



Full Length Article

The generation of benzene carboxylic acids from lignite and the change in structural characteristics of the lignite during oxidation



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HIGHLIGHTS

- Distribution of benzene carboxylic acids (BCAs) was obtained with alkali-oxygen oxidation of lignite.
- Relationship between distribution of BCAs and lignite structure was studied.
- The structural changes of lignite during alkali-oxygen oxidation was investigated with ¹³C NMR.
- The structural properties of residues and humic acids with oxidation time were revealed.

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ABSTRACT

Production of carboxylic acids (including 12 types of benzene carboxylic acids (BCAs) and small-molecule fatty acids) from lignite via oxidation has been widely studied, but few studies addressed the relationship between distribution of BCAs and structure of lignite. This work studies alkali-oxygen oxidation of Xiaolongtan lignite and distributions of BCAs with ¹³C NMR as well as the relationship between the distributions of BCAs and the lignite structures. The results indicate that the dominant aromatic structures in the lignite are naphthalene and benzene with a mole ratio of around 3, and an alkyl-substituted degree of aromatic rings of 0.359. These structure characters determine that the yields of benzene tricarboxylic acids, benzene tetracarboxylic acids, benzene pentacarboxylic acid and mellitic acid are more than those of other BCAs. In the oxidation process, the organic matter of lignite is first converted to humic acids (HAs), then to water soluble acids, and last to carboxylic acids. The last conversion step is the rate-controlling step. Analyses of the residues and HAs indicate that C–O bond of lignite is easily cleaved. The aromatic structures (except condensed aromatic rings) are easily depolymerized from lignite, but the condensed aromatic rings and long alkyl chains are difficult to be oxidized. With an increase in oxidation time, in the residues, the contents of aromatic structures decrease, but the contents of condensed aromatic rings and long alkyl chains both increase. While in HAs, the contents of condensed aromatic rings increase, but the average methylene chain length (C_n) decreases.

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1. Introduction

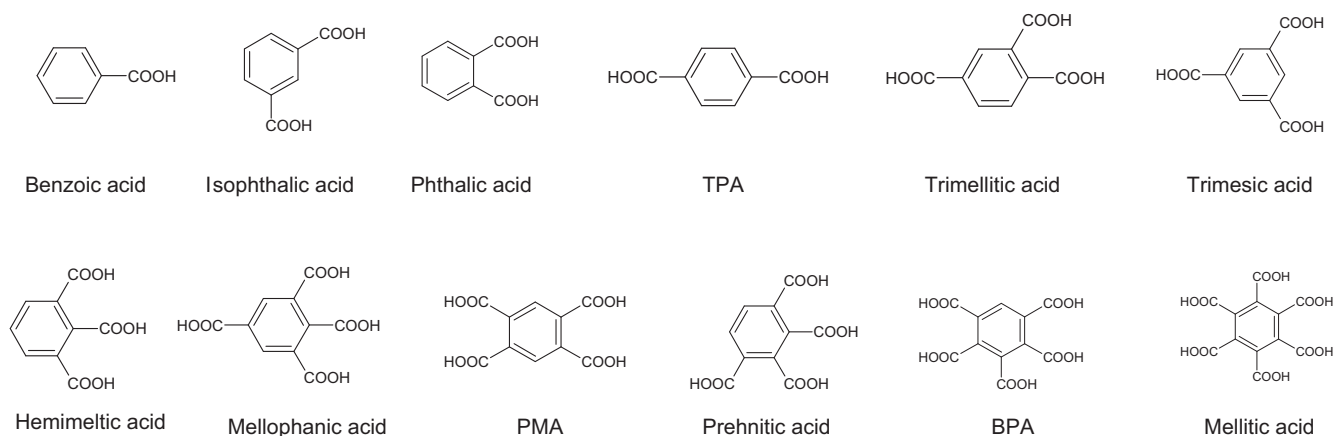
Coal is an important fossil energy and resource, and its structures and applications have been widely studied [1,2]. Lignite is a kind of low-rank coal and not favorable for traditional uses of high-rank coal, such as gasification and electric power generation due to its high oxygen content, high water content, low calorific value, and easy spontaneous combustion [1,3–5]. In light of its properties, lignite is favorable for manufacturing oxygen-containing carboxylic acids (CAs), including benzene carboxylic

acids (BCAs, whose structures are shown in Scheme 1) and small-molecule fatty acids, via oxidation [6–14].

