Formation of Benzenecarboxylic Acids from Bituminous Coal by Means of Oxygen-oxidation in Alkaline Medium

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The oxidation of coal has been an important method of studying the structure of coal and of obtaining products such as benzenecarboxylic acids. The first systematic work was that of Fischer[1] and Schrader who used air to oxidize suspensions of coal in aqueous sodium carbonate. Oxidation of coal in alkaline permanganate solution was carried out by Bone[2] and coworkers, and most of the benzenecarboxylic acids were isolated. Oxygen-oxidation in aqueous caustic alkali was carried out by Howard[3] and coworkers, who obtained aromatic polycarboxylic acids in good yield from bituminous coal. It is hoped that better reaction methods and conditions will be found by further detailed experiments.

In this paper oxygen-oxidation of coal carried out in aqueous solution of sodium or potassium carbonate, in order to investigate the influence of reaction conditions, is discussed. Various benzenecarboxylic acids were separated from the oxidized product and were identified.

Experimental

The sample used in the experiment was a Japanese bituminous coal, Shikamachi, the analytical result of which is given below:—

Moisture 1.2%; Ash 19.8%; C (d. a. f.) 87.3%; H(d. a. f.) 5.4%.

Oxidation Procedure A.—A suspension of 6 g. of coal (through 100 mesh) in 200 ml. of sodium carbonate aqueous solution of various concentrations was treated with oxygen (initial pressure 30 kg./cm^2/0°C) at 250°C for 90 min. in a 600 ml. shaking type autoclave (agitation frequency 100/min.).

Oxidation Procedure B. — A suspension of 85 g. of coal in 1.5 l. of aqueous solution of sodium or potassium carbonate was treated with oxygen at 250~280°C in a 3 l. autoclave electro-magnatically agitated; the reaction gases discharged continuously from the vessel at the rate of 2 l./min. were found to contain about 30% (average) of carbon dioxide.

Analysis of Oxidation Products. — The reaction product was filtered to remove residue and the filtrate was acidified with sulfuric acid to pH 1.5. Water-insoluble acids were filtered off and weighed after vacuum drying. The filtrate was saturated with sodium sulfate at 25°C and extracted twice with methyl ethyl ketone equal to 80% of the volume of the total filtrate. The total acids extracted were considered to represent "Aromatic acids" after vacuum drying at 100°C and removal of oxalic acid. Oxalic acid was precipitated with acetic acid and calcium chloride, and the precipitate was decomposed with sulfuric acid and titrated with permanganate solution. The oxalic acid was confirmed as dihydrate by the determination of equivalent weight 64 and melting point 100~101°C.

Esterification of Aromatic Acid.—150 g. of aromatic acids were dissolved in a mixture of 450 g. of methanol and 36 g. of sulfuric acid and kept at 110°C for 5 hr. The reaction products were extracted with ethylene dichloride and aqueous solution of sodium carbonate. The acidic esters were re-esterified under similar conditions repeatedly.

Results and Discussion

Reaction Conditions. — The results of procedure A are shown in Fig. 1. An increase in the ratio of sodium carbonate to coal caused an increment in the reaction rate as well as in the yield of aromatic acids. The ratio of 8.7 : 1 corresponds approximately to the weight of sodium carbonate required to convert all the carbon dioxide into sodium bicarbonate. The yield of oxalic acid was 1.4% when the ratio was 10 : 1, but less than 0.5% when it was lower 7 : 1. When sodium hydroxide was used, the yields of products were as shown in Table I.

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[1] F. Fischer and H. Schrader, *Gesammelte Abhandlungen zur Kenntnis der Kohle*, **4**, (1920); **5**, (1922).

[2] W. A. Bone, L. Horton and S. G. Ward, *Proc. Roy. Soc.*, **A127**, 480 (1930).

[3] H. C. Howard et al., *J. Am. Chem. Soc.*, **61**, 2398 (1939); *Ind. Eng. Chem.*, **44**, 2784 (1952).

