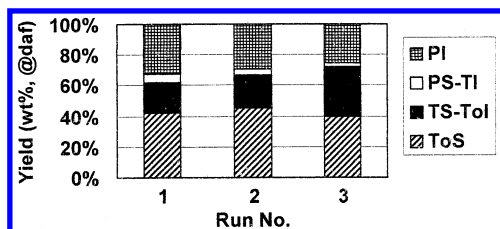


Figure 2. Changes in conversion yields by the addition of cumene hydroperoxide at 350 °C. Conditions as in Table 2. (ToS: toluene-solubles; TS·ToI: tetrahydrofuran-solubles and toluene-insolubles; PS·TI: pyridine-solubles and tetrahydrofuran-insolubles; and PI: pyridine-insolubles).

These experimental conditions are listed in Table 2. All Runs were repeated, and their yields were reproducible within ± 3 wt %.

The coal was heated under nitrogen in tetralin at 350 °C for 0.5 h (Run 1). About 42 wt % of toluene-solubles (ToS), 62 wt % of THF-solubles (TS), and 66 wt % of pyridine-solubles (PS) were obtained after this treatment as shown in Figure 2. Cumene hydroperoxide (CHP) was added in the amount of 1.6% in tetralin and treated under the same condition as for Run 2. The yields of ToS, TS, and PS increased 2–5 wt % compared to those in Run 1. When CHP was added in the amount of 8% (Run 3), the yields of TS and PS further increased 2–4%, but the yield of ToS decreased as shown in Figure 2.

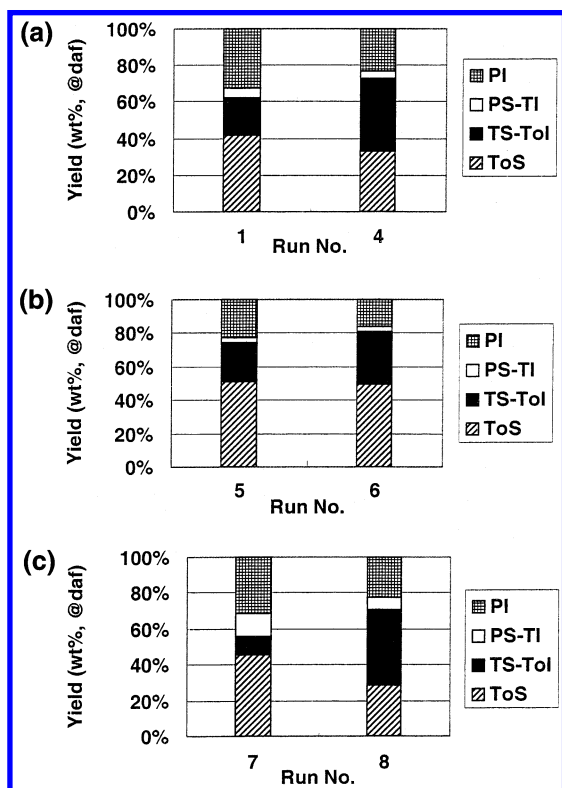


Figure 3. Conversion yields by the addition of hydrogen peroxide at 350 °C. Conditions as in Table 2. (ToS: toluene-solubles; TS·ToI: tetrahydrofuran-solubles and toluene-insolubles; PS·TI: pyridine-solubles and tetrahydrofuran-insolubles; and PI: pyridine-insolubles).

ture. The product was filtered and transferred to an extraction thimble and Soxhlet-extracted under a nitrogen atmosphere with 200-mL cyclohexane, toluene, tetrahydrofuran (THF) and pyridine for 24 h, respectively. Extracts after evaporation of solvents and residues were dried under vacuum at 95 °C overnight. Cyclohexane-solubles (CyS), toluene-solubles (ToS), toluene-solubles and cyclohexane-insolubles (ToS·CyI), THF-solubles and toluene-insolubles (TS·ToI), pyridine-solubles and THF-insolubles (PS·TI), THF-insolubles (TI), and pyridine-insolubles (PI) were calculated from these respective residues.

Another peroxide, hydrogen peroxide (3% in water), was used instead of CHP. An amount of 3000 ppm of hydrogen peroxide was added in tetralin and treated under the same conditions for Run 4 (Figure 3a). The yields of PS significantly increased to 77 wt % by the addition of H₂O₂ in the solvent, whereas the ToS yield decreased from 42 to 32 wt %, resulting in an increase in the TS·ToI (THF-solubles and toluene-insolubles) yield. When the same experiments were carried out for 2 h instead of 0.5 h, and without the presence of hydrogen peroxide, yields of ToS, TS, and PS increased more than 10%, respectively (Run 5) (Figure 3b). For Run 6, 3000 ppm H₂O₂ was added in tetralin, and the mixture was heated for 2 h. The same effect of H₂O₂ on conversion was again observed for this longer soaking. Experiments under the same conditions were repeated in the coal liquid in place of tetralin, and tested both with and without H₂O₂ (Runs 8 and 7) (Figure 3c). The same trend was again observed in the coal liquid when H₂O₂ was present. The outcome was that the total conversion increased, and the ToS yield decreased. The change in the yields using H₂O₂ is consistent with the results obtained from experiments using CHP.

From both results using H₂O₂ and CHP, the effect of these additives on conversion, based on pyridine-solubles, is positive for soaking at 350 °C. Radicals are undesirable species in coal liquefaction according to the currently accepted concept.¹³ It is thought that coal radicals on adjacent molecules recombines, forming more stable, higher-molecular-mass material. The role of radicals, however, may not be as simple as expected if these additives produce radicals under the conditions used. The underlying theory is that the effect may be a function of a degree of coal dissolution and temperature.

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