OXIDATION OF COALS WITH NITRATE IN CONCENTRATED CAUSTIC SODA SOLUTIONS AT ELEVATED TEMPERATURES.

H. Kawamura, A. Okuwaki, O. Horie, A. Amano and T. Okabe

Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Sendai 980, Japan.

Introduction

Molten alkali nitrate, a strong oxidizing agent having low melting point, is interesting to use as an oxidizing agent and solvent in the oxidation reactions of both inorganic and organic compounds. Previously, we have applied caustic soda-sodium nitrate melt to the production of chromate or oxyacids of manganese. In the present paper, we have examined it for the oxidation of coals, thereby studing the effects of rank, reaction temperature, concentrations of caustic soda and sodium nitrate, and pre-oxidation on the yields of oxidation products. Benzenecarboxylic acids in the products are currently noted as important raw chemicals.

Experiment

Three kinds of foreign coals, Latrobe coal(Australia), Amax coal(U.S.A.), and Goonyella coal(Australia) were used. Their properties are shown in Table 1. Coal(100-150mesh) 5g, caustic soda 150g, sodium nitrate 0-38g, and water 40g were placed in an autoclave(SUS 304) equipped with a mechanical stirrer, were maintained at 150-300°C for 3 hrs. Alkaline solutions of reaction products were analysed for residue, humic acids(water-soluble acids of high molecular weight), and aromatic acids obtained by two stages methyl ethyl ketone extraction from acidified solutions of oxidation products. Nitrate and nitrite in the alkaline solutions were also determined. Aromatic acids were first esterificated by diazomethane. Benzenepolycarboxylic acids were then determined as esters by temperature programmed gas chromatography using a SE-30 column.

Table 1. Analyses of sample coals

Sample	Ultimate analyses(% d.a.f.)				Ash
	C	H	N	O	(%d)
Latrobe coal(Victoria)	64.10	4.85	0.09	30.96	1.06
Amax coal(Utah)	76.53	5.22	1.77	16.48	8.87
Goonyella coal(Q'land)	85.49	5.05	2.07	7.39	7.04

Results and Discussion

Listed in Table 2 are the results obtained for Latrobe coal. Latrobe coal was found to be easily soluble in the concentrated alkaline solutions leaving a small amount of residue. Aromatic acids as well as humic acids was formed in good yield even in the absence of sodium nitrate. Upon further oxidation at raising temperature and increasing amount of nitrate, however, humic acids gave rise to aromatic acids. The maximum yield of aromatic acids was thus reached at 200°C and 7g of sodium nitrate. The ratio of aromatic acids/humic acids reached maximum at 250°C and 18-38g of sodium nitrate, but the yield of aromatic acids became much higher at the amount of sodium nitrate less than 18-38g. On the other hand, nitrate was reduced by the carbonaceous materials to nitrite and further to nitrogen and ammonia depending on the reaction conditions. In the absence of water, the coal was converted to carbon dioxide and water with the concurrent reduction of nitrate to nitrogen as shown in Table 3. The maximum yield of aromatic acids was

Table 2. Oxidation of Latrobe coal

	Temp. (°C)	Coal (g)	$NaNO_3$ (g)	Yields to coal(wt%) Residue	Humic acids	Aromatic acids	Mol ratios to initial NO_3^-(%) NO_3^-	NO_2^-
L-1	150[a]	10.43	17.36	8	30	30	46.6	46.1
L-2		12.58	44.74	8	43	25	79.7	18.4
L-3		12.58	94.37	2	43	28	74.8	16.4
L-4	200	5.035	0	9	40	30	-	-
L-5		5.019	6.97	4	30	63	0	48.8
L-6		5.084	17.79	3	20	60	17.6	74.3
L-7		5.034	37.80	3	17	35	46.3	49.2
L-8	b	5.029	17.97	2	11	53	0	85.8
L-9	c	5.008	17.94	5	10	36	0	89.1
L-10	250	5.024	0	4	29	38	-	-
L-11		5.020	6.95	3	17	55	0	19.5
L-12		5.024	17.92	2	6	50	3.8	86.3
L-13		5.029	37.82	2	2	19	10.1	82.0

a ;·NaOH 400g, b; 6hr, c; 9hr

Table 3. Effect of caustic soda concentration on oxidation of Latrobe coal
(Temp. 250°C. NaOH 5.5g, $NaNO_3$ 6.3g, time 3hr in a 15ml autoclave)

