



## Mechanistic influences of different solvents on microwave-assisted extraction of Shenfu low-rank coal



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### ABSTRACT

Microwave-assisted extractions (MAEs) were carried out on Shenfu (SF) low-rank coal using four types of solvent, namely tetrahydrofuran, methanol, dichloromethane and ethyl acetate. Comparison with the traditional thermal extractions (TEs) indicated that MAEs were much more efficient in extracting organic components of SF coal. A large amount of aromatic compounds with 2–3 rings and rich branched alkanes could be extracted from coal by MAE. The results also showed that solvent polarity and the interaction between solvent and functional groups abundant in the extracts were the two main factors leading to differences of their MAE. Among the studied solvents, tetrahydrofuran could extract much more amount of polar compounds and its solution was rich in highly-condensed polycyclic aromatic compounds (PACs) with  $\geq 4$  rings. And this feature had relationship with its strongest interaction with the C–O bond. Ethyl acetate, in contrast, showed strong interaction with the C=O bonds and had good potential for the extraction of low-polarity compounds especially PACs with two aromatic rings and aliphatic compounds with long alkane chains. And for methanol and dichloromethane, their solvent polarity played dominant roles during the MAE procedures. The results provided more detailed mechanistic influences of different solvents on MAE of coal, and would help for the identification of a suitable solvent for efficient detection of components in organic substances, especially the extraordinary complex compounds in coal.

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### 1. Introduction

Coal is an important energy resource in many countries, especially in China. The clean and efficient utilization of coal requires a better knowledge of the organic molecular structure (OMS) of coal [1,2]. Although the OMS of coal has been studied for about 70 years [1], the task is still very challenging and needs further exploration because of extreme complexity of coal.

Finding a suitable solvent and an efficient extraction method is a critical process in the study of OMS of coal [3,4]. For example, solvents such as pyridine [4], *N*-methyl-2-pyrrolidinone (NMP) [5], carbon disulfide/*N*-methyl-2-pyrrolidinone (CS<sub>2</sub>/NMP) [6], etc. are efficient for the extraction of coal. However, there is an argument that nanoclusters and aggregates exist in the solutions obtained through extraction of

high-yield solvents such as pyridine, CS<sub>2</sub>/NMP, etc. [7,8]. Obtaining comprehensive analytical data on the composition of those high-yield extracts is a formidable task, even though many analytical techniques are available [9]. Thus, finding a mild extraction method using suitable solvents to obtain optimum amount of extract with little chemical changes and conveniently detectable by subsequent analysis is necessary to get a more detailed information on the OMS of coal.

Microwave heating has been widely used for mild reaction in many research areas [10]. When heating the complex reactant (coal mixed with a solvent) in a closed vessel, the internal pressure increases due to the higher vapor pressure of the solvent, thus enabling the temperature of the reactant to rise above the solvent's boiling point [11,12]. Meanwhile, the relatively high extraction temperature (generally  $\geq 100$  °C) can reduce solvent viscosity and surface tension, which in turn enhance solvent's ability to penetrate into the sample's matrix, thus enhancing the mass transfer of the solutes [12,13]. It was also reported that microwave heating can generate micropores and increase pore volume and surface area of coal [14], which can further enhance penetration of solvent into the coal matrix. In view of the conveniently detectable necessity, as opposed to pyridine, etc. soft low-boiling

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solvents such as tetrahydrofuran, methanol, dichloromethane, etc. have been successfully used for the chemical characterization of OMS in coal in previous works using the microwave-assisted extraction (MAE) [13,15–17]. For example, with the help of MAE using various solvents, a wide range of alkane hydrocarbons and an abundance of alkylated aromatic compounds in coal samples were detected in previous work [13], relatively high-condensed polycyclic aromatic compounds (PACs) in the mobile phase could be separated and comprehensively detected [17,18]. Despite these compelling results on the detection of OMS in coal using MAE method, the influences of different solvents on the MAE procedure at molecular level are still unclear, while the extraction mechanisms of many solvents remain obscure. Further research into the extraction characteristics of the solvent during MAE procedure of coal must be carried out to help us identify a suitable solvent for future researches on the OMS of coal.

In this study, Shenfu (SF) low-rank coal was chosen for the extractions due to its huge reserves and a wide range of uses, especially in China. To investigate the extraction mechanisms, four solvents with different physicochemical properties were used for microwave-assisted and traditional thermal extractions. Extracts were divided into three parts, namely, oil (non-polar and/or low-polar components), resin and polar components (PC, including asphaltenes and preasphaltenes in this work) with the help of column liquid chromatography technique. Distributions of n-alkanes and PACs in oil fractions were investigated through the analysis of gas chromatography/mass spectrometry (GC/MS). Aromatic systems in the diverse extracts were distinguished by ultraviolet (UV) fluorescence spectroscopy, while the residues were analyzed via Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) to study the changes of functional groups in coal after MAE.

## 2. Experimental

### 2.1. Samples

The low-rank coal used in this work was obtained from Shenfu coal mine in China. The coal was firstly ground to <75  $\mu\text{m}$ , and dried in vacuum at 80  $^{\circ}\text{C}$  for 12 h before the experiments. The results of ultimate and proximate analyses of Shenfu coal are shown in Table 1.

