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Oxidative depolymerization of Shenfu subbituminous coal and its thermal dissolution insoluble fraction

Chun-Xiu Pan [a],*, Hua-Long Liu [a], Qian Liu [a], Heng-Fu Shui [a], Zhi-Cai Wang [a], Zhi-Ping Lei [a], Shi-Gang Kang [a], Xian-Yong Wei [b]

[a] School of Chemistry & Chemical Engineering, Anhui University of Technology, Ma'anshan 243002, Anhui, China
[b] Key Laboratory of Coal Processing and Efficient Utilization, Ministry of Education, China University of Mining & Technology, Xuzhou 221116, Jiangsu, China

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ABSTRACT

The oxidative depolymerizations of Shenfu subbituminous coal (SSBC) and its thermal dissolution insoluble (TDI), which obtained by thermal dissolution (TD) in 1-methylnaphthalene at 320 °C, were investigated with H_2O_2 aqueous solution as oxidant under different conditions. Their products were characterized by FTIR, ultimate analyses and acidic functional groups determination. Further, the detailed comparison of oxidative depolymerizations of SSBC and its TDI was carried out with 20% H_2O_2 at 60 °C. The water solubles (WSs) were esterified, and subsequently analyzed by GC/MS in order to understand the macromolecular structural features of SSBC. The results revealed that compared with SSBC, the TDI contained more phenolic hydroxyls and showed higher oxidation reactivity. It suggested that the phenolic hydroxyl should be the active site of oxidative depolymerization, and thermal dissolution generated substantial phenolic hydroxyls in TDI by the rupture of C_{al}–OAr. The WS from the oxidation of SSBC mainly consists of monocyclic aromatic acids, while the WS from TDI contains much amount of alkanoic acids and α,ω-dicarboxylic acids. Especially the substantial oxalic acid and malonic acid identified in the WS from TDI suggested that significant amount of the aromatic rings in the macromolecules of SSBC could be coupled directly or connected by monomethylene bridge.

1. Introduction

Oxidative depolymerization has been paid more attention as an effective technique to reveal the coal structure and obtain high value-added compounds [1–16]. The key to understand the coal structure is to study the kind and distribution of the bridge bonds, aliphatic structures and aromatic clusters. It was concluded that oxidation would convert aromatic carbons bonded to alkylene bridges or pendant alkyl groups into corresponding α,ω-alkanedicarboxylic acids (ADAs) or alkanoic acids (AAs). By comparison of the oxidations of a lignite and a bituminous coal with NaOCl as oxidant, Gong et al. [1] suggested that the amounts of phenyl group, bridge bonds and hydroaromatic structures in lignite were much higher than those in bituminous coal. Hayashi et al. [2,3] described the relationship between the decrease in the number of bridges and clusters and the increase in the proportion of low-molecular-mass network fragments through O_2 oxidation. Several researchers [4–7] have claimed that H_2O_2 oxidation could decompose the covalent bonds and contribute to the breakdown of the associated macromolecular structure. Rutheniumion catalyzed oxidation (RICO) was introduced to the field of the fuel chemistry by Stock [8]. Murata et al. [9–11] conducted the RICOs of different rank coals. The analysis of RICO products indicated that the distribution of alkylene bridge bonds is similar to each other and the most popular bridge is dimethylene bridges, which can be oxidized to give high yield of succinic acid. The RICO of Shenfu subbituminous coal [12,13] suggested that it is rich in α,ω-diarylalkanes with carbon number of methylene linkage from 2 to 4. The investigation of RICO of Huolinguole lignite suggested that $-CH_2CH_2-$ and $-CH_2CH_2CH_2-$ are dominant bridged linkages [14]. It is commonly considered that the numbers of longer alkyl chains and bridges in lignite are greater than those in subbituminous coal and monomethylene bridge has been thought the most popular alkylene bridge bonds in subbituminous coal [15]. But as far as we know, there was little direct experiment evidence to support the view. It was proposed that malonic acid produced from monomethylene bridge in RICO is unstable, that is the reason why no malonic acid was detected in the RICO products [15].

