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Full Length Article

Molecular structure characterization of the tetrahydrofuran-microwave-extracted portions from three Chinese low-rank coals

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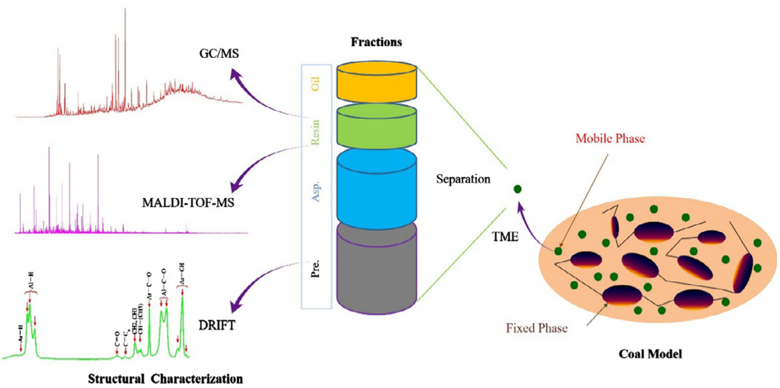
HIGHLIGHTS

- The TME portions were rich in highly branched aliphatic hydrocarbons.
- Aromatic structures in the TME portions were mainly *para*-alkyl substituted.
- C—O bonds were the main oxygen-containing structures in the TME portions.
- AMW of specific fraction had positive relationship with parameter I_2.

GRAPHICAL ABSTRACT



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ABSTRACT

The existence form and structure properties of mobile phase (MP) in low-rank coals (LRCs) can significantly influence the initial stage of thermal conversion. In the present work, three Chinese LRCs, namely, Shenfu, Zhundong and Hongshaquan, were extracted with tetrahydrofuran using the microwave-assisted heating. The tetrahydrofuran-microwave-extracted (TME) portion as the representative of MP was further separated to four fractions defined as oil, resin, asphaltene and preasphaltene, respectively. Diffuse reflectance Fourier transform-infrared spectroscopy (DRIFT), gas chromatography/mass spectrometer (GC/MS), matrix-assisted laser desorption ionization time-of-flight mass spectrometer (MALDI-TOF-MS) and X-ray photoelectron spectroscopy (XPS) were used to comprehensively investigate the molecular characteristics of the derived materials. The results indicated that the studied TME portions were mainly consisted of asphaltenes and rich in highly branched aliphatic hydrocarbons due to the relatively low CH_2/CH_3 and H_{ar}/H_{al} ratios. *Para*-alkyl substituted aromatic structures with 1–2 rings were the main aromatic structures in the TME portions. C—O bonds were the main oxygen-containing structures in the TME portions and could be more likely seen in aliphatic compounds. Combining the MALDI-TOF-MS and DRIFT analyses, the ratio of aliphatic side chains and aromatic hydrogens ($3000–2800\ cm^{-1}/900–700\ cm^{-1}$, I_2) derived from IR spectra seemed to be a suitable parameter for assessing the average molecular weight (AMW) of the specific fraction in TME portion of LRCs when

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the ratio of C═O/C─O was at very low level. The results made a further explanation for the detailed chemical structure of mobile phase in coal and could be helpful for studying the formation mechanism of volatiles during pyrolysis process.

1. Introduction

Because of high moisture and low calorific value, the use of low-rank coals (LRCs) is still constrained in many domains such as power generation [1]. However, the great scale and worldwide distribution ensure the fact that LRCs are still important energy and chemical resources in this century [2]. Thus, the clean and efficient utilization of LRCs is one of the most urgent tasks for researchers. Upgrading, pyrolysis, liquefaction and gasification are the main potentially available thermal conversion approaches for the clean and efficient utilization of LRCs [3,4]. Extensive researches have proved that chemical structure of coal can significantly influence the process of these thermal conversions [5–7].

Based on the host-gust model of coal [8], only the mobile phase and the peripheral structures of the fixed phase are decomposed in the initial stage of pyrolysis [9], which will produce a great deal of free radicals to influence the whole thermal conversion [10,11]. The mobile phase itself can certainly influence the pyrolysis characteristics of coal [12], while the oxygen functional groups in the mobile phase play very important roles during the pyrolysis process [10]. Furthermore, the raw coal mainly consists of two parts (<800 Da and 1000–4000 Da components [13]), but only the smaller molecules will melt and potentially be vaporized as tar at low temperature (<400 °C) [13]. The volatile tar (200–450 Da) and acetone-soluble extract (250–500 Da) obtained from 400 to 500 °C pyrolysis have common species as those identified in the raw coal [14]. The fluidity and subsequent re-solidification during coking should rely on <1000 Da compounds of raw coal [14]. Overall, the structure features of mobile phase in the raw coal can significantly influence the thermal conversion process especially the steps for the formation of volatiles. However, the detailed chemical structure of mobile phase remains unclear particularly due to its complexity [15] and the limitation of analytical instruments [16].

