

Selective Bond Cleavage of Coal by Controlled Low-Temperature Air Oxidation

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Recent efforts to find low temperature routes to liquefy coal have led to a renewal of interest in oxidative methods. Air oxidation of coal has been used to effect desulfurization(1). Application of low temperature air oxidation to SRC (Solvent Refined Coal)(2) and some coals(3) have shown that coal is easily oxidized in solvent with radical initiators at 50° and without initiators at 100–200°C. Subsequent thermolysis of the oxidized SRC for instance, leads to significant production of low molecular weight compounds(2). The attraction of the air oxidation routes to coal liquids are two fold: inexpensive reagent(air) and low-temperature and pressure conditions. However, the oxidation must be controlled or severe loss of C and H can occur. It is worthwhile to note that the well known basic water oxidations of coal(4,5) produced high yields of benzene carboxylic acids but also gave CO₂ amounting to approximately 50% of the available carbon.

Under mild conditions, oxidation of coal in pyridine should proceed principally at benzylic positions. Many organic sulfur forms should also oxidize readily near 100°C(1,6,7). Upon thermolysis, as noted above, SRC which was oxidized in quinoline has been shown to produce as much as 32% by wt. of compounds with molecular weights less than 210. Thus a two step scheme which involves first low-temperature air oxidation followed by a higher temperature pyrolysis step could lead to significant yields of low molecular weight compounds. We would now like to present our results which extend the two step oxidation-thermolysis scheme to SRC and several raw coals using pyridine as solvent. It should be noted that all of our work thus far has been performed using small batch scale reactors and greater control over reactive intermediates might be achieved using flow reactors(9).

Experimental

The coals used in this work were obtained courtesy of the Pennsylvania State University, College of Earth and Mineral Sciences. Ultimate analyses (performed by Pennsylvania State University) are shown in Table I. Also shown are the total quantity of pyridine solubles of each coal used determined by soxhlet extraction. SRC was obtained from a Western Kentucky coal (Lot No. AL-3-35-77) and was supplied courtesy of Catalytic, Inc.

Complete details of the apparatus, experimental details and analytical methods have been reported elsewhere(2). Briefly, air is passed through a solution (SRC) or suspension (coal) of substrate in pyridine which is maintained at approx. 100°C. At the end of the oxidation period, the solution and the remaining residue are thermolyzed in the absence of air. The coals were oxidized and thermolyzed as 10% (wt/wt) slurries. Low molecular weight products (below 210) are quantitatively analyzed by gas chromatography using an internal standard.

Results

All coals and SRC oxidized smoothly at 100°C in pyridine. By monitoring the vent gases from our oxidation reactor for O₂, CO₂, CO and H₂O (2) we can determine how much oxygen reacted with the coal. The oxygen gas balance data for six coals and SRC oxidized in pyridine are presented in Table II. The vent gas from our

oxidation reactor passes through a condenser which is maintained at 0°C prior to gas analysis. Consequently very little water vapor escapes the condenser to be analyzed. While the water vapor content of the vent gases can be measured in all cases the total oxygen content represented by this water vapor is negligible and is therefore not reported in Table II. Water analysis of the pyridine solvent both before and after oxidation must be performed to close the oxygen balance. It seems unlikely however that all of the remaining oxygen can be accounted for by water.

It should be noted that these oxidations are quite mild. The evolved carbon (as carbon oxides) from the Sub-Bituminous B coal for instance, represents 0.001% of the available carbon on a mmf basis (Table I). The extent of oxidation, assuming negligible water production, is only 0.6% by weight for the Hi Volatile C bituminous coal. The extent of oxidation of the raw coals in this work is less than that observed for SRC in quinoline (2) or in pyridine at 100° (Table II). Thus, these are indeed mild, controlled oxidation conditions and should be compared again with the much more severe base catalyzed oxidations performed by others (4,5).

While sulfur moieties should oxidize readily under these conditions we do not expect SO₂ to be evolved at these temperatures (1,6,7). In prior work (2) in quinoline solution, SRC showed no evidence of sulfur dioxide evolution while oxidizing at temperatures as high as 180°C (10). While the substrate in the above case was low in sulfur and therefore evolved SO₂ might have gone undetected, it appears most unlikely that 180° is sufficient to cause appreciable SO₂ extrusion from sulfones (7).