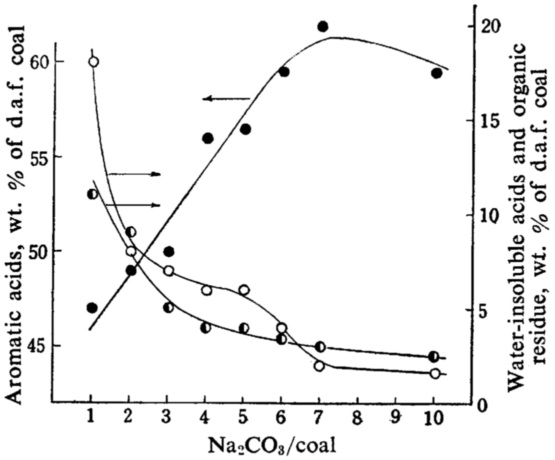

Fig. 1. Influence of the ratio of sodium carbonate to coal.
Procedure A
● Aromatic acids
○ Water-insoluble acids
◐ Organic residue

Table I. The yields of oxidation products using sodium hydroxide aqueous solution
Procedure A, NaOH/coal=3.4

Yields, wt. % of d.a.f. coal
Aromatic acids 61.3%, Water-insoluble acids 6.8%, Oxalic acid 13.2%, Organic residue 1.2%, Carbon dioxide carbon/coal carbon 0.498

Accordingly, it is seen that if enough sodium carbonate is present, the yield of aromatic acids is the same as in the case of sodium hydroxide.

A portion (200 ml.) of the reaction product from procedure B* was resubmitted to oxidation under two different conditions (Table II) to investigate the influence of alkali on the decomposition of the acids produced. It was observed that when the ratio of alkali to coal was small the decomposition rate of aromatic acids and water-insoluble acids was high.

Table II. Oxidation of reaction product

Oxidation condition	Yield of acids, wt. % of d.a.f. coal: Water-insoluble acids	Yield of acids, wt. % of d.a.f. coal: Aromatic acids
Before reoxidation	61.2	34.2
Procedure A	0.8	17.0
Procedure A 34 g. of NaOH added	3.4	55.2

During oxidation reaction equilibrium was reached:

$$Na_2CO_3+CO_2+H_2O \rightleftarrows 2NaHCO_3$$

So it was inferred that bleeding the reactor to remove carbon dioxide would result in good yield of aromatic acids, even when the ratio of alkali to coal was not large. Results of procedure B are shown in Fig. 2. The relations were found to be independent of the kind of alkali at the same molar ratio, when the normality of solution was chosen instead of alkali coal weight ratio. Good acids yields were obtained when the ratio of alkali to coal was higher than 2:1.

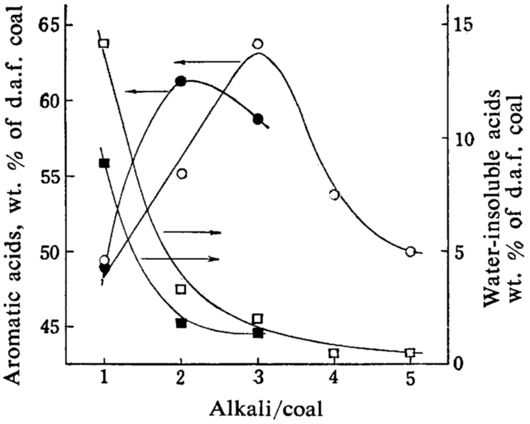

Fig. 2. Influence of the ratio of alkali to coal.
Procedure B, 270°C, 120 min.,
Oxygen partial pressure (average) 14 kg./cm^2 (K$_2$CO$_3$), 17 kg./cm^2 (Na$_2$CO$_3$),
Agitation frequency 85/min.
● Aromatic acids (Na$_2$CO$_3$)
○ Aromatic acids (K$_2$CO$_3$)
■ Water-insoluble acids (Na$_2$CO$_3$)
□ Water-insoluble acids (K$_2$CO$_3$)

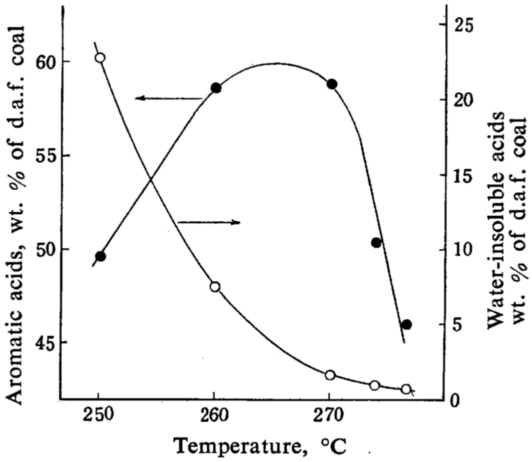

Fig. 3. Influence of temperature.
Procedure B, 120 min. Na$_2$CO$_3$ 255 g.
Oxygen partial pressure (average) 17 kg./cm^2, Agitation frequency 85/min.
● Aromatic acids
○ Water-insoluble acids

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* 250°C, 120 min., Na$_2$CO$_3$/coal=1, oxygen partial pressure 10 kg./cm^2, agitation frequency 85/min.

