Journal of Analytical and Applied Pyrolysis xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Effects of extractable compounds on the structure and pyrolysis behaviours of two Xinjiang coal

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ARTICLE INFO

Keywords:
Extractable compounds
Pyridine vapor swelling
Structure
Coal pyrolysis
Xinjiang coal

ABSTRACT

The extractable compounds are a very important part of coal and play an important role in the pyrolysis of coal. To further understand the effect of the extracts on the structure and pyrolysis behaviours of coal, Naomaohu (NMH) lignite and Hutubi (HTB) bituminous coal were extracted with pyridine and swollen with its solvent vapor. The pyrolysis process was performed in a fixed-bed reactor. Thermogravimetric analysis (TGA) of the coal samples was carried out on a thermogravimetric (TG) analyser. The pore structure characteristics of the coal samples and their chars obtained from pyrolysis at different temperatures were measured by the mercury intrusion porosimetry (MIP) method. The components of the pyrolysis gas were detected by gas chromatography (GC). It was found that the extraction and swelling processes enlarged the pore size and improved the porosity of the coals to some extent. Compared with the pyrolysis of the raw coal, that of the swollen coal resulted in a higher tar yield owing to the destruction of the cross-linked structure and the variations in the coal structure; the tar yield for the pyrolysis of all the residues decreased significantly, but the gas yield increased, where the volume of the CO gas mainly increased. The NMH residue char obtained from pyrolysis of the residue at different temperatures had a lower proportion of micropores than the HTB residue char. The extractable compounds will be converted to gas-phase (e.g. volatiles) and liquid-phase (e.g. colloids) products during the pyrolysis process, which could stabilise the free radical fragments, form coke in the pore structure of the char and increase the number of new micropores formed.

1. Introduction

Pyrolysis is an essential step in the thermal conversion of coal, and studies of this process have been performed for hundreds of years [1]. To gain insight into the structure and composition of different types of coal, previous researchers have proposed over one hundred models for the coal molecular structure [2]. Based on the two-phase (host-guest) model, coal is composed of a fixed phase and a mobile phase, which can be separated by solvent extraction [3]. Previous studies showed that the mobile phase mainly refers to extractable compounds with molecular weights less than 500, including hydrocarbons and oxygenates that are free or embedded in the host network structure of the coal macromolecules [4,5].

These parts of coal exhibit high thermal plasticity and decomposability, and the formation of colloids and the cohesiveness of coal depend to a large extent on the content of extractable compounds [6–8]. The content of extractable compounds also has a significant effect on the caking property of coal. When the extraction yields in mixed solvents decrease, the caking indexes of coal decrease [9]. However, there is still a poor understanding of the complexity of these chemical and physical decomposition processes of coal, especially the interactions between each part [1]. The pyrolysis behaviours of the extracts and residue of coal are very different [10–12]. The extracts can be directly volatilised, converted to gas-phase products, or cracked into smaller molecules during thermal decomposition, which plays an important role in serving as mobile hydrogen donors to stabilise the radical fragments that split from the coal macrostructure [13]. The extraction residue is mainly composed of macromolecules, and its pyrolysis behaviour involves polycondensation reactions and free radical reaction processes [11,12]. There are different contributors to the formation of pyrolysis products, such as tar and gas, but the extracts and extraction residue also interact with each other through hydrogen donation and mass transfer [14]. However, there are few research reports that compare the swollen coal (in-situ extractable compounds in

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https://doi.org/10.1016/j.jaap.2018.04.012
Received 26 February 2018; Received in revised form 13 April 2018; Accepted 16 April 2018

coal structure) and extraction residue (removal of the extracts from coal) to further investigate the structure of coal and gain insight into the pyrolysis behaviours of coal. The extractable compounds can influence the physical and chemical structure. Those will influence the pyrolysis behaviours of coal, such as pyrolysis product distribution, the secondary reaction and the formation of char structure, particularly the formation and accumulation of the liquid phase (e.g. colloids) during the pyrolysis process. The content of extracts would have a significant impact on the liquid products, where the destruction of the cross-linked structure will increase their yield and the enlarging of the pore structure will decrease the coke formation in coal during the coal process.

In this study, two Xinjiang coals, Naomaohu (NMH) lignite and Hutubi (HTB) bituminous coal, with different coal ranks and extraction yields were chosen. The extractable compounds were separated by pyridine extraction. To avoid displacing the extractable compounds from the coal structure and to compare them with the residue and raw coal, the coal was swollen with pyridine vapor. The pyrolysis products, especially the pyrolysis gas, were collected and analysed. The coal samples and their char from pyrolysis at different temperatures were measured to understand the effect of the extractable compounds on the formation of the char structure.

2. Material and methods

2.1. Coal samples

The Naomaohu (NMH) lignite and Hutubi (HTB) bituminous coal, collected from Xinjiang, China, were crushed, sieved to < 74 μm and dried at 80 °C in a vacuum oven to constant weight before use. Their proximate and ultimate analyses are given in Table 1.

