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In-situ analysis of volatile products from lignite pyrolysis with pyrolysis-vacuum ultraviolet photoionization and electron impact mass spectrometry

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ABSTRACT

Pyrolytic species of two kinds of lignites (samples A and B) are investigated in-situ with pyrolysis-vacuum ultraviolet photoionization/electron impact mass spectrometry (PVUVPI/EIMS). Mass spectra of pyrolytic fragments are measured during temperature-programmed pyrolysis process of two lignite samples and the intensity profiles of the pyrolytic species are estimated in different temperatures. Experimental results show that H_2, H_2O, CO, and CO_2 are dominant inorganic gaseous products and their characteristic temperatures are in accord with the temperatures of related chemical bonds cleavage. Mononuclear aromatics are dominant organic pyrolysis products, and many olefin species are also identified. The differences between samples A and B on macromolecular structures make the distribution of pyrolytic products different. In addition, the peak of H_2S and CH_3SH are both clearly observed in mass spectra of sample B, which could come from thioether bonds decomposition. This work also illustrates that the PVUVPI/EIMS performs very well in in-situ analysis pyrolytic products.

1. Introduction

Pyrolysis as an efficient and clean utilization technology for coal processing has attracted more and more attention. It also plays an important role in coal thermal process due to the pyrolysis process occurs in the majority of coal applications. In addition, studies on pyrolysis mechanism provide useful information about macromolecular structure of coal, which will promote the development of coal conversion techniques [1–6]. However, until now, it is still hard to understand the mechanism of coal pyrolysis because of the complexity, heterogeneity, and variability of coal [7].

Pyrolysis of coal has been extensively studied by thermogravimetric (TG) analysis [8], mass spectrometry (MS), and Fourier transform infrared (FTIR) spectrometry. As the common analysis method, TG is employed to get the information about the weight loss and pyrolysis reactivity of coal [9–12]; FTIR is introduced to obtain the vibrational spectra of chemical bonds in coal [13,14]. Zhao et al. used the TG and FTIR to investigate the pyrolysis behavior of three weakly reductive coals (WRCs) from northwest China and one reductive Pingshuo (PS) [4]. Compared with TG and FTIR, the main advantage of MS is at pyrolytic product analysis [15], especially it will become more powerful when couples with other analytic techniques. Bläsing et al. studied the evolution of inorganic species during German hard coals pyrolysis by using the molecular beam (MB)–MS, and concluded that the composition and reaction atmosphere played an important role in the release of Na-, K-, Cl-, and S-species [16]. Zhao et al. applied TG–MS to investigate thermolysis of the vitrinites and inertinites which separated from three WRCs and PS coal [17]. Chen et al. used inductively coupled-plasma (ICP)-MS to study the release and enrichment behavior of 44 trace elements during coal pyrolysis of Yima coal, and found that the evolution ratio of rear earth elements were very low [18,19]. Moreover, the gas chromatography (GC)–MS has been extensively used during coal pyrolysis process [20–23]. Wang et al. investigated the tar formation mechanism in coal pyrolysis coupled with CO_2 reforming of methane (CRMP) by using GC–MS, and deduced that the interaction of free radicals between coal pyrolysis and CO_2 reforming of methane made the higher tar yield in CRMP process [24,25]. In addition, more useful information about coal pyrolytic behavior can be taken by GC–MS combined with other analytic techniques (like FTIR [26] and TG [27]). However, most previous MS selected the electron-impact (EI) as ionization source and its high electron energy (70 eV) could ionize most volatile species and produced many fragments. Moreover, the electron energy resolution of electron gun was low.

To overcome the disadvantages of EI, vacuum ultraviolet photoionization (VUVPI) has attracted great interest as an alternative ionization technique [28–30]. Generally, VUV light mainly consist of three types: laser VUV light, rare-gas-discharge light, and synchrotron VUV light. With the help of VUV ionization technique, mass spectrum provides better analytic results for coal pyrolysis process [31–35]. Streibel et al. combined MS with electron beam pumped rare gas excimer lamp to get

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pyrolytic information about lignum, coal, and polymer [31]. Jia et al. [36] studied Huainan and Yima coals pyrolytic properties by using MS coupled with synchrotron radiation, and illustrated that the different macromolecular network structures of two bituminous coals made the different pyrolytic products.

In this work, two kinds of lignites were selected to study the pyrolysis performances and structural characteristics of low rank coals. VUVPI/EIMS is employed to identify the pyrolysis products. VUV lamp combined with time-of-flight (TOF)-MS is utilized to detect major organic products and reduce ionized fragments. EI-MS can detect many small molecules such as CO_2, CO, H_2O, CH_4 and H_2, which are not accessible by VUVPI–MS. Furthermore, the alternate easily between VUVPI and EI ionization will improve the performance of in-situ gas analysis in MS.

2. Experimental

2.1. Lignite samples analysis

Two lignite samples A and B were selected from coal sample library of China Huadian Electric Power Research Institute. Both lignite samples are grinded to pass 100 mesh. As shown in Table 1, two lignites have high volatile matter, and sample A has higher carbon content, lower volatile matter and lower sulfur content than sample B.

2.2. TG analysis

TG analysis was carried out by a Mettler Toledo TGA/SDTA851e analyzer. In TG experiment, the lignite sample is about 12 mg and temperature is from 30 to 850 °C with a heating rate of 10 °C/min under 60 ml/min nitrogen atmosphere.

2.3. FTIR analysis

FTIR spectra of two lignites are measured by an EQUINOX55 spectrometer using KBr pellet technique. The ratio of samples to KBr is about 1:150. The spectra are recorded from 4000 cm^{-1} to 400 cm^{-1} at 2 cm^{-1} resolution.