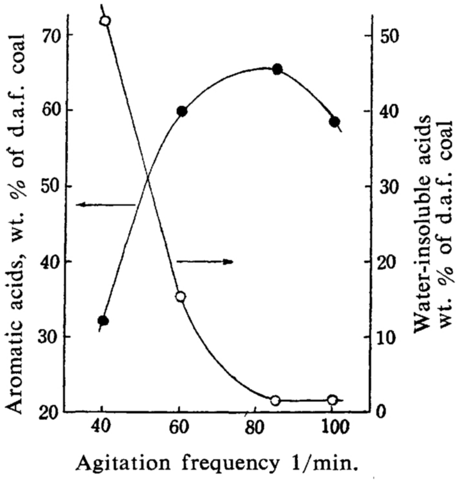

Fig. 4. Influence of agitation.
Procedure B, K_2CO_3 255 g., 270°C, 120 min.,
Oxygen partial pressure (average) 14 kg./cm^2
● Aromatic acids
○ Water-insoluble acids

Generally, the reaction rate was doubled for every 10°C rise in temperature. There is also an optimum temperature as shown in Fig. 3. The effect of agitation is also important as shown in Fig. 4.

TABLE III. REACTION CONDITIONS FOR OPTIMUM YIELDS OF AROMATIC ACIDS

Reaction conditions		
Alkali used	Na_2CO_3	K_2CO_3
Alkali/Coal (wt. basis)	3	3
Temperature (°C)	270	270
Time (min.)	120	120
Total pressure (kg./cm^2)	70	72
Oxygen pressure (average, kg./cm^2)	14	14
Agitation frequency (per min.)	85	85
Yield (wt. % of d.a.f. coal)		
Aromatic acids	60.8	63.9
Water-insoluble acids	3.8	2.1
Oxalic acid	0.2	2.8
Organic residue	3.1	1.5

TABLE IV. PROPERTIES OF ACIDS PRODUCED UNDER OPTIMUM CONDITIONS

		Aromatic acids	Water-insoluble acids
Color		yellow	dark brown
Elementary analysis	C(%)	54.5	66.0
	H(%)	3.7	3.0
Molecular weight		250	—
Equivalent weight		80	130

Remarks: Ash contents of these acids were less than 0.1%.

Details of the optimum reaction conditions and the yield of products are given in Table III. The properties of the acids are given in Table IV.

The coal oxidation process may be expressed as follows: Coal $\xrightarrow{\text{I}}$ Water-insoluble acids $\xrightarrow{\text{II}}$ Aromatic acids $\xrightarrow{\text{III}}$ CO_2, H_2O. If the ratios of the reaction speeds of these steps are independent of any reaction factors, good correlation between the yields of products should be observed. The relations between water-insoluble acids and aromatic acids are plotted in Fig. 5, and found the mechanism of the reaction is not changed by altering temperature, pressure and agitation. When the alkali coal ratio is 1 : 1, the first step becomes slow and the third fast. The oxidation mechanism depends upon the ratio of alkali to coal.

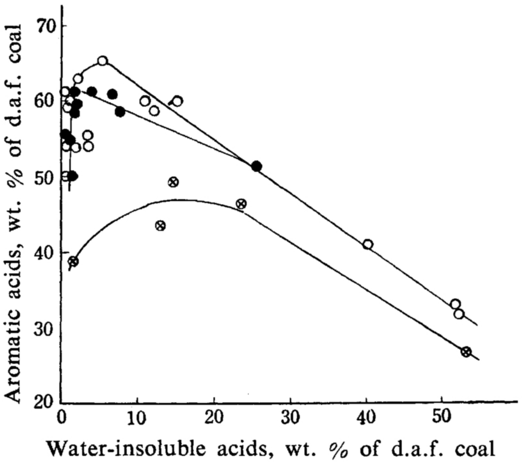

Fig. 5. Relations between water-insoluble acids and aromatic acids.
Procedure B, 250~280°C, 120 min.,
Oxygen partial pressure (average) 7~21 kg./cm^2, Agitation frequency 55~100/min.
○ K_2CO_3/coal=2~5
⊗ K_2CO_3/coal=1
● Na_2CO_3/coal=2 or 3

Separation of Benzenecarboxylic Acids.—From the industrial point of view, the most favorable oxidation medium may be sodium carbonate, because of its smaller corrosive effect, low cost and the possibility of its easy recovery. Benzenecarboxylic acids were separated from the aromatic acids which were obtained by the sodium carbonate process under the optimum conditions.