Meanwhile, it is well known that both macromolecular networks and low molecular weight compounds (LMWC) are presented in coal structure. The LMWC can be separated from the macromolecular networks by means of extraction [16]. But most of the previous works are focused on the oxidation of raw coal. It is liable to be confused to investigate the network structures of coal by oxidation without removal of the LMWC. Thus, we presented a two-step depolymerization method

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* Corresponding author.
E-mail address: panchunxiu@sina.com (C.-X. Pan).

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Table 1
Proximate and ultimate analyses (wt.%) of SSBC.

Proximate analysis			Ultimate analysis (daf)				
M_{ad}	A_d	V_{daf}	C	H	N	O^a	$S_{t,\,d}$
8.2	6.9	31.9	79.4	4.7	1.7	>13.8	0.4

daf: dry and ash-free base; M_{ad}: moisture (air dried base); A_d: ash (dry base, *i.e.*, moisture-free base); V_{daf}: volatile matter (dry and ash-free base); $S_{t,\,d}$: total sulfur (dry base); ^{a} by difference.

including thermal dissolution (TD) and subsequent oxidation to understand the macromolecular structure of Xianfeng lignite (XL) [17]. The high yields of succinic and malonic acids in water-soluble products indicated that there are not only a lot of dimethylene bridges but also a certain amount of monomethylene bridges in XL. In this work, further examination was performed on the H_2O_2 oxidations of Shenfu subbituminous coal (SSBC) and its thermal dissolution insoluble (TDI) to understand the macromolecular structural features of subbituminous coal.

2. Experimental

2.1. Materials

SSBC was collected from Shenfu coal field, China. It was pulverized to pass through a 200-mesh sieve and dried in a vacuum at 80 °C for 24 h. All reagents used in the study are analytical reagents. Table 1 lists the proximate and ultimate analyses of SSBC.

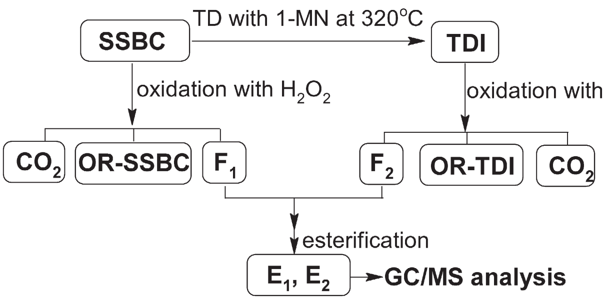
2.2. Experimental procedure

Scheme 1 shows the experiment procedures including TD, oxidation, and subsequent treatments, detailed information can be available in our previous works [17,18]. TD of SSBC in 1-methylnaphthalene (1-MN) solvent was carried out at 320 °C to obtain the TDI. The TD yield (daf, *i.e.*, dried and ash-free) of SSBC was 46.0% [18]. The dried SSBC and its TDI were oxidized with H_2O_2 aqueous solution as oxidant. CO_2 released from the reaction system was collected in a U-shaped tube packed with soda-lime. The reaction mixture was filtered and washed with H_2O to afford filter cake, then it was dried in a vacuum at 80 °C for 24 h to obtain the oxidation residue (OR). The effect of different temperatures (40 °C, 60 °C and 80 °C) on oxidation was carried out with 30% H_2O_2. The effect of different H_2O_2 concentration on oxidation was studied at 60 °C. The oxidation conversion (1) and the yield of CO_2 (y_{CO2}) based on coal sample before oxidation were calculated according to the masses of SSBC or TDI ($m_{0,}$ daf), the corresponding OR ($m_{1,}$ daf) and CO_2 (m_{CO2}).

$$\text{Conversion} = (m_0 - m_1)/m_0 \quad (1)$$

$$y_{CO2} = m_{CO2} \times 12/44/(m_0 \times C) \quad (2)$$

where C is the carbon content of coal sample before oxidation. The experimental error is within 3%.



