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Investigation of mechanism and kinetics of non-isothermal low temperature pyrolysis of perhydrous bituminous coal by in-situ FTIR

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ABSTRACT

Perhydrous coal has advantages as a fuel source and raw material for hydrocarbon production over other coal with similar rank. Good understanding of thermal characterization of perhydrous coal can provide important information for control of the pollutants release and enhancement of the conversion rate of coal during its utilization. A perhydrous bituminous coal from Dingji Coal Mine, China was selected for the investigation of the non-isothermal pyrolysis process below 500 °C in N_2 flow by in-situ transmission FIIR. Evolutions of the main functional groups in coal, including aliphatic groups, aromatic C=C and C—H, carbonyl, C—O and hydroxyl could be divided into several stages. The thermal characterization of each stage was discussed. The aliphatic groups and aromatic C=C content decreased slightly with the volatilization of small molecules below 400 °C, while the amount of aromatic C—H increased with the loss of substituent groups. The conversion of C—O to C=O contributes to the slight increase in the C=O amount below 370 °C, and the decrease of hydroxyl was attributed to loss of water and the condensation and elimination of hydroxyl groups. The amount of all functional groups except for the aromatic C—H declined rapidly with the cracking of C—C bonds after 400 °C. The kinetic characterization of pyrolysis stages for three functional groups, including aliphatic groups, C—O and hydroxyl, was studied with modified integral method. Activation energy of pyrolysis stages of the three functional groups increased with rising temperature. Kinetics for the different stages of functional groups were fitted with different kinetic models. The initial loss of aliphatic groups and C—O was controlled by diffusion. Then, the reaction of the three functional groups fitted on the first-order or third-order reaction models. The results obtained by in-situ FTIR revealed more detail information about thermal characterization and kinetic characterization and can be expected to lead to good understanding of pyrolysis of a perhydrous coal.

1. Introduction

Perhydrous coal is a type of coal that is enriched with hydrogen (4.6–5.6, wt.%) or has a higher atomic ratio of hydrogen and carbon (H/C) compared to other types of coal of similar rank [1]. The hydrogen enrichment gives rise to the modifications in the macromolecular structure of the coal, thus affecting the properties and behavior of the coal [2,3], such as high calorific value [4], higher volatile matter content and enhancement of oil/tar potential [2]. Perhydrous coal was used as a good fuel source and applied in the field of hydrocarbon generation [5].

However, the complexity of coal composition and structure limits its utilization, and consumption of with large quantities of coal releases a high amount of pollutants such as SO_2, CO_2 and organic matter [6]. Thermal decomposition may be the initial step during the main processes of coal utilization including combustion and gasification [7]. Good understanding the mechanism of coal pyrolysis can help controlling the release of pollutants and enhance the conversion rate of coal, beneficial for clean and effective utilization of coal. Additionally, the decomposition reaction of can provide basic information concerning the structure of perhydrous coal molecules [8]. Furthermore, there is a similarity between the artificial pyrolysis and natural coalification, so that pyrolysis was often employed to study coalification process [9,10].

In the past decades, many studies have addressed the pyrolysis of coal. General pyrolysis reactions and processes were established [11–13] and can be summarized as follows. At low temperature, some weak non-covalent bonds such as hydrogen bond are cracked and reduced. Compounds bonded by these weak bonds are slightly vaporized and released from solid coal. With rising temperature, bridge bonds begin to be cleaved, resulting in the formation of free radical groups and subsequent production of gas, tar and char.

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Finally, the solid residue undergoes further condensation reactions with the release of secondary gases (mainly CO and H_2). Nevertheless, studies focusing on the detailed information about reactions and processes during pyrolysis have been limited, especially in the case of dynamic processes. Thermo gravity analysis (TGA) [14] was applied in investigation of the mechanism and kinetic characterization of coal pyrolysis. However, the results based on TGA are macroscopic and do not provide the information on the correlation between the coal structure and reactions. The coal pyrolysis model of Functional Group-Depolymerization Vaporization Crosslinking (FG-DVC) firstly proposed by Solomon established the correlation between coal structure and reactions and characterized the reaction of functional groups as the main processes of coal pyrolysis [12]. Nevertheless, this model is based on the evolution of the gas product by TGA-Fourier Transform Infrared Spectroscopy (TGA-FTIR) [15] and TGA-Mass Spectrum (TGA-MS) [16]. However, data obtained using these two characterization methods can not directly reflect the changes in solid coal during heating process, while in-situ transmission FTIR can determine the direct changes in the solid coal. Some reports on in-situ FTIR measurement have been published [17–20]. Unlike ex-situ FTIR, the in-situ FTIR can reflect the online evolution of functional groups, and using ex-situ FTIR make the presence of secondary reactions inevitable during the coal processing [21–24]. In addition, Qi et al. reported smoother and more precise curve of evolution of functional groups obtained by in-situ FTIR than that obtained by ex-situ FTIR during coal oxidation [25].