By the first and second esterification 128 g. of neutral esters (Fraction A) were obtained, and by the third and fourth 15 g. (Fraction B) were obtained. Residual acidic materials were completely hydrolysed with alkali and 6 g. of acids (Fraction C) were recovered.

TABLE V. ANALYTICAL CHARACTERISTICS OF ISOLATED ACIDS AND ESTERS

Component	Elementary analysis (%)		Equivalent weight	Melting point	Remarks
	C	H			
Phthalic acid	57.45 (57.45)	3.66 (3.64)	83 (83)	Anhydride 131°C *p*-Nitrobenzyl ester 155°C	
Isophthalic acid	57.69 (57.45)	3.45 (3.64)	83 (83)	Dimethyl ester 65°C *p*-Nitrobenzyl ester 201∼202°C	Barium salt water-soluble
Terephthalic acid	57.53 (57.45)	3.45 (3.64)	83 (83)	Dimethyl ester 139∼140°C	
Trimellitic acid	51.52 (51.41)	3.01 (2.85)	70.5 (70)	Acid 224∼225°C	Barium salt water-soluble
Hemimellitic acid trimethyl ester	56.80 (57.14)	4.57 (4.78)	84 (84)	Trimethyl ester 100°C	
Trimesic acid trimethyl ester	51.21 (51.41)	2.84 (2.85)	83.5 (84)	Trimethyl ester 143∼144°C	
1, 2, 3, 4-Benzenetetracarboxylic acid tetramethyl ester	54.35 (54.19)	4.83 (4.52)	77.5 (77.5)	Acid 237∼240°C Tetramethyl ester 130°C	
1, 2, 3, 5-Benzenetetracarboxylic acid tetramethyl ester	54.42 (54.19)	4.76 (4.52)	78.2 (77.5)	Tetramethyl ester 112∼113°C	
1, 2, 4, 5-Benzenetetracarboxylic acid tetramethyl ester	54.28 (54.19)	4.67 (4.52)	77.9 (77.5)	Tetramethyl ester 141.5°C	
Benzenepentacarboxylic acid pentamethyl ester	52.31 (52.18)	4.01 (4.38)	74.6 (73.5)	Pentamethyl ester 147∼148°C	
Mellitic acid			56.8 (57.0)	Acid 282∼285°C	Insoluble in ammonia
Naphthalenetricarboxylic acid	60.54 (60.00)	3.59 (3.08)	87.0 (86.7)		Naphthalene was obtained after decarboxylation*.

Figures in brackets have been calculated.

* Dissolved in aqueous solution of sodium carbonate and treated at 450°C.

Fraction A was separated into nine fractions by means of vacuum distillation at 120∼300°C (packed column, I. d. 10 mm., height 26 cm.). From the distillate nine benzenecarboxylic acids (di-, tri- and tetra-) were isolated by means of solubility difference, using acids, barium salts or methyl esters in solution, and identified (Table V). Infrared spectra of the benzenecarboxylic acids were compared with those of the pure substances and confirmed the identifications. Traces of benzoic acid were isolated by means of counter-current distribution (solvent: ethyl ether and water) from phthalic acid fraction. Naphthalenecarboxylic acid was separated as follows; the ethyl ether soluble part of a distillate (4 mmHg, 225∼300°C) was hydrolysed, the filtrate of barium salts in solution was extracted with ethyl ether after acidification, and the extracted acid in ethyl ether solution was purified by washing with water.

Fraction B was submitted to chromatography (column alumina, developer carbon tetrachloride) and recrystallization, and as a result benzene tetra- and penta-carboxylic acids were isolated. From Fraction C mellitic acid was isolated.

The yields of benzenecarboxylic acids from the aromatic acids were as follows:

Benzenedicarboxylic acids		7.1%
Phthalic acid	5.9%	
Isophthalic acid	1.1%	
Terephthalic acid	0.1%	
Benzenetricarboxylic acids		16.2%
Hemimellitic acid	4.9%	
Trimellitic acid	10.9%	
Trimesic acid	0.4%	
Benzenetetracarboxylic acids mainly 1, 2, 4, 5- and 1, 2, 3, 4-		17.3%
Benzenepentacarboxylic acid		1.9%
Mellitic acid		0.3%

The total yield of benzenecarboxylic acids was 43% of aromatic acids and 25% of coal (d.a.f.). The ratio of di- tri- and tetra-benzenecarboxylic acids was approximately 1 : 2 : 2.

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