2.4. PVUVPI/EIMS apparatus

Lignite pyrolysis was carried out in an in-situ pyrolysis VUVPI/EIMS (PVUVPI/EIMS) apparatus. As shown in Fig. 1, the PVUVPI/EIMS consists of two parts: a pyrolytic furnace electronically heated by a tungsten heater and TOF–MS. In this experiment, a 4 mm inner diameter alumina sample tube is employed to make 10 mg lignite sample into the pyrolytic furnace. Volatile species pass a repeller plate with ~1 mm nozzle and enter ionization region, finally the ions generated by EI or VUVPI are guided into homemade TOF–MS. In this work, the photon energy of charge lamp is 10.6 eV, and the energy of EI source is 70 eV. The pyrolytic furnace is powered by a precise electric source and adjusted at interval of 10 mV. The temperature of sample tube is heated from room temperature to 850 °C with a heating rate of 5 °C/min controlled by computer. The mass spectrum and sample temperature are acquired and recorded per second. Each spectrum is an accumulation of 10,000 spectra gathered at interval of 100 μs. The typical pressure of the pyrolytic furnace is kept at 2×10^{-4} Pa to prevent secondary reactions.

Table 1
Proximate and ultimate analyses of lignite samples.

Sample	Proximate analysis (wt.%)			Ultimate analysis (wt.% daf)				$S_{t,d}$
	M_{ad}	A_d	V_{daf}	C	H	N	O^a	
A	9.24	15.48	42.03	72.12	4.08	0.75	>22.63	0.42
B	9.76	26.99	60.49	63.73	5.16	1.36	>27.03	2.72

daf: dry and ash-free base; M_{ad}: moisture (air dried base); A_d: ash (dry base, i.e., moisture-free base); V_{daf}: volatile matter (dry and ash-free base); $S_{t,d}$: total sulfur (dry base); ^{a}By difference.

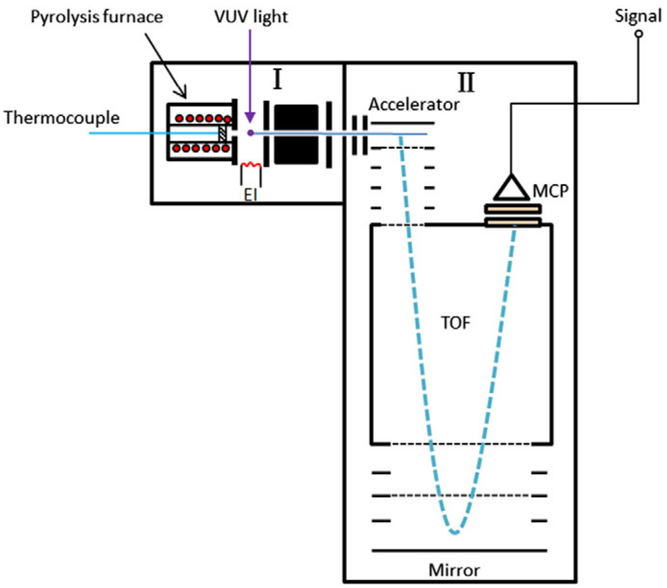

Fig. 1. Schematic diagram of lignite pyrolysis apparatus, I:pyrolysis chamber; II: time-of-flight mass analysis chamber.

3. Results and discussion

Volatile inorganic and organic species evolved from two lignite samples are detected by MS with increasing temperature. The photon energy of mass spectrums is taken at 10.6 eV, which can ionize most species and reduce ionized fragments. As demonstrated in Fig. 2, the TG results show that there is a remarkable volatilization before 200 °C, which may be the moisture in lignite sample, and the second major weight loss appears from 200 to 600 °C in two lignite samples pyrolysis processes. The gaseous species smaller than m/z 200 are main analytic objects in the experiment due to the transfer efficiency of larger species is too low. The FTIR spectra of two lignites are displayed in Fig. 3. Clearly, two samples have abundant oxygen functional groups (3000–3650 cm^{-1}) and aromatic structures (1600 cm^{-1} and 1500 cm^{-1}). The intensities of peaks attributed to oxygen functional groups in sample B are stronger than those in sample A, which corresponds with the results of proximate and ultimate analysis. Moreover, sample B contains more aliphatic C–H vibrations (2918, 2854 and 1442 cm^{-1}) than sample A, indicating more aliphatic moiety in sample B.

3.1. Evolved gas analysis by EI-MS

The CO_2, CO, H_2O, CH_4 and H_2 are selected as main analysis objects, and the evolution of those molecules can reflect the structure of coal sample. As shown in Fig. 4, the peak and formation temperatures of pyrolytic species of two lignite samples are similar, which illustrates the analogous structure of two lignite samples. As shown in Fig. 4(a), the release profile of CO_2 presents one peak-shape signal intensity. The initial release temperature of CO_2 is at 100 °C and the temperature with maximum intensity is at around 250 °C. CO_2 is mainly from two parts: the decomposition of carboxyl and the carboxylate groups at low temperatures, and the thermal dissociation of stable ether structures, quinones and oxygen-bearing heterocycles at high temperatures [37].

The two lignite samples show the similar CO evolution profile as in Fig. 4(b), which have double peak in signal intensity profile. The double peak shape profile illustrates that the evolution of CO occurs at different stages. At lower temperatures, CO is from the decomposition of aryl ether linkages (Ar–O) [38]; at higher temperatures, oxygen content