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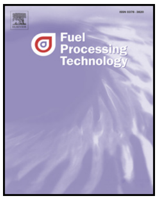

Research article

Impacts of chemical fractionation on Zhundong coal's chemical structure and pyrolysis reactivity

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The investigation to the structure change of coal during demineralization is the prerequisite in evaluating the minerals' catalytic action in pyrolysis. In the study, Zhundong raw coal samples were first treated using the chemical fractionation method, and then the pyrolysis reactivities of the samples were measured on a thermogravimetric analyser (TGA). In order to understand the chemical structures of the samples, the Fourier transform infrared spectroscopy (FT-IR) and a series of original infrared structure parameters were employed. Finally, a correlation was established between the infrared structural parameters and the pyrolysis reactivity. It is indicated that the characteristic of Zhundong coal is different from other low-rank coals in inorganic mineral composition and chemical structure of organic matter. Dilute sulfuric acid washing can increase the carboxyl group and phenolic hydroxyl group contents, but has insignificant impacts on aliphatic hydrogen content, aromatic hydrogen content, and hydrogen atom distributions in aliphatic and aromatic structures. Washing process using concentrated HCl/HF can further increase the carboxyl group content but has little impact on the phenolic hydroxyl group content. In addition, the washing can also shorten the aliphatic side chains and bridge bonds, causing the aromatic ring fusing lower and substitution higher. Dilute sulfuric acid and concentrated HCl/HF washings increase the pyrolysis reactivity of Zhundong coal. Finally, a correlation was regressed between the infrared structural parameter *S* and the pyrolysis reactivity, which was proved to be effective to predict the pyrolysis reactivity of coal.

1. Introduction

Coal is a mixture with complex structures including organic macromolecule networks and inorganic matters. Although the inorganic matters take a very small proportion in the coal, it is well reported that the alkali and alkaline earth metals (AAEM) have obvious catalytic action in the thermal conversion of coal, i.e. pyrolysis, gasification, etc. [1–6], and the catalysis becomes stronger as the coal rank drops [7–10]. The AAEM species in the coal occur mainly in three states: water soluble state (chlorides, etc.), ion exchangeable state (carboxylates, etc.), and insoluble state (clay minerals, etc.). Most of the recent studies related to the catalysis of AAEM are based on the comparison of thermal conversion reactivities between the demineralized coal (by chemical process to remove AAEM) and the raw coal or the coal supporting metallic elements under the same external conditions. However, if the organic structure of the coal changes much during demineralization, attributing the reactivity variation only to the removing of AAEM may be questionable. So, it is significant to estimate the impact of demineralization on the chemical structure before the coal proceeds to its thermal conversion, however the related study is inefficient. The existing papers also give inconsistent conclusions. Some believe that the HCl/HF-based demineralization has little impact on the organic macromolecule structures of the coal [11–13], some consider that it will reduce aliphatic structures [14,15], and some others conclude it will produce more alkyl side chains and carboxyl groups [16–19]. The variety of the coal is one of the main reasons leading to the inconsistency as different kinds of coal have different organic macromolecule networks and AAEM modes of occurrence.

Zhundong coal is a kind of low-rank coal abundantly reversed in east Junggar Basin, Xinjiang, China [20]. It is estimated that the coal can be used for more than 100 years in China in today's consumption rate. Zhundong coal has distinct chemical feathers both in organic matters and in inorganic minerals, including: (1) up to 40–70% of the fusinite and semifusinite contents [20,21]; (2) high AAEM content [22–26], especially high sodium content in ash [24]. However, few studies have been focused on the impacts of demineralization on the chemical structure and pyrolysis of Zhundong coal.

In the study, the three states of AAEM in Zhundong coal were removed by chemical fractionation method gradually, and the chemical

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structures and pyrolysis of obtained samples were studied using FT-IR and TGA.

2. Experimental procedures

2.1. Sample preparation

In preparing for this experiment, 4 experimental samples were first treated from raw Zhundong coal sample, one following another.

1) R-form sample. Raw coal sample was first crushed, ground and screened to particles in diameters between 106 and 150 μm. After drying at 35 °C for 24 h, they were kept in a polytetrafluoroethylene (PTFE) sample bottle at 4 °C, labeled as R-form sample.
2) W-form sample. W-form sample was prepared by putting R-form sample into the deionized water at ratio of 1 g/25 ml. After being stirred in nitrogen for 24 h, the solutable AAEM were removed. With the same steps as stated above, W-form sample was collected and labeled.
3) H-form sample. In preparing H-form sample, W-form sample was first put into 0.1 mol/l dilute sulfuric acid (in 1 g/20 ml), and was put in nitrogen. After being continuously stirred for 24 h, the ion exchangeable AAEM were removed. Then after being filtered, collected, and washed repeatedly by deionized water, H-form sample was obtained and labeled.
4) D-form sample. H-form sample, mixed with 37% hydrochloric acid (in 1 g/20 ml), was put again in nitrogen and stirred continuously for 24 h. Afterwards the filtered sample was put into 40% hydrofluoric acid and then 37% hydrochloric acid so as to remove the insoluble AAEM. After being washed repeatedly using deionized water, D-form sample was collected and labeled.