Oxidation of lignite in aqueous alkali solutions with O₂, commonly referred as alkali-oxygen oxidation, has been widely studied to produce CAs [7,12,15–18]. For example, Zhang et al. [14] carried out alkali-oxygen oxidation of Huolinhe lignite at 240 °C and an alkali/coal mass ratio of 3/1, and obtained a BCAs yield of 22.5 wt % in 30 min. Franke et al. [19] studied alkali-oxygen oxidation of several coals at a NaOH/coal mass ratio of 6.71/1 and 250 °C, and obtained approximately 45% yield (based on carbon) of water soluble acids (WSAs). In our previous researches [16,17], oxidation of a lignite was carried out in an aqueous NaOH solution at 240 °C

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Scheme 1. The structures of BCAs obtained from selective oxidation of coal. Abbreviations: BPA, benzenepentacarboxylic acid; IPA, isophthalic acid; PMA, pyromellitic acid; TPA, terephthalic acid.

and a NaOH/coal mass ratio of 3/1, and yielded approximately 20 wt% BCAs and 40 wt% small-molecule fatty acids.

In the studies of alkali-oxygen oxidation of lignite, researchers paid more attention to increase BCAs yield rather than the relationship between BCAs yield and lignite's structure. Little information was reported on the degradation law and the structural changes of lignite during the oxidation.

In this work, oxidation of lignite is studied to investigate its conversion and distributions of BCAs. The structural parameters of the lignite, determined by ^{13}C NMR analysis, are correlated with the distributions of BCAs as well as that of humic acids (HAs) during the oxidation.

2. Experimental

2.1. Materials

The lignite used is Xiaolongtan lignite (XLT) from Yunnan province of China. Its proximate and ultimate analyses are shown in Table 1. The lignite was pulverized to pass a 200 mesh sieve before use. Sodium hydroxide (NaOH, 98%, AR), concentrated sulfuric acid (H_2SO_4 , 98%, AR), phosphoric acid (H_3PO_4 , $\geq 85\%$, AR), acetonitrile ($\text{C}_2\text{H}_3\text{N}$, 99.9%, GR) and isopropanol ($\text{C}_3\text{H}_7\text{OH}$, 99.9%, GR) were purchased from Beijing Chemical Plant. Oxygen (O_2 , 99.995%) was supplied by Beijing Beiwen Gases Co., Ltd. (Beijing, China). All the reagents were used without further purification.

2.2. Oxidation of lignite

Oxidation of the lignite was carried out in a high-pressure batch reactor made with Hastelloy (HC276), supplied by Haiyan Petroleum Scientific Research Co., Ltd., Jiangsu, China. The reactor is 50 cm^3 in inner volume and equipped with a magnetic stirrer. In a typical experiment, 1.00 g lignite, 3.00 g NaOH, and 20.0 cm^3 distilled water were loaded into the reactor. Next, the reactor was sealed and purged with O_2 . After that, O_2 was charged into the

reactor to a desired pressure. Then, the reactor was placed into a furnace and heated at a rate of approximately 13–15 $^\circ\text{C}/\text{min}$ to a desired temperature that was monitored by a K type thermocouple with an accuracy of ± 1 $^\circ\text{C}$. When the desired temperature was reached, the reaction time was recorded. During the reaction, the mixture was stirred at a constant speed of 500 rpm. After the reaction, the reactor was transferred into a cold water bath to quickly stop the reaction. When the reactor reached room temperature, the mixture in the reactor was transferred to a beaker and separated by a filter of 0.45 μm in pore size. The filtrate was adjusted to pH of 1.5 by titrating with concentrated sulfuric acid and then diluted for further analysis. The filtration residue was washed with distilled water and dried in air.

2.3. Analyses of humic acids, water soluble acids, and CO_2

As shown above, after the oxidation of lignite, the mixture in the reactor was separated to yield filtrate (I) and a residue. The carbon content of the filtrate (I) was analyzed with a total organic carbon analyzer (TOC, Shimadzu TOC-L CPN, Japan). The filtrate (I) is an alkaline solution and hence produced CO_2 is also soluble in the solution. Based on the inorganic carbon content (analyzed with TOC) of the solution, the CO_2 yield was obtained. The filtrate (I) was adjusted to pH of 1.5 by titrating with concentrated sulfuric acid and insoluble substances occurred. Then filtration of the mixtures was performed to obtain a filtrate (II) and solid substances. These filtrate (II) and solid substances were water soluble acids and humic acids, respectively. The humic acids and water soluble acids were quantitatively analyzed using TOC for carbon contents.

2.4. Analysis of CAs

BCAs and small-molecule fatty acids in liquid samples were analyzed by a high-performance liquid chromatography (HPLC, Waters 2695, USA) using different methods. A binary gradient elution procedure was used for BCAs. The mobile phase was acetonitrile.

Table 1
Proximate and ultimate analyses of XLT.

Proximate analysis/wt%			Ultimate analysis/wt%, in daf basis				
M_{ad}	A_{d}	V_{daf}	C	H	O*	N	S
16.4	14.5	50.7	73.7	3.9	20.1	1.3	1.0

XLT: Xiaolongtan lignite. ad: air-dry basis; d: dry basis; daf: dry-and-ash-free basis. M: moisture; A: ash; V: volatile matter content.

* By difference.

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