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A new in-situ pyrolytic time-of-flight mass spectrometer instrument for study on coal pyrolysis

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ABSTRACT

This paper reports a novel in-situ pyrolytic time-of-flight mass spectrometers which is applied on coal pyrolysis studies. The pyrolytic products of Zhundong (ZD), Xilinguole (XLGL) and Shenhua (SH) coals were investigated using both electron ionization (EI) and vacuum ultraviolet photon ionization (VIV-PI) method. The evolutions of H_2O, CO_2, CO, CH_4 and H_2 from pyrolysis of these three coals were analyzed using electron ionization. The qualitative and quantitive performance of our device was discussed by comparing DTG data and ion current curve which was gathered from mass-spectrum. The distribution and evolution of the organic products during pyrolysis were investigated using PI. We found that 1 or 2 ring aromatic compounds were dominant pyrolytic products of the three coals, while some olefin and alkynes products were also observed. Through analyzing the distribution and evolution behavior of organic pyrolytic products, the differences in macromolecular structures of those coals and its influence on pyrolytic process was discussed. The condensation of olefin during coal pyrolytic process was also observed. This work demonstrates the good performance of our in-situ pyrolytic time of flight mass spectrometer on studying of coal pyrolysis.

1. Introduction

Pyrolysis of coal is the initial, accompanying reaction of a number of coal conversion processes such as hydrogenation, combustion and gasification. Coal structures are viewed as three-dimensional cross linking networks, commonly called coal macromolecules, with low molecular mass species scattered inside [1–3]. However, due to the complexity of coal structures, it is very difficult to describe coal pyrolysis process clearly. Model compounds are often used to give an insight into the complex processes that occur in process of coal pyrolyis [4,5]. However, interesting results have been obtained in this way, the picture is still a simplified one and some important aspects of coal structure, such as the interactions between different surface groups and cross-links, are omitted in the case of single compounds.

Many advanced techniques have been applied to characterizing the chemical properties and structures of products from coal pyrolysis directly. Thermogravimetric analysis (TG) is a useful technique employed in coal research [6–8], by measuring the weight loss as function of temperature or time, some information of chemical and physical phenomena occurring in coals can be revealed. However, the structure and component of coal are very complex and the temperature of different decomposition process overlap with each other, the evolution of individual compounds cannot be discerned from the thermo analytical curves. Fourier transform infrared spectroscopy (FTIR) is one of the most powerful and versatile techniques for the characterization of coal. By the vibration spectra, information on coal structure and the main structural changes that take place during the thermocoversion process can be given [9–15]. Although the chemical information such as C—H bond of aromatic/aliphatic and oxygen-containing structures can be provided, more detail information such as molecular structure is unachievable by FTIR method.

Mass spectrometer is a powerful tool to identify the pyrolytic products of coal. For organic compounds, so far the most commonly used technique for analyzing the pyrolytic products of coal is gas chromatography/mass spectrometry (GC/MS) and thermogravimetric/mass spectrometry (TG/MS) [4,16–18], because of their high sensitivity and good resolution. Most of those mass spectrometry methods utilize the quad-pole analyzer and electron impact ionization (EI) method. Many pyrolytic products of coal contain O, N and S. This requires the resolution of MS instrument exceeds 2000, while the resolution of majority of quad-pole analyzer are less than 1000. However, with high sensitivity, the EI creates com-

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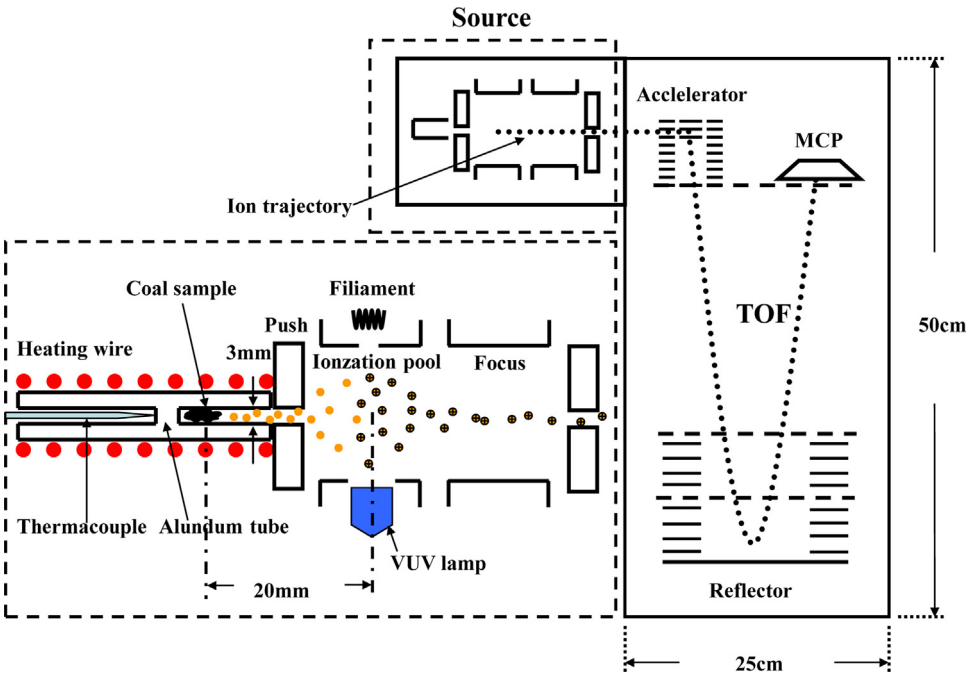

