CO-OXIDATIVE DEPOLYMERIZATION OF COAL

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Introduction

Recently a number of industry-sponsored coal conversion projects have suffered set-backs in the acquisition of government financial support that have all but dismantled the synfuels industry in the United States. Although the requirement for reduced sulfur emissions can be identified as one of the problems currently holding back the development of direct coal liquefaction processes, it is the prohibitively high cost associated with liquefaction technology which has been the stumbling block for private corporate investors and governmental agencies.

In undertaking this project, we proposed to explore the possibility that a useful feedstock could be prepared from coal using a totally different approach to the basic problem involved in fracturing the complex and highly crosslinked coal matrix. Rather than relying on thermal bond cleavage and hydrogen transfer under high pressure, we believed that a mild, limited oxidation process could achieve the desired depolymerization of coal. Under special conditions involving a solvent capable of undergoing free radical oxidative chain reactions, C-C bond cleavage in the coal might be achieved. Oxidation of coal, even mild oxidation, is generally undesirable. Progressive oxidation results in destructive degradation - lost heating value and swelling properties, and even ignition (1,2). A number of studies of controlled oxidation of coal have been made (3-6). From these studies, it was apparent that even controlled oxidation is not satisfactory for the liquefaction of coal.

It is important, however, that coal oxidation is believed to be a free radical process (7-16). From polymer chemistry it is well known that a chain reaction, similar to those proposed for coal conversion reactions at high temperatures, occur readily between two reactive substrates under oxidizing conditions, and at temperatures well below 400-450°C (the temperature range used commonly to achieve coal thermolysis). Figure 1 illustrates the system we proposed (17). R_1H and R_2H represent two hydrocarbon substrates--in our case a solvent and coal. Free radical initiation to produce $R_1\bullet$ is a relatively low energy process. The reaction with pure oxygen or air to form $R_1OO\bullet$ has an activation energy of ~0. Abstraction of hydrogen can involve labile carbon-hydrogen bonds in either R_1H or R_2H, and the cycles shown in the figure can be repeated a number of times. The products of this co-oxidative free radical chain reaction are hydroperoxides. Cumene (isopropyl benzene) is a hydrocarbon which is known to undergo the kind of oxidation reaction described in Figure 1. We have chosen it as our principle solvent. Using an initiator, and in some cases a small quantity of a transition metal ion, cumene hydroperoxide can be produced at 80°-100°C (18). In dilute acid at a temperature as low as 60°C, the decomposition of cumene hydroperoxide results in C-C bond scission. Thus, we proposed that analogous scission could be induced in the coal matrix subsequent to the oxidative formation of the coal hydroperoxide, R_2OOH. We predicted that the C-H bond energy of tertiary (-CH-) and secondary ($-CH_2-$) bridging sites in coal is comparable to that of the C-H bond in cumene.

Experimental

Co-oxidation. Three coals were selected for this study. All were western Kentucky hvB or hvC bituminous coals obtained from the coal bank at Western Kentucky University. The elemental analysis for each coal is given in Table I. The coals

were not dried before use. Determination of the optimum conditions for co-oxidation involved a number of variables: solvent, temperature, pressure, and reaction time were identified as the four principle variables. These were varied within limits selected as a useful range for ultimate commercial application. Temperatures were tested in the range 30-185°C; gas pressures were varied from 1-7 atmospheres (0.1-0.7 MPa); reaction times were 0.5-24 hours. Solvents tested are listed in Table II.

Typically, 10 g coal (-60 mesh), 100 ml solvent, and 1.0 g of initiator were used. For reactions at atmospheric pressure, air or oxygen was passed continuously into the reaction slurry at a rate sufficient to maintain a moderately turbulent system. At elevated temperatures (above the normal b.p. of the solvent) or pressures, the reactants were charged to a 300 ml stainless steel Parr reactor (equipped with mechanical stirring and temperature control) which was sealed and pressurized with oxygen as desired. The free radical initiators which were used in each temperature range were azobisisobutyronitrile (65-88°C), ditertiary butyl peroxide (117-143°C), tert-butyl hydroperoxide (121-147°C) and cumene hydroperoxide (154-194°C)(19).

After each reaction, the slurry was cooled and filtered to recover the coal. The coal was washed with acetone and was dried for a minimum of 16 hours at 150°C in an evacuated drying oven.