2.2. Analyses of samples

2.2.1. FT-IR analysis

For FT-IR analysis, coal samples were first blended with KBr powder at mass ratio 1:200 (coal sample to KBr). Each time, 200 mg of mixture was pressed to a pallet at a pressure of 90,000 N/cm^2. A Nicolet 5700 FT-IR spectroscopy whose measuring range, resolution and numbers of scan were 4000–400 cm^{-1}, 4 cm^{-1} and 32 respectively was adopted to analyse the samples.

2.2.2. TG analysis

TG analyses were carried out on a Mettler-Toledo TGA/SDTA851^e analyser. In each test, 18 mg of sample was filled into a custom-made platonic crucible and kept heating from ambient temperature to 1000 °C at 40 °C/min with the highly pure argon (99.999%) surrounding the sample as protective gas.

Table 1
Proximate and ultimate analyses of four coal samples.

Coal sample	Proximate analysis (wt.%, ad)				Ultimate analysis (wt.%, daf)				
	M	A	V	FC	C	H	O[a]	N	S
R-form	9.31	5.61	38.92	46.16	73.39	3.98	20.80	1.21	0.62
W-form	9.12	3.79	39.46	47.63	72.52	3.77	21.86	1.09	0.76
H-form	5.43	1.55	39.67	53.35	72.91	3.89	21.53	1.02	0.65
D-form	5.08	0.53	40.42	53.97	72.25	4.10	21.95	0.96	0.74

[a] The oxygen concentration in coal was obtained by difference.

3. Results and discussions

3.1. Proximate, ultimate and ash composition analysis

It is indicated in Table 1 that the ash contents of R-form, W-form, H-form, and D-form coal are 5.61%, 3.79%, 1.55% and 0.53%, respectively, which means the chemical fractionation method mentioned in Section 2.1 can well remove the minerals from Zhundong coal. In addition, moisture content shows such a tendency as R-form ≈ W-form > H-form ≈ D-form. Especially from W-form to H-form, moisture content drops sharply. Allardice et al. [27] find that the coal's moisture retention has falling tendency when they adopted dilute sulfuric acid to wash out the soluble inorganic salts and exchangeable metal ions in similar procedure as we used. That seems to imply the washing method with dilute sulfuric acid can effectively reduce the exchangeable ions contained in the organic matters and the moisture retention [26]. The variations of elemental compositions of four samples are not obvious, this indicates that the ultimate analysis as a method based on the macroscopic chemical properties of samples, sometimes may be inefficient to reveal the structural changes of coal's macromolecule network.

In order to avoid the significant volatilization of AAEM, R-form, W-form, and H-form samples were subjected to a low-temperature and low-speed ashing process (which kept heating from ambient temperature to 550 °C at 2 °C/min, and holding for 8 h), and then, the inductively coupled plasma optical emission spectroscopy (ICP-OES) method was used to analyse the main constituents in their ashes. As shown in Table 2, compared with R-form coal, the sodium in W-form coal is obviously low, indicating that a fairly large proportion of sodium in Zhundong coal exists in water soluble state. While in the ash of H-form sample, the contents of calcium, magnesium and sodium are low, but the contents of silicon and aluminum are high, indicating that the dilute sulfuric acid washing can effectively remove the ion exchangeable AAEM species. That implies the residual components in the ash are mainly insoluble clay minerals [26]. Since R-form coal has low potassium content, the removals of potassium by deionized water and dilute sulfuric acid from R-form coal are relatively limited. In addition, the removals of ferrum and titanium are also unobvious, which implies an inconsiderable portion of these metals exist in the water soluble and ion exchangeable forms.

3.2. Infrared spectroscopy

Nowadays, infrared spectroscopy has been used as a powerful tool in examining the structure of coal [16–19,28–30]. As shown in Fig. 1, W-form coal is similar to R-form coal in the shape of infrared spectrum, which indicates the deionized water washing has almost no impacts on Zhundong coal's structure except on the removal of some soluble minerals. However, the spectra of H-form and D-form coal samples show significant differences from that of R-form coal, which mainly focus on wavenumbers 1709, 1451, 1403, 1107, 1032, 1009 and 600–400 cm^{-1}. The preliminary evaluation of the peak intensities can be made on the basis of the peaks' heights relative to that of the highest and relatively stable one which is near 1610 cm^{-1} and caused by the stretching vibration of C═C in aromatic rings [13]. The peak corresponding to 1709 cm^{-1} is caused by the stretching vibration of carboxylic acid's carbonyl group (C═O) [13]. For the four spectra, the

Table 2
Ash composition analysis of four coal samples.

Coal sample	Ash composition (wt.%)									
	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	SO_3	P_2O_5
R-form	22.82	14.93	26.71	6.81	5.96	0.63	13.19	5.62	0.03	0.16
W-form	23.14	15.04	28.20	7.11	2.32	0.56	13.87	5.81	0.02	0.14
H-form	43.97	27.58	4.86	1.47	0.56	0.58	13.05	4.89	0.03	0.11
D-form	–	–	–	–	–	–	–	–	–	–

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