

OXIDATIONS OF COALS AT AMBIENT TEMPERATURES

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INTRODUCTION

This paper extends the work of Liotta, Brons, and Isaacs (1) on the weathering of coal. They crushed freshly-mined Illinois No. 6 Coal (Monterrey Mine) to a maximum size of 6.4 mm, spread it over the ground, and allowed it to weather with daily mixing. Samples were removed periodically and Soxhlet-extracted with tetrahydrofuran. The amount extracted (dmmf basis) decreased from 21.3% at zero time to 14.5% at 56 days and then did not change further. During the exposure, the dmmf carbon content of the coal decreased from 69.3 to 66.9% and its oxygen content increased from 9.0 to 11.3%. No new carbonyl groups were found by FTIR and the phenol and carboxyl contents did not change. The authors propose that free alkyl radicals react with nearby hydroperoxide groups to give ether crosslinks and hydroxyl radicals. However, the alkyl radicals should react much faster with oxygen than with coal. This paper describes some related experiments done to obtain material balances and better control of conditions.

EXPERIMENTAL

In my work samples of about 5 g of coal were exposed in Pyrex-covered Petrie dishes (area 61 cm²) either in a dark cabinet at 23°C or to ambient temperatures on the roof of the laboratory. For a density of 1.35 g/cm³, the average thickness of the coal layers was ~0.6 mm. The samples on the roof were also covered by a Pyrex beaker for rain protection and were agitated about twice a week. Each sample suffered a loss from a wind gust during agitation. To measure changes in carbon and oxygen contents, I then had to assume that there was no change in mineral matter during exposure. One coal was 100-200 Tyler mesh Illinois No. 6, Herrin Mine, PSOC 1098; the other was ~200 mesh from the Wyodak Mine at Cambell, Wyoming. In general, the analyses reported are on coal samples dried over anhydrous calcium sulfate at about 2000 Pa (15 torr) and room temperature, but the oxidations were done at ambient humidities.

The remaining oxidized coals are similar to the initial coals. The probe chosen was the solubilities of the coals in pyridine (1 day extraction at 100°C) and benzylamine (1 week extraction at 100°C) as in another paper.(2) Most of the solvents from the soluble and insoluble coal fractions were removed at reduced pressure. The residues were then neutralized with aqueous HCl, washed three times each with 3 M HCl and 3 M NH₃ and dried as indicated previously. The washings removed about half of the mineral matter but caused no significant change in the organic material.(2)

RESULTS

Analyses of the aged and unaged coals are in Table 1 with oxygen and sulfur together determined by difference (1.55% organic S in Illinois 6, 0.45% in Wyodak). Weight changes are shown in Figure 1. The figure shows that there was little change during the cool and cloudy season but that change was relatively fast during clear, warm weather.

Table 2 shows the weight changes normalized to 100 g of initial coal and also shows the carbon contents of the coals. In 311 days in the dark at 23°C, Illinois No. 6 coal lost about 0.14% of its original weight and 0.90% of its original carbon. Wyodak lost 1.5% of its weight and 5.2% of its carbon. However, in 282 days to sunlight, the Illinois

coal lost 17% of its weight and 23% of its original carbon. The corresponding numbers for Wyodak coal are 26% of its weight, 15% of its carbon. In the light experiments, the calculations assume that there was no change in mineral matter during exposure. Neither sample changed much in total O + S content. These results show that both moderately dried coals, and especially the Illinois coal, are fairly stable to ambient air in the dark at room temperature but that both are unstable in sunlight.