Determination of Hydroperoxides

For reactions using cumene, gas chromatographic analysis of the reaction filtrate was used to detect the extent of oxidation of the solvent. The titrimetric method described by Lundberg (20) was used to detect hydroperoxides in the coal after co-oxidation. For this test, 2 g sodium iodide and 25 ml acetic acid were purged 5 minutes with nitrogen. The dried, co-oxidized coal was slurried in the solution for a minimum of 25 minutes and the nitrogen purge was continued. The solution was decanted and immediately titrated potentiometrically with sodium thiosulfate. A blank was run as well as a test using a 1% solution of commercial cumene hydroperoxide.

Oxygen Uptake Analysis

Elemental analysis of co-oxidized coal was carried out. This data is included in Table I. Infrared analysis was carried out on selected samples of co-oxidized coal. A 1% by weight KBr sample was prepared. A Nicolet 10-MX FT-IR was used to obtain the spectra.

Hydroperoxide Decomposition

The decomposition, via C-C bond scission, of hydroperoxides is critical to the success of this process. Although hydroperoxides are generally thermally unstable and can be decomposed by heat, several methods were tested using co-oxidized coal. These are shown in Table III.

Determination of Depolymerization

Soxhlet extraction in refluxing N,N-dimethylformamide (DMF) was used to determine whether co-oxidation had increased the extractability of the coal. Duplicate samples (~5g) were weighed into pre-dried and pre-weighed cellulose extraction thimbles. Extraction with DMF was carried out for 24 hours. The DMF was replaced by methanol which was used to rinse the coal for a minimum of 6 hours. The thimbles and residue were dried in vacuo at 150°C. The weight loss was used to calculate the weight percent extracted. Extraction values reported here are relative to the extractibility of the raw coal.

Table I

Analyses of Coals before and after Co-oxidation (Selected Trials)

Coal (Trial)	M**	VM	Ash	C	H	N	S	O**
9100	7.09	40.6	8.36	74.08	5.11	1.50	3.59	7.34
(1-40[a])	1.67	37.01	7.68	73.72	5.05	1.68	2.93	8.94
9036	5.33	46.8	6.44	76.48	5.37	1.60	3.29	6.79
(253[b])	0.87	36.59	5.71	75.38	5.09	2.08	2.71	9.03
7827	2.84	35.88	9.49	74.49	5.22	1.53	3.33	5.94
(66[c])	2.01	36.64	9.28	75.20	5.24	1.50	3.10	5.68
(A-1[d])	0.45	37.06	9.32	73.59	5.00	1.58	3.19	7.32
(A-2[e])	1.08	35.86	9.51	73.10	4.98	1.56	3.01	7.84

**Moisture, as determined; Oxygen by difference; other values on dry basis
[a]2 hr., 1 atm., 90°C, 10:1 (v/w) Cumene:Coal
[b]15 hr., 1 atm., 115°C, 10:1 (v/w) Cumene:Coal + 0.1M $Co(ac)_2$ and 0.1 M HBr
[c]0.5 hr., 20 psig. O_2, 165°C, 15:1 (v/w) Cumene:Coal
[d]3 hr., 1 atm., 90°C 15:1 (v/w) Cumene:Coal
[e]2 hr., 20 psig. O_2, 115°C, 2:1 (v/w) Cumene:Coal, + 0.1M $Co(ac)_2$ and 0.1M HBr

Table II

Solvent Screening[a]

Solvent	Change in Extractibility, %[b]
Cumene	+ 7
Benzonitrile	-18
o-dichlorobenzene	-16
Diphenylmethane	- 4
Fluorene	0[c], -2[d], -10[e]
Tetralin	+ 1
Diphenylether	- 2

[a]Oxidation: 2 hr., 100°C, 1 atm., 10:1 (v/w) Cumene:Coal
[b]24 hour Soxhlet extraction, 6 hr. MeOH rinse, 150°C vac. dry; % = Wt. sample - Wt. ressid./Wt. sample x 100. Value shown is relative to the extraction of unoxidized coal.
[c]20% (w/v) in Cumene
[d]20% (w/v) in o-dichlorobenzene
[e]20% (w/v) in benzonitrile

Results

Table II through Table VI summarize the results of approximately 200 reaction trials. Each piece of data was determined by multiple trials. Table II shows that cumene was the most effective solvent tested. Benzonitrile, o-dichlorobenzene and diphenylether were tested because of their relatively higher boiling point. They were not expected to participate in co-oxidation.

