



Study of oxidization of coal–pitch by O₃

Wang Yaoling^a, Chen Sishun^b, Ding Mingjie^{a,*}, Xu Zhan^a

^a School of Chemical and Material Engineering, Henan University of Urban Construction, Pingdingshan 467036, China

^b Department of Light Industry, Luohe Vocational Technology College, Luohe 462002, China



ARTICLE INFO

Article history:

Received 10 November 2015

Received in revised form 12 December 2015

Accepted 16 March 2016

Available online 25 May 2016

Keywords:

Study

Coal–pitch

Ozone oxidation

Depolymerization

ABSTRACT

For the purpose of obtaining small molecular and oxygen-containing aromatic compounds, taking a toluene-extracted coal pitch as the research object, the oxidation of coal–pitch by ozone (O₃) in formic acid was studied. The coal–pitch sample and the oxidized pitch residue were characterized by elementary analysis and Fourier transform infrared spectroscopy (FTIR), while the small molecular products were analyzed by a gas chromatography–mass spectrometer (GC–MS). The results show that the highest oxygen content of oxidized coal pitch had been acquired at a reaction temperature of 50 °C, an O₃ flow rate of 6300 mg/h and a reaction time of 4 h. Quite a lot of hydroxyls and carbonyls were introduced into the structure of the oxidized coal–pitch, while the small molecules produced mainly involve nonpolar aromatic compounds, aromatic anhydride and quinone compounds. It is speculated that the mechanism is direct electrophilic oxidation in which the molecules of O₃ directly attack the aromatic ring at its carbon atoms with high electron density, and then generate hydroxyl or carbonyl until the aromatic ring cracks. This study shows that O₃ can make the fused aromatic ring of coal–pitch become oxidized and depolymerized, and hence the ozonization of coal–pitch can be a potential method for obtaining oxygen-containing aromatic compounds.

© 2016 Published by Elsevier B.V. on behalf of China University of Mining & Technology.

1. Introduction

The huge coal coking industry of China generates great amounts of coal tar every year [1], about 50–60% of which is transformed into coal pitch in further processing. The main uses of coal pitch are ordinary and inferior asphalts, some of which can be converted into high-quality asphalts for preparing high value-added needle coke and carbon fiber after purification and modification [2–6]. Most of the rest are still inferior asphalts with no better utilization than for the use of road or building asphalt and waterproof coatings [7]. It is therefore of great significance for the coal coking industry to research and develop new and effective applications for coal–pitch.

Coal–pitches are mainly composed of polycyclic aromatic hydrocarbons and heterocyclic aromatic compounds of oxygen, sulfur and nitrogen, which can be oxidized to prepare corresponding aldehydes, ketones, aromatic acids, quinones, epoxides and peroxides, etc., many of which are important chemical intermediates [8,9]. Previous studies on coal–pitch oxidation have mainly been carried out using air or oxygen for the purposes of improving the degree of molecular polymerization and enhancing the

softening point to prepare the isotropic coal–pitch [2,10]. Oshika and Okuwaki performed an investigation of two-step oxidation of coal–tar pitch using an O₂/NaOH system, in which the pitch was oxidized with oxygen firstly in water and then in a NaOH solution, which yielded 51–79% (by weight) of water-soluble aromatic acids (WSAA) under optimum conditions. About 40–50% of the WSAA were benzene carboxylic acids [11]. This study proved the possibility of obtaining some small-molecular oxygen-containing aromatic chemicals by oxidation of coal–pitch.

In addition, the study of coal oxidation can be used for references to the coal–pitch oxidation to some extent. Initial studies on coal oxidation were carried out for research into depolymerizing the macromolecular structure of coal and coal chemistry, or for coal desulfurization, while coal oxidation for fine chemicals has drawn more attention only in recent years [12–15]. The Wei Xianyong group had studied the oxidation of different coals under mild conditions using NaClO, H₂O₂ and RICO as oxidizing agents and obtained high yields of small molecule aromatic acids [16–23]. These results can guide the study of oxidation of coal and coal–pitch to some extent.

Ozone (O₃) dissolved in water can produce some active particles with strong oxidation capability, such as the hydroxyl radical, and single atomic oxygen, and has mainly been used for the degradation of organic substances in wastewater [24,25]. Semenova et al.

* Corresponding author. Tel.: +86 18537505593.

E-mail address: dingmj2004@126.com (M. Ding).

studied the ozonation of lignite to prepare and modify the multi-purpose humic acid, and found that about 90% of the organic matter in lignite was converted to soluble products in polar organic solvents, most of which are of aromatic acids [26]. Patrakov et al. treated coal organic matter with O_3 , and then studied the influence of ozone treatment on the liquefaction effect of the coal, and found that the oxygen content in the forms of ether and quinone groups is increased for low and middle rank coals, and concluded that the ozonation of coals could depolymerize the large macromolecules in coal and promote the formation of weak polar bonds in the coal structure [27]. Both the studies above showed the possibility of coal–pitch oxidation by O_3 , and made us think of obtaining aromatic quinone compounds by coal–pitch ozonation.

Based on the above considerations, this paper describes an experimental study of coal–pitch ozonation in formic acid solvent, the results of which show that the method can effectively convert the aromatic structure of coal–pitch into small molecule aromatic acid and a certain number of quinone products.