	Coal (g)	Water (g)	Yields to coal(wt%) Residue	Humic acids	Aromatic acids	Mol ratios to initial NO_3^-(%) NO_3^-	NO_2^-
L-14	2.013	0	1	0	1	0.6	5.6
L-15	2.032	1.4	1	15	40	13.7	52.7
L-16	2.012	2.6	2	16	49	21.4	50.4
L-17	2.015	3.4	3	15	52	29.6	46.8
L-18	2.032	6.4	5	15	40	42.4	29.5

reached at caustic soda concentration of about 60-70% under which the ratios of aromatic acids / humic acids were about 3. It was confirmed that even under the high ratio of coal to the solvent shown in Table 3, Latrobe coal underwent the oxidation by nitrate.

Amax coal was only poorly soluble in concentrated caustic soda solutions and the yields of humic acids and aromatic acids were very low in the absence of sodium nitrate. The amounts of the intermediates increased with increasing amount of sodium nitrate as shown in Table 4.

Table 4. Oxidation of Amax coal

	Temp. (°C)	Coal (g)	$NaNO_3$ (g)	Yields to coal(wt%) Residue	Humic acids	Aromatic acids	Mol ratios to initial NO_3^-(%) NO_3^-	NO_2^-
A-1	150	5.082	21.95	83	1	0	94.1	5.9
A-2	200	4.935	0	78	2	4	-	-
A-3		5.167	7.07	41	14	12	18.1	70.4
A-4		5.294	14.20	22	15	9	39.3	50.5
A-5		5.192	21.18	14	42	23	41.4	54.2
A-6		5.295	38.05	16	25	13	72.5	27.5
A-7	a	4.983	22.18	70	4	4	92.2	5.9
A-8	b	5.084	21.49	14	23	14	49.8	43.9
A-9	c	5.014	21.60	16	45	21	38.6	56.3
A-10	250	5.091	0	78	4	6	-	-
A-11		5.123	7.11	13	33	25	0	55.5
A-12		5.138	21.72	5	36	29	0.8	95.3
A-13		5.100	37.83	10	20	27	19.3	71.5

a; 1hr, b; 6hr, c; 9hr

The formation of the intermediates reached at its maximum with 21g sodium nitrate. The maximum yield of aromatic acids was reached at 250°C, but lower than that obserbed for Latrobe coal. The ratios of aromatic acids/humic acids were consistently lower than those for Latrobe coal.

Goonyella coal, sparingly soluble under the hydrothermal conditions, was treated in caustic soda-sodium nitrate melts at 300°C. More than 50% of Goonyella coal was recovered as residue giving rise to only as low as 2-6% of intermediary formation of humic acids and aromatic acids, since the latter were readily oxidized. Consequently, it seems difficult to obtain aromatic acids in good yield directly from a higher rank coal such as Goonyella coal by the oxidation with nitrate in caustic melts.

When Goonyella coal and Amax coal preoxidized in air were reacted with nitrate in concentrated caustic soda solutions at 250°C for 3hrs, the yields of the oxidation products were improved remarkably as shown in Table 5.

Table 5. Oxidation of the coals pre-oxidized in air

	Coal (g)	Wt. loss on oxidn. (wt%)	Temp. (°C)	$NaNO_3$ (g)	Yields to coal(wt%) Residue	Humic acids	Aromatic acids	Mol ratios to initial NO_3^-(%) NO_3^-	NO_2^-
Goonyella coal: Air oxidation; 300°C, 5hr									
G-1	5.320	5.4	250	0	21	36	10	-	-
G-2	5.321	4.8		6.59	18	30	28	0	68.5
G-3	5.319	2.8		17.94	6	27	42	0	90.0
G-4	5.318	4.9		37.72	6	8	24	22.5	65.9
G-5	5.492	5.4	300	17.90	4	19	25	0	62.8
Amax coal: Air oxidation; 300°C, 5hr									
A-14	5.529	17.5	250	17.91	6	12	42	0	90.1
Amax coal: Air oxidation; 250°C, 5hr									
A-15	5.507	4.9	250	17.93	4	20	53	0	82.9

Air-preoxidized Goonyella coal dissolved appreaciably in the alkaline solutions and formed the intermediates. Humic acids decreased with increasing amount of sodium nitrate. Aromatic acids, however, reached maximum at 18g of sodium nitrate. When air-preoxidized Amax coal was used, the yields of aromatic acids were considerably improved. The drastic increase in the oxygen content from 7.4 to 28.3% and the appearence of carbonyl absorption in IR range upon the preoxidation of Goonyella coal suggest the significant structural and constitutional changes in a manner suitable for the oxidation.