The oxidized solutions and recovered residue were then placed in small stainless steel tubes which were fitted with Swagelok valves. The tubes were subjected to several freeze (-78°)-pump-thaw cycles then pressurized to 500 psig (room temperature) with hydrogen. The slurries were then heated to 415° for 3 hours. After cooling, the recovered solutions were quantitatively analyzed by gas chromatography. The results are reported in Table III. The conversion represents the yield, on a weight basis, of compounds whose molecular weight is less than approximately 210. In runs performed with raw coals, but not with SRC, some formation of pyridine (solvent) dimers was observed. The coals which gave the higher yields of low molecular weight compounds also appear to produce more pyridine dimer. Oxidized SRC was heated at two different temperatures. As observed previously using quinoline as solvent (2), only when the thermolysis temperature is above 400° are appreciable yields of low molecular weight compounds observed (Table III).

Discussion

All coals and SRC used in this work oxidized smoothly at 100° in pyridine. The coals of higher rank absorbed more oxygen than those of lower rank (Table II). The SRC absorbed more oxygen than any coal and appeared to be as reactive in pyridine at 100° as in quinoline at temperatures up to 150° (2). This difference in reactivity toward liquid phase air oxidation between SRC and the coals listed in Table I is probably not connected with oxygen transport within coal pores (9). Rather the difference in reactivity appears to be structure related. SRC has a lower oxygen content than any of our coals (11) and probably a lower phenolic oxygen content (12). Similarly, higher rank coals which absorb more oxygen than lower rank coals (Table II) appear also to have a lower content of phenolic oxygen. Hindered phenols are well known liquid phase oxidation inhibitors (13) so that this explanation is consistent with the observed oxidation behavior of the coals and SRC.

The oxidized solutions and recovered residue (coals only) were then thermolyzed in stainless steel tubes for 3 hours. Initial experiments with SRC at 350° showed that only small amounts of low molecular weight compounds were produced. At 415°

a dramatic increase in the observed production of low molecular weight products was observed. In an earlier paper we suggested that at temperatures over 400° thermal decarboxylation of acids, which were produced during oxidation, followed by rapid quenching of the radicals could account for the observed results (2). The same pattern of reactivity is exhibited by SRC in the present work. Recently, Campbell (14) has shown that CO₂ is evolved from the organic portion of sub-bituminous coal only at temperature above 400°. Presumably, thermal decarboxylation also explains this data.

Thermolysis of some of the oxidized coals produced some interesting results. The two higher rank coals (Table III) produced more low molecular weight compounds than the lower rank coal studied. The yields of low molecular weight material were always higher if the substrate were subjected to the mild oxidation prior to thermolysis. However, thermolysis of the raw coals at 415 induced dimerization and some trimerization (15) of the solvent, pyridine. The quantity of bipyridine formed roughly follows the pattern of oxidative reactivity of the coals- more oxygen absorbed, more bipyridine formed. Interestingly, no bipyridine was observed from the thermolysis of any SRC at 415 but biquinolines formed at 450° with SRC in quinoline.

The degree of solvent involvement reported in Table III is significant. Bipyridines distill in the same region as major products and if not removed would lead to high N content of the product. One way in which the bipyridines could be formed is by H atom abstraction from a solvent molecule in a coal pore by a 'hot' radical. Self-reaction with another solvent molecule in close proximity rather than quenching with hydrogen might be the preferred reaction pathway. We attempted to suppress bipyridine formation by addition of some tetrahydropyridine to the thermolysis slurries. The observed formation of bipyridines was reduced by a factor of about 2 when tetrahydropyridine was present in 10 wt % in the oxidized or unoxidized (raw coal + pyridine) slurries of the Hi Vol A and Hi Vol C coals. The observed yields of low molecular weight material were also reduced. However, the substrates used in the latter experiments had inadvertently been allowed to remain at room temperature for approximately two months. We had observed that these solutions and residues are easily degraded even at freezer temperatures in short periods of time.

The data presented in Table III demonstrate that coal can be fragmented to yield significant quantities of low molecular weight material. Since the reported yields from the oxidized and thermolyzed runs are all higher than the pyridine soxhlet extracts, on a weight basis, we can say that the two step process employed here definitely attacks some of the polymeric coal structure. Work is now in progress to replicate these results but on a much larger scale so that the yield of distillate (not gc yield) material can be reported. Similarly the residue after thermolysis will be examined for sulfur content. Finally it should be noted that the soxhlet extractable material from the Hi Vol A coal contains about 1% by weight of low molecular weight (less than 210) compounds.