Table IV shows the effect of temperature and the effect of pressure above atmospheric (1 atm - 0.101 MPa - 14.696 psig). No enhanced solubility is indicated by the data at a temperature above 100°C or above atmospheric pressure of air (or oxygen).

Table III

Effect of Post-Treatment on Extraction of Co-oxidized Coal[a]

Treatment	Change in Extractability, %[b]
Thermolysis at 260°C 10 min.	-18 to +5
Sat'd aq. KI in HoAc/$CHCl_3$	
25°C	
2 - 15 hrs.	-2 to 0
60°C	
2% H_2SO_4 in acetone; 60°C, 2 hr.	+4
N_2H_4 neat or 10% in O-Cl_2Benzene	
25°C	
2 - 24 hrs.	+4
60°C	

[a]Oxidation: 2 hr. at 100°C, 1 atm. O_2, 10:1 (v/w) Cumene:Coal
[b]24 hour Soxhlet extraction, 6 hr. MeOH rinse, 150°C vac dry; % = Wt. sample-Wt. resid./Wt. sample x 100. Value shown is relative to the extraction of unoxidized coal.

Table V summarizes the results of trials using various combinations of mixed solvents tested. Dimethylformamide drastically inhibited the oxidation of cumene itself, and has been reported to undergo free radical addition reactions (21). Of the other solvent systems, acetic acid in dioxane showed the most promise. Overall, however, there was little evidence that this type of reaction medium could overcome the barrier being consistently encountered.

The data in Table VI show that the extractability of the coal has been enhanced by the co-oxidation reactions which were carried out in the presence of aqueous or alcoholic base in addition to cumene. Subsequent trials showed, however, that the action of the alkaline medium alone, even in a nitrogen atmosphere, also led to an observed increase in the solubility of the treated coal.

Table IV

Effect of Temperature, Pressure, and Time on Co-oxidation of Coal[a]

Trial	Temp. °C	O_2 Press. atm	time, hrs.	% Extracted[b]
22	100	1	2	-2
23	130	1	2	0
41	130	6.8	1	+8
65	168	2.7	0.5	-6
69	185	1.7	1.0	-7
71	130	3.4	0.5	-6
72	85	1	0.5	-7
73	31	2.9	0.5	-4
75	69	2.6	0.5	-5
113	85	1	6.5	+1
78	160	1	0.75	-8

[a]1:10 w/v coal:cumene and appropriate initiator.
[b]Relative to extractability of raw coal into DMF.

Table V

Effect of using Mixed Solvents on the Extraction of Co-oxidized Coal

Solvent System	Change in Extractability, %a
--- 85°C, 1 atm., 20:1 (v/w) Solvent: Coal ---	
25% DMF in Cumene	
2.25 hr.	-10
22 hr.	+ 7
26 hr.	+ 2
11% DMF in Cumene	
21 hr.	- 3
27 hr.	+ 5
--- 75°C, 2.25 hr., 1 atm., 20:1 (v/w) Solvent:Coal ---	
Dioxane	- 6
4:1 (v/v) Dioxane:4-picoline	-12
15:4:1 (v/v) Dioxane:Picoline:CS_2	-18
4:1 (v/v) Dioxane:ethylenediamine	-14
4:1 (v/v) Dioxane:acetic acid	- 2

[a]24 hour Soxhlet extraction, 6 hr. MeOH rinse, 150°C vac. dry; % = Wt. sample-Wt. resid./Wt. sample x 100. Value shown is relative to the extraction of unoxidized coal.

Table VI

Effect of Base on the Co-oxidation of Coal[a]

Trial	Base[b]	Temp, °C	O_2Press, atm	Time, hrs	%Ext'd[c]
45	pH 10 Na_2CO_3	100	1	1.5	+13
46	pH 10 Na_2CO_3	100	1	3	+ 4
52	pH 10 Buffer	100	1	1	+18
81	pH 10 Buffer	160	1.5	0.75	-10
84	pH 10 Buffer	160	1	0.75	- 9
91	10% KOH in t-butyl alcohol	130	1.5	0.75	- 9
94	10% KOH in t-butyl alcohol	85	1	3	+ 6
95	10% KOH in t-butyl alcohol	85	1	1	+10
85	pH 10 Buffered	100	1	1	- 6
96	10% KOH in t-butyl alcohol[d]	85	1	1	+13
121	10% KOH in t-butyl alcohol[d]	85	1	1	+17
107	10% KOH in t-butyl alcohol[e]	85	1	1	+ 7

[a]1:10 w/v coal:cumene, appropriate initiator.
[b]2:1 base:solvent.
[c]Relative to extractability of raw coal into DMF.
[d]No cumene present.
[e]No cumene or O_2 present. (N_2)

Table III shows that no appreciable quantity of hydroperoxide was detected in co-oxidized coal or solvent, and also shows that thermolysis of co-oxidized coal at 260°C did not exhibit a positive effect on the subsequent extraction of the coal.