From the results described it was made clear that the oxidation became more difficult for coals of higher rank. In general, it is well known in the oxidation of coal that the following stages proceed successively and the constitution of coal is closely related to its reactivity.

$$\text{coal} \xrightarrow{\text{I}} \text{water insoluble acids} \xrightarrow{\text{II}} \text{water soluble acids} \xrightarrow{\text{III}} CO_2,\ H_2O$$

Latrobe coal is very active as it contains a large amount of oxygen in the form of active functional groups such as phenolic hydroxide and carboxylic acid. The rate of dissolution in concentrated caustic soda solutions was very fast. The reactions I and II thus take place smoothly, and humic acids and aromatic acids could be obtained in good yield. When Amax coal, being higher rank than Latrobe coal, was used, the rate of dissolution was slow, but the rates of oxidations of humic acids and aromatic acids were relatively fast resulting in a lower yield of the intermediate oxygen compounds. The trend was found re-

markable in the case of Goonyella coal which was placed at the highest rank among the samples tested.

The composition of benzenepolycarboxylic acids in aromatic acids was shown in Table 6.

Table 6. Determination of benzenecarboxylic acids in aromatic acids

Specimen	Ratios of benzenecarboxylic acids in aromatic acids									Yield to coal
	Di-				Tri-		Tetra-		Sum	
	1,2-	1,3-1,4-	1,2,3-	1,2,4-	1,3,5-	1,2,3,4-	1,2,3,5-	1,2,4,5-	(wt%)	(wt%)
L-6	0.8	0.3	0.7	2.2	0.5	1.1	1.5	2.1	9.2	5.5
L-8	0.7	0.4	0.5	1.7	0.5	0.8	1.1	1.7	7.4	3.9
L-12	1.2	1.0	0.8	3.6	1.2	1.2	1.3	2.6	12.9	6.5
L-13	2.6	0.8	0.6	3.9	2.3	1.3	2.1	4.8	18.4	3.5
A-5	1.7	1.2	1.0	3.8	0.8	1.1	1.3	2.0	12.9	3.0
A-12	0.8	1.3	1.4	5.0	1.2	1.5	1.4	2.5	15.1	4.4
A-15	1.6	1.7	1.6	5.6	1.3	1.7	1.5	2.5	17.5	9.3
G-8	1.9	2.0	1.8	6.9	1.4	1.9	2.0	2.8	20.7	8.7
G-10	1.5	0.6	0.8	3.4	0.8	0.9	1.0	1.2	10.2	2.6

Neither benzoic acid was detected by gas chromatographic analysis, nor was detected water-soluble acids such as citric acid in the raffinates on the methyl ethyl ketone extraction by permangamate titration. The sum of the contents of the benzenecarboxylic acids reached a maximum of 20.7% in the air-preoxidized Goonyella coal. However, the best yield of benzenecarboxylic acids was obtained in the case of similarly treated Amax coal. When Latrobe coal was used, both the content of benzenecarboxylic acids in aromatic acids and the yield of benzenecarboxylic acids to the raw coal were not high. Furthermore, the content of benzenetetracarboxylic acids was the highest in the benzenecarboxylic acids for Latrobe coal, that of tricarboxylic acids, however, was the highest for air-preoxidized Amax coal and Goonyella coal.

Concentrations of caustic soda used in the present study might be too high to obtain benzenecarboxylic acids in good yield. But the following results are concluded. In the oxidation of coals with the present method, a low rank coal such as Latrobe coal dissolves easily and forms humic acids and aromatic acids in good yield. In order to obtain benzenecarboxylic acids, however, it is profitable to use an air-preoxidized high ranked coal such as Amax coal and Goonyella coal.