References

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12. Generally, phenolic oxygen content decreases with rank but can be as high as approximately 4% for coals that are 85% carbon; eg, L. Blom, L. Edelhausen and D. W. van Krevelen, *Fuel*, 36, 135 (1957).
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15. Field ionization mass spectrometric analysis of some of these thermolyzed samples demonstrated the presence of pyridine trimers.

Table I

Elemental Analyses of Coals

Coal, PSU No. - Type	Ultimate Analysis ¹			Soxhlet Extract, wt %		
	C	H	N			
PSOC 314 - Hi Vol A bituminous	81.5	6.1	1.7	0.72	10.2 ³	24 ⁴
PSOC 237 - Hi Vol B Bituminous	81.9	5.5	1.8	0.6	10.2	15
PSOC 316 - Hi Vol C Bituminous	78.3	5.4	2.3	0.5	13.5	11
PSOC 230 - Sub Bituminous B	76.3	5.0	1.1	0.5	17.1	7
PSOC 101 - Sub Bituminous C	75.7	5.1	0.9	0.3	18.1	-----
PSOC 247 - Lignite	75.5	4.8	1.5	0.5	17.6	6

1, wt %; elemental analysis data (dmf basis - direct basis) were kindly provided by the Pennsylvania State University, College of Earth and Mineral Sciences. 2, Organic sulfur. 3, Oxygen by difference. 4, wt % extracted, in pyridine, based on weight of raw coal (coals were allowed to air dry to constant weight at room temperature prior to extraction); conditions - N₂ atmosphere, exhaustive extraction (> 12 hrs).

Table II

Partial Oxygen Balances for Oxidation of SRC and Various Coals in Pyridine at 100°C⁴

<u>Substrate</u>	<u>O₂Absorbed, mmoles</u>	<u>Evolved Gases, mmoles³</u>	
		<u>CO₂</u>	<u>CO</u>
SRC	5.1	0.5(.4) ²	-nm ¹
Hi Vol A Bituminous	2.8	0.5(.4)	0.04(.01) ²
Hi Vol B Bituminous	4.0	0.6(.4)	0.06(.02)
Hi Vol C Bituminous	4.1	0.6(.4)	0.05(.01)
Sub Bituminous B	3.1	0.9(.6)	0.05(.01)
Sub Bituminous C	2.5	0.9(.7)	0.05(.01)
Lignite	2.3	0.8(.6)	0.04(.01)

¹, Not measured. ², Numbers in parenthesis in this column refer to the calculated amount of O₂ in mmoles, accounted for in this gas. ³, A negligible amount of water was evolved in the oxidation gases. Karl-Fischer water analysis of the suspensions before and after oxidation remain to be performed. ⁴, Oxidation conditions: 100°C, 250 ml/min air flow, 3 hours, pyridine solvent.

Table III

Liquefaction Yields from SRC and Various Coals

<u>Substrate</u>	<u>Oxidized¹</u>	<u>Thermolyzed², °C</u>	<u>Conversion, %³</u>	<u>Wt % Bipyridines Formed⁴</u>
SRC	No	415	1	n.f. ⁵
SRC	Yes	350	7	n.f.
SRC	Yes	415	36	n.f.
Hi Vol A Bit.	No	415	15	0.9
Hi Vol A Bit.	Yes	415	32	0.4
Hi Vol C Bit.	No	415	12	0.3
Hi Vol C Bit.	Yes	415	19	1.8
Sub-Bit. B	No	415	4	0.2
Sub-Bit. B	Yes	415	10	0.2

1, Oxidized in pyridine maintained at 100°C, for 3 hours with air. 2, Oxidized solution and residue (for raw coals) heated for 3 hours at indicated temperature in Swagelok sealed stainless steel tubes. Tubes pressurized to approx. 500 psig (r.t.) with H₂ after several freeze (-78°C)-pump-thaw cycles. 3, Based on amount of coal and corrected for bipyridines formed. 4, Identified by retention time on two different columns; based on total amount of pyridine present. 5, Not found.