Fig. 1. Schematic diagram of in-situ pryrolytic time-of-flight mass spectrometer apparatus.

plex fragment peaks at same time, which bring in great obstacle to analyzing, especially in the situation of multi-analyte.

Time of flight mass spectrometer (TOF-MS) has the advantage of high speed and high resolution. In 1968, Joy et al. using laser heating and TOF studied the pyrolytic products of coal particles [19,20]. Free radicals of molecular weight of about 100 was observed. Although important results were achieved, the ionization method used by Joy et al. was still not fragment free. It is difficult to identify certain *M*/*Z* peak is pyrolytic product or fragment created by electron impact. Recently, high resolution TOF-MS combined with synchrotron vacuum ultraviolet (SVUV) photoionization were used for coal and biomass pyrolyzation [21]. The SVUV photoionization has many advantages for the online analysis of complex chemical systems, such as broad tunable photon energy range, good energy resolution, and high photon flux. Fragment-free mass spectra can be obtained, and isotopes can be characterized using the tunable SVUV light due to their different ionization energies. The VUV lamp is an acceptable alternator when the SVUV light is unachievable, but the photon flux of VUV lamp is about 10^3 times lower than SVUV. In order to achieve enough signal intensity when using VUV lamp, a much more efficient ion transfer system is needed.

In summary, the main disadvantages of those analytical methods based on MS are non in-situ detection, low resolution, unsoft ionization and high cost. In this work, to overcome those obstacles, a novel high-resolution time-of-flight mass spectrometer with both vacuum ultraviolet (VUV) photoionization and electron ionization (EI) has been developed to analyze the coal pyrolytic products. To avoid reactions between pyrolytic products and increase the ion transfer efficiency, the ion source and the pyrolytic device were integrated together and miniaturized. Using this new designed instrument, pyrolytic behaviors of 3 common coal of China were studied based on the temperature-products profile.

2. Experimental

2.1. In-situ pyrolytic ion source

As shown in Fig. 1, a high resolution mini time-of-flight mass spectrometer with an in-situ pyrolytic ion source was built for study of coal pyrolysis. The apparatus consists of a source chamber and a TOF chamber. Each chamber was pumped by a turbo pump with pumping speed of 300 L/S. The background vacuum of source chamber and TOF chamber was 1×10^{-5} Pa and 3×10^{-5} Pa respectively. Coal samples of about 3 mg were placed in an alundum tube with isolation in the middle to avoid catalyzing the pyrolytic products of coal by thermocouple (platinum). The alundum tube is heated by heating wire and the temperature is measured by a K-type thermocouple. The power of heating is adjusted in real time by computer to obtain smooth heating rate. The gas phase products passed through a hole with diameter of 1 mm and entered the ionization pool, and then ions produced by electron beam (EI) or VUV light (photoionization, PI) were guided into TOF mass analyzer by ion transfer/focus lens.

The VUV light was generated by a VUV lamp (Heraeus, Ltd., Germany) with photon energy of 10.6 eV and average photon flux of 10^{10} photons/s. The electron beam was generated through thermionic emission by heating a wire filament that has an electric current running through it. The electron was accelerated to 70 eV in the region between the filament and the entrance of ionization pool. For pyrolytic products such as H_2O, CO_2, CO, CH_4 and H_2, to study those spices whose ionization energy is higher than 10.6 eV, electron ionization was chosen. For more complex organic products which are produced during coal pyrolysis, the multiple-overlapped fragment peaks of EI make the assignment very difficult. So the photonionization is chosen to study those products.

2.2. TOF mass analyzer

The mass analyzer of this instrument is a homemade orthogonal acceleration time-of-flight mass spectrometer. The detail information of this technology was described elsewhere [22,23]. In our experiment, the pulse is provided by a homemade high voltage pulse generator. The repetition rate of the pulses is optimized to 10 kHz in this experiment. Ions are detected by a microchannel plate (MCP) detector. The ion signal is recorded by an ADC (analog-to-digital converter) data acquisition card (FCFR-9982, Fcctec Technology) after being amplified with a preamplifier (SR445A, SRS).