### 2.2. Chemicals

Solvents used in this work were tetrahydrofuran (THF), methanol (MT), ethyl acetate (EA), dichloromethane (DCM), cyclohexane and n-hexane. They were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) as analytical reagents and purified before use. The physicochemical properties of solvents [13,19] used for extractions are listed in Table 2.

### 2.3. Extraction procedures

#### 2.3.1. Thermal extraction (TE)

Thermal extraction was carried out in a glass flask which was connected to a water-cooled reflux condenser. Coal sample (5 g  $\pm$  0.01 g) was mixed with one specific solvent (50 ml) in a glass flask, and the mixture was heated by electric jacket at its boiling point for 1 h. Magnetic stirring was used to ensure that coal mixed with solvent thoroughly, and the temperature of the coal/solvent mixture was homogenized.

After extraction, the entire system was cooled to room temperature. The reaction mixture was then centrifuged at 12,000 rpm for 5 min, after which the supernatant was filtered through polytetrafluoroethylene (PTFE) membrane (0.45  $\mu\text{m}$ ) to obtain solvent containing extract. The residue was washed with fresh solvent 3–5 times until the supernatant became colorless, followed by drying at 80  $^{\circ}\text{C}$  in vacuum to remove the solvent. The filtered supernatants were combined and concentrated to 5 ml volume using a R134 rotary evaporator. Then, the solvent in extract was removed from the concentrated solution in vacuum drying oven.

#### 2.3.2. Microwave-assisted extraction (MAE)

Microwave-assisted extraction was performed in a microwave oven with temperature measurement and time control. Coal (5.0 g  $\pm$  0.01 g) and solvent (50 ml) were charged into a PTFE tube (100 ml) to be extracted at 100  $^{\circ}\text{C}$  for 30 min. After cooling to room temperature, the reaction mixture underwent the same process as described above for thermal extraction. The residues ( $R_{\text{THF}}$ ,  $R_{\text{MT}}$ ,  $R_{\text{DCM}}$  and  $R_{\text{EA}}$  for THF, MT, DCM and EA, respectively) were kept under 4  $^{\circ}\text{C}$  before their subsequent DRIFT analyses, while the extracts ( $E_{\text{THF}}$ ,  $E_{\text{MT}}$ ,  $E_{\text{DCM}}$  and  $E_{\text{EA}}$  for THF, MT, DCM and EA, respectively) underwent further separation (as described in 2.4).

For both TE and MAE methods, three replicate experiments using the four solvents were carried out in the same way to avoid random errors. The extraction yields were determined by the weight of extract and coal (dry ash-free basis) using the following Eq. (1):

$$\text{Yield (wt\%)} = [\text{extract(g)}/\text{coal(g)}(\text{daf})] \times 100 \quad (1)$$

### 2.4. Separation of extract

It was reported that the removal of polar fraction (asphaltene and preasphaltene) in extract is necessary for further fractionation [11]. In this work, n-hexane was used to isolate polar components (PC) from the extract [11]. N-hexane containing maltenes were filtered into a pre-weighed glass vial, and the PC was also recovered from the filter membrane to a pre-weighed glass vial, followed by drying in vacuum to remove the solvent.

A Pasteur pipette (length = 300 mm, diameter = 5 mm) filled with 1.5 g of aluminum oxide (100–200 mesh, pH = 4.5) was used for the column liquid chromatography of maltenes. The aluminum oxide was washed with cyclohexane and DCM successively, followed by drying at 140  $^{\circ}\text{C}$  for 1 h before use. The dried maltene was first eluted with 5 ml of DCM to obtain oil fraction. The column was then eluted with DCM/MT (50:50, vol/vol) to obtain resin fraction. Each fraction was collected with a pre-weighed glass vial. This was followed by overnight drying in vacuum to remove the solvent. The mass of fractions were obtained by weighing the empty and filled vials.

### 2.5. Gas chromatography/mass spectrometry (GC/MS) analysis

The oil fractions were recovered with n-hexane for subsequent analysis using a 7890A/5975C GC/MS equipped with a capillary column which was coated with HP-5MS (cross-link 5% PH ME siloxane, 30 m  $\times$  0.25 mm inner diameter, 0.25  $\mu\text{m}$  film thickness). Carrier gas was helium flowing at a constant rate of 1 ml/min. The injection volume was 1  $\mu\text{l}$  with a split ratio of 5:1 and a split flow of 50 ml/min. The injector temperature was 300  $^{\circ}\text{C}$ . The temperature of the GC oven was

**Table 1**  
Proximate and ultimate analyses (wt%) of SF coal.

Sample	Proximate analysis (wt%, air-dry basis)				Ultimate analysis (wt%, air-dry basis)					H/C
	Volatile	Moisture	Ash	Fixed carbon	C	H	O <sup>a</sup>	N	S	
SF	33.85	6.85	4.90	54.40	68.78	4.03	14.06	0.75	0.63	0.703

<sup>a</sup> By difference.

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