Mild solvent extraction has been considered as a suitable way to study the structure features of the mobile phase of coal [16,17]. For example, with the help of fractional Soxhlet extraction, considerable number of valuable and/or noteworthy compounds from LRCs can be successfully separated and further enriched [18–20]. Additionally, a more detailed chemical structure of the target components can be obtained by microwave-assisted extraction [21] which will afford higher efficiency than other methods. Unfortunately, many molecular characterization of mobile phase in the above-mentioned coals still cannot be fully evaluated in these literatures [18–21]. For example, compounds with high polarity or high vaporization point (such as heterocyclic pyridines, quinolines, and benzoquinolines) are rarely considered because they are difficult to be adequately detected by gas chromatography/mass spectrometer (GC/MS) [22,23]. Thus, separation is necessary for comprehensive study of the structure of the extracts [23]. With the help of separation methods such as column liquid chromatography, the maltenes in the extracts can be isolated and enriched to several parts with similar features [23]. Consequently, extensive information can be obtained by comparative analysis of those fractions [24,25]. In addition, combined with many ordinary analytical methods, diffuse reflectance Fourier transform-infrared spectroscopy (DRIFT) [26,27] and matrix-assisted laser desorption ionization time-of-flight mass spectrometer (MALDI-TOF-MS) [16,28] can be used to achieve more detailed and comprehensive information about molecular characteristic of LRCs.

In order to comprehensively study the structure composition of mobile phase in LRCs, three Chinese coals with relatively high volatile content were selected for tetrahydrofuran-microwave-extrac tion. Based on column liquid chromatography, the extracts were further separated and analyzed by MALDI-TOF-MS, GC/MS and DRIFT. X-ray photoelectron spectroscopy (XPS) was also applied to identify the functional groups of the raw coals and their extraction residues.

2. Experimental section

2.1. Materials and pretreatment

LRCs used in this work were from Shenfu (SF), Zhundong (ZD) and Hongshaquan (HSQ) mines in China. They were ground to <75 μm before being dried in vacuo at 80 °C for 12 h. The ultimate and proximate analyses of the LRCs are listed in Table 1. Solvents used in this work included tetrahydrofuran (THF), n-hexane, toluene, dichloromethane, and methanol (Chemical Reagent Co., Ltd., Shanghai, China).

2.2. Tetrahydrofuran-microwave-extraction (TME)

TME was performed in a microwave extraction apparatus (MDS-6G/SMART, Sineo Microwave Chemistry Science and Technology Ltd.). Coal (5.00 ± 0.05 g) and THF (50 ml) were charged into a PTEF tube (100 ml) to be extracted at 100 °C for 30 min. After extraction, the entire system was cooled down to room temperature, and the reaction mixture was filtered through membrane filter (0.45 μm) to obtain solvent containing extract. Then, the residue was washed with fresh solvent 3–5 times until the supernatant became colorless. The filtered supernatants were combined and concentrated to 5 ml using a R134 rotary evaporator. The concentrated solution was then transferred to a 10 ml pre-weighted glass vial and dried in vacuum at 40 °C for 12 h to remove the residual solvent. Meanwhile, the solid residue was also heated in vacuum at 80 °C for 12 h to remove the solvent.

2.3. Separation process

It was reported that the removal of polar compounds (asphaltene and preasphaltene in this paper) is necessary for further fractionation [29]. In this work, n-hexane was used to eliminate polar fraction from the extract [29]. N-hexane containing maltene was filtered into a pre-weighted glass vial, followed by drying in vacuum to remove the solvent. The insoluble substance was sequentially dissolved with toluene. The toluene soluble and insoluble fractions were defined as asphaltene (asp.) and preasphaltene (pre.), respectively [23]. The dried maltene was subsequently separated by column liquid chromatography.

The column chromatography isolation of maltene was conducted by using a Pasteur pipette (length = 300 mm, diameter = 5 mm) filled with 1.5 g of aluminum oxide (100–200 mesh, pH = 4.5). The elution process was in accordance with the literature [29] orderly using dichloromethane and dichloromethane/metha-