2.2. Pre-treatment of coal samples

Generally, there are five kinds of binding forces exist in coal, including covalent bond force and four non-covalent bond forces: van der Waals force, hydrogen bond force, ion crosslinking force and π ~ π electron interaction. Toshimasa Takanohashi et al. [15] found that acetic acid, methoxyacetic acid and other organic acids can effectively destroy the coal in the carboxylic acid ion crosslinking bond, which is conducive to the solvent extraction process.

The coal samples were pretreated with low-concentration organic acid to destroy ion crosslinking force and the procedure for pre-treatment is as follows: the coal samples were pretreated with 20% (v) acetic acid for 48 h at room temperature, filtered and washed with deionised water until the filtrate was neutral, and dried at 80 °C in a vacuum oven.

2.3. Extraction and swelling

Approximately 30 g of coal and 300 mL of pyridine were added to a Soxhlet vessel (500 mL). The apparatus was heated in an oil bath to approximately 140 °C and removed from the bath when the circulating solvent become clear. Ethanol was used to remove the remaining pyridine. The extracts and residue were dried at 110 °C in a vacuum oven to constant weight. Finally, the extraction yield of the NMH coal and the HTB coal were 16.58% and 6.51%, respectively. Approximately 50 g of coal was put in a glass thimble under a flow of pyridine vapor. The apparatus was maintained at 135 °C for 12 h to avoid solvent condensation. Pyridine was purified by distillation before use.

Table 1
Proximate and ultimate analyses of the coal samples.

Sample	Proximate analyses/wt.%			Ultimate analysis w_{daf}/%				
	M_{ad}	A_d	V_{daf}	C	H	O[a]	N	S
NMH	16.09	8.76	37.59	64.90	6.42	26.75	1.05	0.88
HTB	2.67	6.12	30.46	76.62	4.37	17.71	0.97	0.33

[a] By difference.

2.4. Pyrolysis experiments

The pyrolysis experiments were performed with approximately 20 g of sample in a fixed-bed reactor. The coal was heated to the desired temperature at a rate of 10 °C min^{-1}, and then the pyrolysis temperature was held for 20 min to remove the volatiles. The liquid products were collected in a cold trap at −10 °C, and tar/water separation was carried out according to the method of ASTM D95–05e1 (2005).

The air bags with a volume of 5 L were pre-vacuumized and closed the valve, and then connected to the pyrolysis apparatus; to commence the pyrolysis experiment and open the valve; after the end of reaction and cooling to room temperature, the valve was closed again. The bag collects all pyrolysis gases during the process of pyrolysis. The procedure for obtaining the gas weight is as follows; the composition and content of pyrolysis gas were detected by gas chromatography; the volume were measured by drainage method; the total weight of pyrolysis gases was calculated based on the composition and volume of detected gas.

The yield of tar, water, gas, and char, calculated according to the dry (d) basis of the coal sample, was defined as follows:

$$y_x = \frac{w_x}{w_0}$$

where x = tar, water, gas, or char, y_x is the yield of the product, and w_x and w_0 are the weights of the pyrolysis products and the sample, respectively.

2.5. Sample analyses

FTIR analyses were performed on a Nicolet 6700 spectrometer (USA, Thermo Scientific Co.) whose measuring range, spectral resolution, and numbers of scan were 4000–400 cm^{-1}, 4 cm^{-1}, and 32, respectively. The coal sample was blended with KBr powder at a mass ratio of 1:100 (coal sample to KBr), pressed to a pellet and then analysed the pellets.

To investigate the pyrolysis process of different coal samples, thermogravimetric (TG) analysis were carried out on a STA-449-F3 Jupiter TG analyser. About 10 mg coal sample was placed in a ceramic crucible, heated from a room temperature up to 110 °C with a heating rate of 10 °C min^{-1}, kept at 110 °C for 30 min to remove water, and then rose the temperature up to 900 °C with the same heating rate. The protective gas of thermal balance and carrier gas are Argon (purity 99.999%) with a flow rate of 20 mL min^{-1} and 100 mL min^{-1}, respectively.

The pyrolysis gases, including H_2, O_2, N_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, were analysed by a gas chromatograph (GC–7890 A, Agilent) equipped with the Agilent G3591-80135/6 column and a thermal conductivity detector (TCD). The column temperature was set an initial temperature of 50 °C, held for 3 min, rose the temperature up to 100 °C at a heating rate of 10 °C min^{-1}, and then kept 14 min. The detector temperature was set to 200 °C and the inlet temperature was kept to 150 °C. Gas injection volume was 1 uL. Area normalization was used for quantitative analysis. The protection gas was Ar with a flow rate of 15 mL min^{-1}.

The mercury intrusion porosimetry (MIP) test was conducted on an AutoPore IV 9500 instrument (Micromeritics Instrument Corporation) with a measuring range of 5 nm–360 μm. A penetrometer (powder, 5 cc sample volume) with a stem volume of 1.836 mL was selected, while sample loading was done to achieve a used stem volume of 25–90% under high pressure intrusion. Samples can be pressurised from 6 psi (41.4 kPa) to 30,500 psi (210.3 MPa) and the mercury contact angle and Hg surface tension during intrusion were assumed to be 130° and