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Investigation of the relationship between infrared structure and pyrolysis reactivity of coals with different ranks

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ABSTRACT

The chemical structures of six coal samples with different ranks were semi-quantitatively characterized by a series of original infrared structural parameters, and the pyrolysis reactivity of the samples were quantitatively characterized by a comprehensive devolatilization index. A correlation was established between the infrared structural parameters and pyrolysis reactivity. The results show that the infrared structural parameter method presented in this paper can reveal the distribution characteristic of chemical bonds in coal effectively. The total content of oxygen-containing functional groups, C—H groups and the inorganic mineral can be satisfactorily characterized by infrared structural parameter, I_{a3}, I_{b4} and I_{d3} respectively. The length of aliphatic side chains or bridge bonds undergoes a Stable-Increased-Decreased process. Good positive correlation was established between the comprehensive infrared structural parameter S and the pyrolysis reactivity, which was proved effective to predict the pyrolysis reactivity of coal over various ranks.

1. Introduction

The relationship between coal structure and reactivity is the most important research area in coal chemistry. Theoretical foundations in the field have been constantly promoting the progress of coal processing and conversion technologies [1]. For a long time, proximate analysis, ultimate analysis and petrographic analysis [2–4] were the most widely used methods for coal structure characterization. Proximate analysis only roughly reflects the behavior of coal conversion by getting the whole contents of moisture, volatile matter, fixed carbon and ash under specified conditions. Ultimate analysis provides the contents of five elements C, H, O, N and S, which are the main elemental compositions of coal on dry ash free basis. Ultimate analysis ignores the information of chemical bonds that indicates the combining ways between atoms. Petrographic analysis divides coal into a number of organic groups and mineral subgroups and gives their respective contents that can speculate the reactivity of coal based on the experience. The three types of methods for coal characterization lack of the exploring in macromolecular bonding structure. As a result, they cannot satisfactorily establish the relationship between the conversion reactivity of coals and their internal bonding information that are essential for chemical reactions.

Pyrolysis is the initial stage of all thermal conversion process of coal that includes a series of complex free radical reactions and highly relative to coal's bonding structure forms. By now, scholars have established a variety of methods for better predictions of pyrolysis reactivity based on their individual experimental purposes. These methods mainly include: (1) yield of solid/liquid/gas phase product [5–10]; (2) production characteristics of components in gas/liquid product [6,11]; (3) temperature corresponding to the maximum release rate of hydrocarbons [7–9,12] and hydrogen index [7,8,12,13] in Rock-Eval pyrolysis; and (4) kinetic parameters [14] and comprehensive devolatilization index [14–15], etc. Unfortunately, no standard method is set up today due to the complexity of coal structure. Among the methods, pyrolysis reactivity index is often defined to combine coal's macromolecular bonding structure and its behavior, which covers the indication of difficulty level and release intensity of a pyrolysis. Kinetic parameters and comprehensive devolatilization index are the main definitions of pyrolysis reactivity index, which have been proved effective in characterizing the pyrolysis reactivity. Comparatively, the latter is more convenient in use.

In terms of the relation between coal's structure and its pyrolysis reactivity, many attempts are found from previous publications, which mainly concentrated in combining the traditional analysis data of coal structure and certain pyrolysis reactivity index. Some scholars [7–10] try to predict yield of volatile matters (V), and others [12] are committed to establish the connection between these data with T_{max} and *HI* of Rock-Eval pyrolysis. However, there are some points worthy of

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Table 1
Proximate and ultimate analyses of six coal samples.

Coal	Proximate analysis (wt.%, d)			Ultimate analysis (wt.%, daf)					Ultimate analysis (wt.%, d)				
	A_d	V_d	FC_d	C_{daf}	H_{daf}	O^a_{daf}	N_{daf}	S_{daf}	C_d	H_d	O^a_d	N_d	S_d
ZD	6.19	40.12	53.69	73.39	3.98	20.80	1.21	0.62	68.85	3.73	19.51	1.14	0.58
CS	16.69	34.77	48.54	75.31	4.02	19.57	0.87	0.23	62.74	3.35	16.30	0.72	0.19
YY	10.02	30.31	59.67	77.32	3.87	17.63	0.71	0.47	69.57	3.48	15.86	0.64	0.42
HY	7.27	34.32	58.41	79.36	5.26	13.86	1.12	0.40	73.59	4.88	12.85	1.04	0.37
YD	11.97	23.45	64.58	87.17	4.92	5.02	2.22	0.67	76.74	4.33	4.42	1.95	0.59
TX	22.34	6.68	70.98	88.84	2.92	4.81	0.69	2.74	68.99	2.27	3.74	0.54	2.13

[a] Calculated by difference; d, dry basis; daf, dry ash-free basis.

consideration. Firstly, data from elemental and petrographic analysis cannot directly give the bonding structure information that determines the activity of coal pyrolysis, so they are not the suitable parameters for coal structure characterization. Secondly, *V* or *HI* only reflect the whole yield of volatile matter or heavy hydrocarbon in coal pyrolysis, but cannot characterize the difficulty level and intensity of their releases, and T_{max} has the same issue. Finally, some structural parameters and the corresponding reactivity indices are based on different objects that makes the theoretical significance of the relation established ambiguous. As a result, considerable scatterings will appear in the data of previous studies, and the relations established between traditional data of coal structure and inappropriate indices of pyrolysis reactivity are empirical and theoretically limited.