Because coal temperatures in sunlight sometimes reached 60°C (annual average about 15°), an effort was made to estimate the effect of solar heating on the light oxidations. The temperature of a thin film of coal in sunlight under Pyrex was measured on a warm (not hot) day in May. The maximum temperature reached was 58.3°C and the temperature exceeded 50°C for about 5 hours. The maximum temperature in the shade was 29°C and the temperature exceeded 25° for 6 hours. To determine the effect of heat alone on oxidation, about 2 g of each coal was also exposed to air with weekly air changes in Pyrex flasks in a brown glass bottle in a thermostat at 60°C. Figure 1 and Tables 1 and 2 show that continuous heating in the dark at 60° caused weight losses that were much smaller than those in sunlight with temperatures above 50° for only 4-6 hours on most days. Thus, the weight losses in sunlight are due mostly to light, not higher temperatures.

Table 2 also lists the solubilities of the initial coals and their oxidation products in pyridine and benzylamine, after correction for excess nitrogen.(2) Some of these corrected carbon contents are too high for reasons unknown. Our previous work(2) shows that pyridine partly dissolves coals at 100° without chemical reaction and that benzylamine dissolves additional coal to the extent that it cleaves ester and ether groups. Thus, the changes in solubility on aging are a measure of chain scission and crosslinking in the surviving coal. In comparison with the unaged coals, the changes are small to moderate. The solubility differences between the unaged coals and those aged in the dark are small and insignificant; little oxidation occurred. However, in comparison with the unaged coals, the light-aged coals give lower recoveries of carbon on extraction, probably because of greater losses of volatile or water-soluble products. The second number in some carbon recoveries counts this missing carbon as soluble carbon.

DISCUSSION

A simple and reasonable explanation of my light results is that my oxidations caused successive oxidation, photolysis, and evaporation of outside layers of coal particles. Penetration of light into the coal particles is apparently severely limited and there was little change in the unexposed coal until it became exposed. I cannot explain the cessation of change after 56 days in the oxidation of Liotta et al.(1) Their large particles and sample sizes and limited penetration of light suggest that much of their oxidation was a thermal dark reaction.

My results with oxidations of dried coals at ambient humidities may seem inconsistent with the well-known spontaneous heating and combustion of coal in storage.(3,4) I suggest some possible explanations: mild drying decreased the oxidizability of my coal; Liotta has suggested that water causes oxidation of pyrite to iron sulfates, which may catalyze oxidation. Both a much faster spontaneous oxidation than mine and limited heat loss appear to be necessary to account for spontaneous combustion in storage. It follows that moderate drying of coal and protection from rain might eliminate combustion in storage.

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Keywords: coal, oxidation, photooxidation, pyridine, benzylamine

REFERENCES

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Table 1

ANALYSES OF COAL PRODUCTS

Coal ^a	%C	%H	%N	%(S+O)	%M	H/C
Illinois No. 6						
Unaged	67.0	4.59	1.22	7.9	19.3	0.817
PS	80.2	6.10	1.98		11.7 ^b	
PI	68.6	4.53	1.89		25.0	
BS	79.0	5.72	2.58		12.7	
BI	65.5	4.52	2.21		27.8	
Aged in dark	66.5	4.54	1.18	8.5	19.4	0.814
PS	79.1	6.00	2.46		12.4	
PI	67.4	4.52	1.86		26.2	
BS	75.2	5.63	3.93		15.3	
BI	67.6	4.61	2.10		25.7	
Aged at 60°	66.2	4.12	1.18	9.1	19.4	0.742
Aged in light	62.2	4.08	0.94	9.5	23.3	0.782
PS	76.8	5.93	1.66		15.6	
PI	65.7	4.31	2.06		28.0	
BS	80.6	6.04	3.85		9.5	
BI	66.0	4.46	2.75		26.8	
Wyodak						
Unaged	65.1	4.70	0.92	20.5	8.8	0.860
PS	77.2	7.77	2.18		12.8	
PI	63.9	4.43	2.88		28.8	
BS	75.4	6.44	3.61		14.5	
BI	69.9	5.14	3.65		21.3	
Aged in dark	62.6	4.53	0.83	23.1	8.9	0.862
PS	76.8	8.87	0.78		13.6	
PI	64.8	4.56	2.50		28.1	
BS	77.1	6.42	4.20		12.3	
BI	70.5	5.14	3.79		20.6	
Aged at 60°	64.2	4.22	0.80	21.8	9.0	0.783
Aged in light	60.7	4.07	0.89	24.4	9.9	0.860
PS	74.6	9.18	1.08		15.2	
NH ₃ -S	59.6	6.35	4.97		29.1	
PI	60.8	4.15	3.13		31.9	
BS	76.4	6.13	4.92		12.5	
BI	67.9	4.85	4.10		23.2	