2. Experimental

2.1. Coal–pitch sample and solvents

The coal–pitch was supplied by Kaifeng Carbon Co. Ltd., China Pingmei Shenma Group in Henan Province. All the samples were sufficiently dried and pulverized to pass through a 100-mesh sieve, then extracted with toluene to remove the small molecules possibly existing in it followed by drying in a vacuum oven at 40 °C for 24 h. The samples were then stored in a desiccator prior to their use in the experiments. The coal–pitch samples mentioned in this paper below refer to this toluene-extracted coal–pitch prepared as described above.

All the solvents, including acetone, ethanol, formic acid and toluene, were commercially purchased and of analytical grade.

Ozone was obtained by a DJ-Q8080 ozone generator made by China Jinhua Instrument Plant, giving a mass flow rate of O_3 of 6300 mg/h with a concentration of 18–20% by weight.

2.2. Ozone oxidation process

The oxidation reaction was carried out in a 250 mL three-necked flask equipped with a reflux condenser, a thermometer and an ozone generator in which 5 g of coal–pitch was ultrasonically dispersed into 120 mL formic acid. The reaction system was heated to the desired temperature by a unitary thermostatic water bath and reacted under magnetic stirring for 4 h.

After the reaction, the produced solid–liquid mixture was statically deposited for enough time, and the upper clear solution was decanted. The lower solid deposit was then extracted with about 100 mL of formic acid, statically deposited and the upper clear solution decanted again. The procedure above was repeated three times. The final sediment, i.e. the oxidized coal–pitch (OCP) was dried in a vacuum oven under room temperature. All the upper clear solution obtained above was merged together, then filtered through a membrane filter with a pore size of 0.45 μm , and the filtrates were evaporated under vacuum by a rotary evaporator to distill off the solvent and obtain a fraction of small molecule products (SMP).

2.3. Analysis methods

2.3.1. Elementary and FTIR analysis

The coal–pitch sample and the OCPs were characterized by an Elementar Vario MACRO Cube element analyzer and a Nicolet iS10 FTIR spectrometer. FTIR analysis was performed using thin

KBr plates as the sample holder prepared by accurately weighed 1 mg of coal pitch sample or OCP sample and 100 mg of KBr. These were ground and mixed uniformly in an agate mortar, then pressed into tablets for testing. The IR scanning range was set from 400 to 4000 cm^{-1} with an accuracy of 0.01 cm^{-1} and frequency of 32 times per second.

2.3.2. GC/MS analysis

The SMP were dissolved with acetone and analyzed on an Agilent 7890/5975C GC/MSD equipped with a DB-35MS capillary column and a quadrupole analyzer. The analysis conditions included an electron bombarding voltage of 70 eV, a helium carrier gas with a flow velocity of 1 mL/s, a split ratio of 20:1, an injection temperature of 300 °C and a mass scanning range from 30 to 500 amu. The column oven of the GC/MSD was heated from 100 to 300 °C at a raising rate 6 of 10 °C/min and then maintained at 300 °C until no peak was observed on the GC. The data were acquired and processed by the workstation software of GC/MS, and the compounds were identified by retrieving in NIST08 spectral library and referring to available references.

3. Results and discussion

3.1. Elemental composition

As listed in Table 1, the elementary analysis of coal pitch and its OCPs at different temperatures shows that the contents of carbon and hydrogen decreased, accompanied by a corresponding increase in the oxygen content. The maximum in oxygen content occurred at 50 °C suggesting that many of the oxygen atoms were introduced into the coal–pitch molecules, and the proper reaction temperature is 50 °C. Thus the following discussions in the present paper focus on the results at 50 °C.

Also as listed in Table 1, the oxygen content of OCPs increased firstly from 25 to 50 °C then decreased slightly after 50 °C, combining together with the decline in O/C after 50 °C, guessing that the oxidation products could not be stable but just an intermediate state in this temperature range, which may be converted into the small molecular products or changed into the oxygen-containing gaseous compounds because the oxidation intensity of coal pitch increased with rising reaction temperature.

3.2. FTIR spectra analysis

The FTIR Spectra of the coal–pitch sample and its OCPs of 50 °C are shown in Fig. 1.

As shown in Fig. 1a, the fused aromatic structure of the coal pitch sample was featured by the obvious absorption of aromatic C–H stretching vibration at 3040 cm^{-1} , the stretching vibration of C=C of the aromatic ring at 1600 cm^{-1} and the C–H deformation vibration of the aromatic ring at 1400 cm^{-1} , while no clear

Table 1
Elementary analysis of coal pitch sample and OCPs.^a

Sample ^b	C (wt%)	H (wt%)	O (wt%)	O/C
0	90.92	4.327	1.327	0.01460
1	76.50	3.631	16.340	0.2136
2	75.84	3.558	17.484	0.2305
3	74.85	3.503	18.243	0.2437
4	79.34	3.604	13.949	0.1758
5	79.18	3.547	13.867	0.1751

Note:

^a By an Elementar Vario Macro Cube element analyzer.

^b 0 refers to coal pitch sample, and 1, 2, 3, 4 and 5 refer to the OCPs of 25 °C, 40 °C, 50 °C, 60 °C and 70 °C in the order.

Download English Version:

<https://daneshyari.com/en/article/275375>

Download Persian Version:

<https://daneshyari.com/article/275375>

[Daneshyari.com](https://daneshyari.com)