However, some scholars still propounded opinions with great reference values in this respect. Liu etc. [16,17] proposed a research train of thought according to the distribution features of chemical bonds in coal structure. He used chemical bond dissociation behavior to describe the pyrolysis reaction and inverse the bonding structure of coal. We highly agree with Liu's research thought. However, we adopted an opposite logic to characterize the distribution of the chemical bonds in coal in the study and established a connection between bonding structure of coal and its pyrolysis reactivity.

Our previous studies [18,19] investigated the chemical structures of a low-rank coal with different particle sizes and chemical treatments based on analysis of Fourier transform infrared spectrometry (FT-IR), and established the relation between the key original infrared structural parameters and pyrolysis reactivity. However, the applicability of this relation to coals with different metamorphism degrees is not validated.

In this paper, chemical structures of six typical Chinese coal and their pyrolysis are investigated by FT-IR and thermogravimetric analysis (TGA). These six kinds of coals are the most important coals widely used in China for gasification with their coal rank from anthracite to lignite. Semi-quantitatively analysis and discussion over the six coal samples and their pyrolysis reactivity is conducted by a series of original infrared structural parameters and the comprehensive devolatilization index. Finally, correlation between the infrared structural parameters and pyrolysis reactivity is established.

2. Experimental

2.1. Sample preparation

Six Chinese coals with different ranks, ZD (sub-bituminous coal), CS (lignite), YY (middle-volatile bituminous coal), HY (middle-volatile bituminous coal), YD (low-volatile bituminous coal), and TX (anthracite) were used in this study. They were dried in air at 40 °C for 48 h and ground in a planetary ball mill at 500 r/min for 30 min. Then after sieved into particles with diameters below 90 μm, all samples were kept in PTFE bottles at 4 °C and labeled with the corresponding abbreviation.

2.2. Analyses of samples

2.2.1. FT-IR analysis

The chemical structures of the samples were measured using a Nicolet 5700 FT-IR spectrometer with the test parameters of 4000–400 cm^{-1} measuring range, 4 cm^{-1} resolution and 32 scan times. The samples were detected by solid KBr pellet method. The mass ratio of KBr to sample was 200:1 and the pellet weight was 200 mg.

2.2.2. TG analysis

A Mettler-Toledo TGA/SDTA851[e] analyser whose temperature accuracy and mass sensitivity were 0.25 °C and 0.1 μg respectively was employed for the pyrolysis experiments on the samples. In each experiment, 18 mg of sample was heated from 25 °C to 1000 °C at 40 °C/min in highly pure nitrogen (> 99.999%).

3. Results and discussion

3.1. Proximate and ultimate analyses

The proximate and ultimate analyses of the samples are presented in Table 1. It is indicated that with the increasing coal rank (i.e. from ZD to TX), carbon content on dry ash-free basis gradually increases, while the corresponding oxygen content decreases. These results are consistent with the trends shown by other studies [20,21]. Hydrogen content shows a complex behavior that basically presents a Stable-Increased-Decreased process. This is a combined result of the natures of botanical precursors, the maturation/oxidation conditions, the degrees of bacterial activities in the sediments, and the surrounding environments during formations of coals [9]. Hydrogen is the most abundant non-carbon element in its number in coal, which has a key impact on pyrolysis reactivity. In some cases, there is a certain positive correlation between the hydrogen content and the volatile matter yield. However, this correlation is frequently weakened by some exceptions [7–10]. As shown in Table 1, compared with YD, ZD has a lower hydrogen content on dry basis, but its volatile matter yield is obviously higher; CS and HY almost have the same volatile matter yields, but the hydrogen content of CS is distinctly lower. In many cases, the relations between them are ambiguous. How to establish a more reasonable relation between the bonding structures of coal and its pyrolysis reactivity in more comprehensive extent becomes necessary.

3.2. Infrared spectroscopy

As shown in Fig. 1, the spectra of six samples exist obvious differences that mainly focus on wavenumbers 2922, 2848, 1707, 1611, 1446, 1264, 1109, 1033, 1009, and 900–700 cm^{-1}. The absorbance peaks near 2922 cm^{-1} and 2848 cm^{-1} originated from the asymmetric and symmetric stretching vibrations of CH_2 structures in alkanes respectively [22]. HY and YD coals' curves are obviously stronger than those on other samples'. This suggests that HY and YD may have more such structures in the organic matter, which are consistent with their