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Pyrolysis characteristics and kinetics of low rank coals by TG-FTIR method

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ABSTRACT

The paper studied the pyrolysis characteristics and kinetics of four typical low rank coals selected from different mines of China using thermogravimetry coupled with Fourier transform infrared spectrometry (TG-FTIR). The chemical structures of the low rank coals were investigated by the FTIR measurements. The FTIR spectra of the low rank coals were divided into four zones and functional groups of the chemical structures were investigated by curve-fitted method. The thermogravimetric (TG) and differential thermogravimetric (DTG) curves of low rank coals indicated that the overall pyrolysis processes could be divided into five stages based on characteristic temperatures and each stage had its unique characteristics. The pyrolysis reactions mainly occurred in the fast pyrolysis stage. The activation energy *E* and frequency factor *A* were calculated by a single first-order reaction model using Doyle integral method. The results showed that the *E* and *A* of the fast pyrolysis stage were the largest, while the obtained *E* of the slow pyrolysis stage was close to that of the fast polycondensation stage. The emissions of CO_2 and CH_4 were detected during pyrolysis process. The results revealed that the evolutions of CO_2 and CH_4 were affected mainly by content of carboxyl groups and content of aliphatic chains in the low rank coals, respectively. The pyrolysis characteristics and kinetics of low rank coals were closely associated with their complex chemical structures.

1. Introduction

Coal is a very important fossil fuel accounting for about 40% of the worldwide power and the demand of coal is continuously increasing in the last decades, especially in China [1]. However, the quantity of the high rank coal is limited and the reserves have been reducing gradually, it is necessary to exploit low rank coal with low degree of metamorphism and low specific energy. It mainly includes lignite and subbituminous coals, which account for almost half of coal reserves throughout the world [2,3]. Low rank coal is usually featured with high moisture content, high ash content and low carbon content, especially exhibits high volatile and low heating value [4,5].

The common utilization technologies of low rank coal are combustion, liquidation, gasification and pyrolysis. As the primary utilization technology of low rank coal, direct combustion is often used for electricity generation in power plants. However, this technology has high cost and low efficiency, even causes environmental problems [4]. Liquidation technology is another important approach to obtain naphtha, diesel oil, liquefied gas, etc. However, large commercial scale application of this technology for low rank coal is limited due to the strict reaction conditions and difficult recycling for catalysts [6]. Coal gasification is a technology requiring gasifying agent to react with low rank coal under certain temperature and pressure to produce a gaseous mixture of oxycarbide, hydrogen and methane, etc. This technology usually requires high temperature and releases pollution gases [7,8]. Pyrolysis is one of the most important thermal conversion processes and it is also the first step in the process of combustion and gasification [9–11]. Large amounts of clean solid, liquid and gas products can be obtained from pyrolysis process, such as high heating value semi-char and hydrogen enriched gaseous products [12–14]. The evolution of gases such as CO_2, CH_4, etc. can be tested by Fourier transform infrared spectrometry coupled with thermogravimetry (TG-FTIR) [15,16].

Pyrolysis characteristics and kinetic models are essential on utilization of low rank coal massively, which are important tools to improve pyrolysis technologies and design pyrolysis reactors [17]. The single reaction model was proposed by Badzioch and has been widely used to investigate pyrolysis kinetic of low rank coal due to its simplicity and accuracy [18–20]. It is a global empirical model and the model correlates the overall weight loss with temperature represented by Arrhenius equation. Kinetic parameters can be determined by a set of thermogravimetric experimental data at a heating rate. In order to well perform the kinetic analysis of pyrolysis process for low rank coal, the overall pyrolysis process is usually divided into different stages [1,21]. Many previous works have been done to investigate the chemical structures of

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low rank coals due to they contain various functional groups [22–24]. Although many studies have been conducted to study pyrolysis kinetic and structure of low rank coal, the mechanism of pyrolysis process hasn't been known clearly. This is mainly attributed to complex chemical structure of low rank coal and complicated chemical reactions during pyrolysis process. Therefore, it is essential to study pyrolysis characteristics and kinetics associated to chemical structures of low rank coals.

In this work, the pyrolysis characteristics of four low rank coals were investigated by TG-FTIR analysis with a non-isothermal temperature program method in N_2 atmosphere. A single first-order reaction model was issued to estimate the kinetic parameters such as activation energy E and frequency factor A. In order to further investigate the relationship of low rank coals pyrolysis characteristics and kinetics with their chemical structures, independent FTIR was carried out to characterize the functional groups of coal samples and coupled FTIR was used to monitor the emission of gases such as CO_2 and CH_4.