In coal structure, aliphatic groups (CH_3, CH_2, CH), aromatic groups (aromatic C—C and C—H), and oxygen-containing groups (hydroxyl, carbonyl, carboxyl and ether) are the most abundant functional groups that appear in the infrared spectrum and are strongly correlated with CO_2, CO and tar [26]. Understanding of the evolution of these functional groups can help optimize thermal treatment of coal processes such as gasification and production of coke and tar.

For kinetic characterization of coal pyrolysis, several methods derived from TGA have been used for isothermal and non-isothermal conditions. These include the Ozawa [27] method and the integral method [28,29]. However, with the exception of the work by Li et al., reports on the kinetic properties based on quantitative assessment of the functional groups are rare [30]. Li et al. investigated the decomposition kinetics of hydrogen bonds by the in-situ diffuse reflectance FT-IR (DRIFT) based on the loss of absorption of different types of hydrogen bonds.

In our previous works, the structural and thermal characterization of perhydrous coal was investigated by TGA-MS [16,31], while in the present study in-situ FTIR was used to investigate the pyrolysis process of a perhydrous bituminous coal under non-isothermal heating condition. The spectra obtained at certain temperatures were deconvolved into peaks assigned to the corresponding functional groups. The main objectives of this study are (a) to investigate the pyrolysis mechanism of perhydrous bituminous coal based on the direct loss of functional groups in solid coal; (b) to establish a kinetic method for evolution of functional groups; (c) to determine kinetic characterization of evolution of functional groups during pyrolysis. The result of this study is expected to provide a useful basis for the optimization of coal treatment.

2. Experimental

2.1. Coal sample

The coal sample (DJ coal) was collected from No. 13 coal seam at Dingji mine, Huainan coalfield, China, which is one of the main mined seams in the Huainan coalfield. The ultimate and proximate analysis results are shown in Table 1. The coal from this seam is classified as high volatile perhydrous bituminous coal and contributes 8% and 9% for the coking and power generation in China, respectively [16]. The sample was ground to <0.096 mm (−160 mesh) before used.

2.2. In-situ transmission FTIR

The in-situ transmission FTIR device includes an FTIR spectrometer (Thermo Nicolet 8700) and a heating accessory (TOPS-IR02, Xiamen Tops Equipment Development Co. Ltd.), i.e., a pressurization in-situ transmission sample cell, sketched in Fig. A.1 (see Appendices). The sample cell is a sealed vessel that can provide different environmental conditions, such as N_2, CO_2, with a system for heating at a set rate. The transmission window is made of CaF_2, which means we cannot obtain the information for frequencies below 1000 cm^{-1}. The heating temperature ranges from the room temperature to 500 °C.

Approximately 1 mg coal sample was finely ground in an agate mortar with dried KBr at a mass ratio of approximately 1:50 (coal to KBr) under an infrared lamp in order to minimize the contribution of water to the spectrum and pressed into a pellet in an evacuated die under 10 MPa pressure for 1 min. The pallet was then placed in the sample cell and fixed in an appropriate position. Prior to heating, high purity N_2 was conducted into the inlet for 30 min to purge the air in the cell. The heating is carried out from 20 °C to 500 °C at a rate of 10 °C/min under an N_2 flow rate of 25 mL/min. FTIR spectra were recorded on the spectrometer at a resolution of 4 cm^{-1} by co-adding 8 scans at certain temperatures. The 25 different temperatures, at which FTIR spectrum was recorded, were determined according to the result of TGA shown in Fig. 1. The density of the temperature points depends on the rate of pyrolysis. Using in-situ FTIR can avoid the error resulting from multiple sampling or the readsorption generated during cooling process and obtain on line data of the remaining sample during pyrolysis.

In addition to the raw coal sample, the coal sample dried at 60 °C under vacuum condition for 12 h was also examined by in-situ FTIR at the same heating rate to investigate the influence of the water in the coal on this method.

Each sample was prepared and determined three times. The relative standard deviations (RSD) of the functional groups at different temperatures were in the range of 3.5–14.2% based on normalized area.

2.3. TGA analysis

TGA analysis under the same heating rate as in-situ FTIR determination was used in this study for the determination of the temperature points during in-situ FTIR determination, as shown in Fig. 1.

3. Result and discussion

The FTIR spectra of coal at different temperatures, shown in Fig. A.2, can only reflect obscure information about the changes

Table 1
The ultimate and proximate analyses of DJ coal.

Proximate analysis (ad), %		Ultimate analysis (daf), %	
Moisture	1.73	Carbon	88.3
Ash	15.09	Hydrogen	6.1
Volatile matter	36.98	Nitrogen	1.4
Fixed carbon	46.51	Oxygen[a]	4.2
		Sulphur	0.6
		Chlorine	0.022

[a] By difference.