Infrared analysis of several samples of co-oxidized coal showed absorbance at about 1670 cm^{-1} which is characteristic of carbonyl signals. This was not observed in IR spectra of unoxidized coal.

Discussion

Co-oxidation. In a two hour period, cumene alone, is oxidized approximately 50%. In the presence of coal, the oxidation of cumene is reduced by one half. Along with the data showing oxygen uptake by the coal (Table I), this indicates that coal oxidation is occurring under these relatively mild conditions. Extraction values, however, were not enhanced, and post-oxidative treatment designed specifically to promote C-C bond cleavage associated with hydroperoxide decomposition were depressingly unsuccessful. Use of swelling solvents, or temperatures and pressures considered 'elevated' in this regard were not effective. Not only is it likely that DMF added to the coal matrix (21), temperatures at or above the boiling point of solvents certainly diminish oxygen solubility, and high pressure may have actually promoted further oxidative crosslinking (4,7). Failure to detect hydroperoxides in the co-oxidized coal does not prove their absence. Penetration by iodide into the pore system may in fact have been minimal. Similarly acid-catalyzed decomposition of hydroperoxides using 2% H_2SO_4 in acetone (18) at 60°C for 1 hour may have been ineffective for the same reason.

It is known that phenolic species are present in coal (22), and phenol is an oxidation product of cumene. Effective inhibition of the free radical reaction may have occurred in the absence of any reagent to neutralize phenolics. The enhanced extraction observed when co-oxidation was carried out in a cumene/KOH (aqueous or isopropyl alcohol) slurry lends support to this notion. However, base alone in the absence of an oxidant is also known to solubilize coal, perhaps by ether or ester hydrolysis (23-25). If keto groups are being formed, as the preliminary IR suggest, some enhanced extraction can be accounted for after alkaline hydrolysis. It is not clear, however, that carbonyl formation should occur in preference to hydroperoxide formation.

Conclusions

At this stage, co-oxidation does not seem to be an effective means of achieving bond cleavage in coal. Three critical features of the process have not been thoroughly investigated, however, and are the object of our on-going research. First, only high rank coals were tested. It is likely that subbituminous or lignitic coals will be more susceptible to co-oxidation and hydroperoxide formation.

Hydroperoxide formation in coal is a relatively facile process. Thermal decomposition of hydroperoxides is also believed to occur at temperature as low as 70°C (26). If this is so, co-oxidation at lower temperatures (~70°C) may be necessary to prevent spontaneous decomposition of hydroperoxides. More important in this regard, is the fact that in this investigation, the co-oxidized coal was always dried at 150°C, and thermolysis was attempted at 250-260°C. Cleavage of hydroperoxides in an inert atmosphere at these temperatures may have indeed cleaved hydroperoxides, but also may have generated free radical species which combined to form more crosslinks in the coal. Not only may thermolysis be achieved at much lower temperatures, the presence of a suitable 'donor' medium, such as cumene or hydrogen, may result in effective depolymerization.

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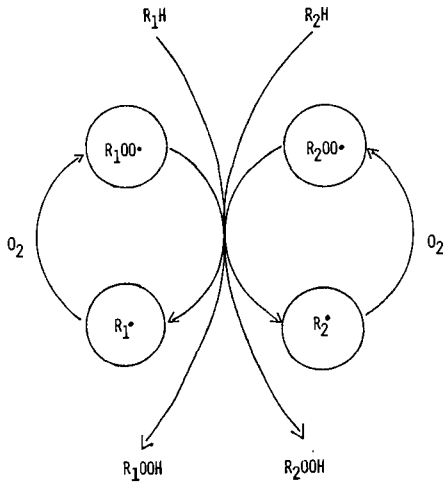

FIGURE 1. AUTOXIDATION OF MIXED SUBSTRATES (17).

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