2. Material and methods

2.1. Coal sample preparation

Four low rank coals chosen from different mines in china were coal NM (lignite from Inner Mongolia of China), coal NX (non-caking coal from Ningxia Province of China), coal HLJ (long-flame coal from Heilongjiang Province of China) and coal SD (long-flame coal from Shandong Province of China), which were listed in approximately increasing order of their carbon contents. Prior to the experiment, all coal samples with particle diameter of 200 meshes were put into a drying oven for four hours at 105 °C. The proximate analysis was measured using a proximate analyzer (SDTGA5000, China) following the Chinese National Standard GB/T 212-2008. The heating value was determined using an oxygen bomb calorimeter (IKA-C200, Germany) according to the Chinese National Standard GB/T 213-2008. The carbon, hydrogen, nitrogen, and sulfur contents of the low rank coals were carried out using an elemental analyzer (Vario EL cube, Germany), and then the oxygen content was calculated by difference. The results of proximate and ultimate analyses of four low rank coals were listed in Table 1. Their moisture content and volatile content were in the range of 3.07–9.49 wt.%, 24.98–31.72 wt.%, respectively. The higher heating values (HHV) of four low rank coals ranged from 16.16 to 24.78 MJ/kg. All coal samples exhibited similar properties with high carbon content (72.15–81.00 wt.%) and low hydrogen content (5.62–7.19 wt.%).

2.2. FTIR and TG-FTIR experiment

The FTIR measurements of low rank coals were performed on a Nicolet iN10 microscopic infrared spectrometer. The scan region ranged from 4000 cm^{-1} to 400 cm^{-1} and the FTIR spectra were recorded by coadding 16 scans at a resolution of 4.0 cm^{-1} using a DTGS detector. A pulverous mixture of coal sample and KBr with mass ratio of 1:100 was used. In order to well study chemical structure and obtain the detailed absorption peak parameters, the FTIR spectra were studied by curve-fitting analysis using Origin 8.5 software. The positions and number of fitted peaks were determined from the second derivative of the experimental spectrum in the selected zone. The fitted peak shape and area were obtained using a Gaussian combination, and they were adjustable by the variance between the experimental curve and fitted curve.

About 10 mg coal sample was carried out on a thermogravimetric analyzer NETZSCH-STA 409 coupled with Fourier transform infrared spectrometer Bruker Tensor 27. N_2 was used as the carrier gas with a flow rate of 50 mL/min. The temperature range was from room temperature to 1050 °C with a temperature-programmed heating rate of 10 °C/min under atmospheric pressure. In order to ensure the repeatability of experimental result, each experiment was repeated three times and the difference was found to be lower than 3%.

Table 1
Proximate and ultimate analyses of coal samples.

	Proximate analysis (wt.%)				Ultimate analysis (wt.%, daf)					HHV(ad)
Coals	M_{ad}	A_{ad}	V_{ad}	FC_{ad}	C	H	O*	N	S	(MJ/kg)
NM	9.34	33.39	25.68	31.59	72.15	7.19	18.21	1.55	0.89	16.16
NX	7.17	12.99	24.98	54.86	76.78	5.62	16.02	0.94	0.64	24.78
HLJ	3.07	25.24	31.72	39.97	80.21	5.77	12.64	1.03	0.35	23.16
SD	9.49	28.97	28.88	32.66	81.00	6.56	9.70	1.85	0.88	20.27

ad: Air dried basis, daf: Dry ash-free basis, *: By difference, HHV: Higher heating value.

2.3. Single reaction model

The non-isothermal kinetic equation for solid coal sample decomposition can be described as follows [25,26]:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{1}$$

where T is the absolute temperature, β is the heating rate, R is the universal gas constant, E is activation energy and A is the frequency factor.

α is the extent of coal sample conversion, and is given by

$$\alpha = \frac{w_0 - w_t}{w_0 - w_f} = \frac{\Delta w}{\Delta w_f} \tag{2}$$

where w_0 is the initial weight of coal sample, w_t is the instantaneous weight at certain time t read from the TGA curve, and w_f is the final weight at the specified end of the reaction.

$f(\alpha)$ is the differential conversion function defined as

$$f(\alpha) = (1-\alpha)^n \tag{3}$$

where n is the reaction order with respect to the solid phase, and the reaction order was assumed $n = 1$ in the later computation.

Using different mathematical treatment such as rearranging Eq. (1), integrating conversion function and temperature function, simplifying temperature integral function with Doyle integral approximate expression, Eq. (1) is rewritten as

$$-\ln(1-\alpha) = \frac{AE}{\beta R}0.00484\exp\left(-\frac{1.0516E}{RT}\right) \tag{4}$$

Taking logarithm of Eq. (4) gives

$$\ln(-\ln(1-\alpha)) = \ln\left(\frac{AE}{\beta R}\right) - 5.3308 - \frac{1.0516E}{RT} \tag{5}$$

The Arrhenius plot of $\ln(-\ln(1\text{-}\alpha))$ versus $-1/T$ becomes a linear line for coal pyrolysis reactions. Thus, the activation energy E and frequency factor A can be calculated from the slope and intercept of the regression line, respectively.

3. Results and discussions

3.1. FTIR analysis

The FTIR analysis was conducted to characterize the functional groups in the complex macromolecular structures of low rank coals. The FTIR spectra of different low rank coals exhibited similar absorption bands and characteristic absorption peaks, as shown in Fig. 1. The FTIR spectra of the coal samples can be divided into four zones, —OH groups stretching vibration (3600–3000 cm^{-1}), aliphatic C—H groups stretching vibration (3000–2800 cm^{-1}), absorption spectrum of oxygen-containing functional groups (1800–1000 cm^{-1}) and aromatic