Scheme 1. Procedures of experiment.

2.3. Sample analyses

The ultimate and FTIR analyses were performed by Vario EL III CHNS and NICOLET6700, respectively. The contents of acidic functional groups were determined by the titration method [19]. The E_1 and E_2 were analyzed by GC/MS (Thermo Trace GC Ultra-ISQ). Compounds were identified by comparing their mass spectra with spectral data in the instrument library. The relative content was determined by the peak area normalization method.

3. Results and discussion

3.1. Oxidation of SSBC and its TDI under different conditions

The H_2O_2 oxidations of SSBC were carried out and it was found that the oxidation activity of SSBC was much lower than that of XL we investigated before. The conversion of SSBC at 40 °C even in 30% H_2O_2 was only 0.8%, while that of XL at 40 °C in 5% H_2O_2 was 55.16% [20]. As shown in Fig. 1, it can also be observed that the conversion and CO_2 yield of TDI-SSBC are markedly higher than those of SSBC at 40 °C. However, the oxidation activity of the TDI from XL obviously decreased after TD [20]. Therefore, the oxidation performances of SSBC and its TDI were significant different from XL and its TDI.

Further, the oxidation of SSBC and its TDI were carried out under different conditions. As shown in Fig. 1a, the conversion and CO_2 yield of SSBC and its TDI increased with the increasing of oxidation temperature. When the temperature was increased to 80 °C, the conversion and CO_2 yield of SSBC significantly increased to 66.2% and 59.9%, the conversion and CO_2 yield of TDI increased to 54.4% and 52.2% respectively. Whether for SSBC or its TDI, as the temperature increased from 60 °C to 80 °C, the CO_2 yield increased faster than the conversion and got a very high value even comparable to the conversion. It is suggested that the water soluble oxidized derivatives could be susceptible to be oxidized to CO_2 at 80 °C. It can also be found that the influences of temperature on CO_2 yield of SSBC and TDI are similar. It was speculated that the oxidation activities of water soluble oxidized derivatives from SSBC and TDI are similar. But compared with SSBC, the conversion of TDI is less affected by oxidation temperature. This may be attributed to the different structural features of SSBC and its TDI. Meanwhile, the oxidation results of SSBC in different concentrations of H_2O_2 aqueous solution at 60 °C (Fig. 1b) show that the conversion and CO_2 yield of SSBC increased with the increasing of H_2O_2 concentration. While the initial H_2O_2 concentration increased to 30%, the CO_2 yield significantly increased. Similar effects of H_2O_2 concentration on the oxidation of TDI can also be observed in Fig. 1b. Although high concentration of H_2O_2 aqueous solution leads to the high production of CO_2, it is obviously that compared with oxidation temperature, the concentration of H_2O_2 shows less influence on the yield of CO_2.

The analysis results of acidic functional groups (Table 2) show that the contents of acidic functional groups of SSBC are all very low. After oxidation at 40 °C, the contents of phenolic OH and COOH of OR-SSBC changed little. While the oxidation temperature increased to 60 °C the contents of phenolic OH and COOH of OR-SSBC increased greatly. However, with the temperature increased to 80 °C, the contents of acidic functional groups of OR-SSBC slightly decreased. Combined with the higher yields of CO_2 at 80 °C, it indicated that deep oxidation such as decarboxylation of carboxylic acids was more likely to occur at 80 °C. Table 2 also shows that as the H_2O_2 concentration increased from 10% to 20% the contents of acidic functional groups of OR-SSBC increased significantly. While the H_2O_2 concentration further increased to 30%, the changes of the contents acidic functional groups of OR were not obvious. It can be explained that the oxidized derivatives (oxygen-containing compounds) especially the ring-hydroxylated products should be active to degrade, so that the contents of acidic functional groups of OR would not increase infinitely along with the increase of oxidation temperature and H_2O_2 concentration.

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