^ap=pyridine; B=benzylamine; S=soluble; I=insoluble

^bNumbers in this column are S + O + M by difference from C + H + N.

Table 2

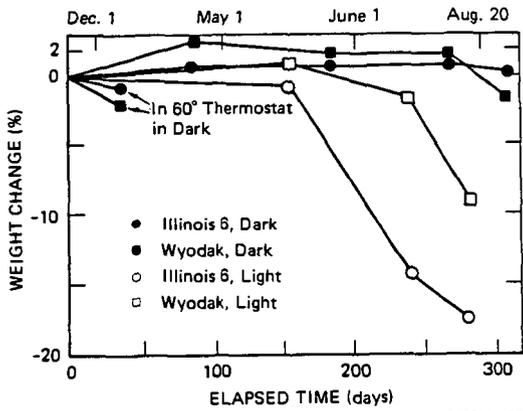
Extractions of Illinois No. 6 and Wyodak Coals at 100°C
Normalized to 100 g coal; corrected for excess nitrogen

Illinois Coal									
g coal, g C, %	<u>311 days in dark at 23°</u>			<u>Unaged</u>			<u>282 days in sunlight</u>		
		99.9	66.4	99.1 ^a	100	67.0	100 ^a	82.7	51.4
Extracted 24 hours with pyridine									
PS	12.0	9.5	14.3	11.7	9.4	14.0	6.5	5.0	8.0
PI	90.6	60.8	91.4	91.5	62.4	93.2	91.4	59.3	95.3
Extracted 1 week with Benzylamine									
BS	33.1	24.5	36.2-37.0 ^b	35.3	28.0	41.8	29.1	23.6	38-40 ^b
BI	62.8	41.8	62.6	61.4	39.5	59.0	58.4	37.4	60.2
Wyodak coal									
g coal, g C, %	98.5	61.7	94.8 ^a	100	65.1	100 ^a	90.7	55.1	84.6 ^a
Extracted 24 hours with pyridine									
PS	4.6	3.5	5.6-15.9 ^b	5.84	4.51	6.9-19.2 ^b	6.8	4.4	7.1-25 ^b
PI	82.8	52.6	84.1	84.4	52.6	80.8	77.0	45.0	74.2
NH ₃ -S ^c	0.81	0.48	0.78				4.6	2.8	6.2
Extracted 1 week with Benzylamine									
BS	19.9	15.2	24.2-33.9 ^b	17.2	12.8	19.7-28.4 ^b	28.6	21.4	35.3-45.3 ^b
BI	61.2	41.4	66.1	69.3	46.6	71.6	52.0	33.2	54.7
Aged 35 days in dark at 60°									
Illinois	99.6	66.0	98.5						
Wyodak	97.8	62.8	96.5						

^aThe three numbers in each group are, respectively, the recovery of coal in grams, recovery of carbon in grams, and the % recovery of carbon, on the basis of original carbon for lines marked a but on the weights or C contents of the a lines for other lines.

^bLast number of pair counts missing carbon as soluble material.

^cSoluble in 3M aqueous NH₃; calculated on basis that excess N comes from NH₂. This product is included in the PS fractions above; dark products calculated from analysis for light products.



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FIGURE 1 WEIGHT CHANGES OF COALS IN THE DARK AT 23°C AND IN OUTSIDE EXPOSURE AT 0 - 60°C
 Dates refer only to light experiments.