



Characterization of Zhundong subbituminous coal by time-of-flight mass spectrometry equipped with atmospheric pressure photoionization ion source



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ABSTRACT

Zhundong subbituminous coal pretreated with aqueous H_2O_2 was oxidized by aqueous NaOCl and sequentially extracted with diethyl ether (DEE) and ethyl acetate (EA) to afford DEE- and EA-extractable fractions and residue. Both extracts were esterified with CH_2N_2 and analyzed using high performance liquid Chromatography/mass spectrometry equipped with electrospray ionization (ESI) or atmospheric pressure photoionization (APPI) ion source. Molecular mass of 60% compounds in the esterified extracts ranged between 200 and 600 Da and more than 20% of the esterified extracts had molecular mass over 600 Da. Toluene and toluene/anisole (vol./vol. = 95/5) were used as dopants for APPI. Low- and non-polar compounds in the esterified extracts were well analyzed using APPI/MS. Compared to toluene/anisole mixture, toluene greatly increased ionization efficiency of APPI. More molecular associations were detected by ESI than by APPI. Heteroatoms were identified in most of the associated species.

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1. Introduction

Coals have been widely used as energy resource and feedstock for chemicals [1]. Coal structures are viewed as three-dimensional crosslinking networks, commonly called coal macromolecules, with low molecular mass (MM) species scattered inside [2]. However, due to the limit of knowledge on the compositions and structures of coals and their derivatives, coal utilization is still with low efficiency and environmental unfriendly [3,4]. A number of recent studies have been aimed at identifying the compositions and structures of coals and coal derivatives. Schmiers and Kopsel used ^{13}C NMR to investigate the macromolecular structure of a brown coal [5]. A structure related to lignin was proposed. Fourier transform infrared (FTIR) spectroscopy was applied to estimate hydrogen bond distribution in coal through the analysis of OH stretching bands [6]. By using the hydrogen bond distribution, the changes in enthalpies associated with the desorption of adsorbed water and the decomposition of COOH groups were well estimated.

Besides NMR and FTIR, mass spectrometry coupled with chromatography has been developed for characterizing components in coals and proven a powerful tool for unknown species identification [2,7,8]. Gas

chromatography/mass spectrometry (GC/MS) has been successfully applied in the determination of organic species in coals [7–9]. But GC/MS can only detect volatile and thermally stable molecules with MM up to 500 Da. The extrapolation of known small-molecule structures to larger masses is usually found to give structures with very different atomic C/H ratios than higher-MM molecules in coals [10]. Most analytical methods, e.g., GC/MS suitable for the detection of species up to 500 Da cannot be adapted to identify molecules with higher MM. For example, GC/MS can only detect less than a quarter of organic species in coal tar pitch [10]. For the analysis of molecules with higher MM, high performance liquid chromatography/mass spectrometry (HPLC/MS) is suitable and effective [11].

HPLC/MS equipped with electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) ion sources is suitable for analyzing polar and medium polar compounds with higher MM, respectively [12]. ESI/MS was used for edible oil analysis. [13]. Isoflavonoids and other phenylpropanoids were analyzed with HPLC-ESI/MS [14]. Maragou et al. compared ESI and APCI in the analysis of pesticide [15]. For the analysis of low- and non-polar molecules such as organic species in coals and their derivatives, developing new ionization methods for MS is needed. APPI is one of the soft ionization techniques available in MS for the analysis of low- and non-polar compounds with MM similar to APCI [16] and it is a possible ionization method to identify molecules which are poorly ionized by ESI and APCI. APPI was applied in the analysis of drugs and corresponding metabolites [17,18], pesticides [19], lipids [20], flavonoids [21] and steroids [22]. It may be used to analyze the low- and non-polar organic species in coals.

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In APPI, the energy of photons emitted from a lamp should be higher than the ionization energy (IE) of analytes [23]. Kr-filled lamp has a suitable IE with 10 eV, which is lower than the IE of major components in air (e.g., nitrogen, 15.58 eV; oxygen, 12.07 eV) and some of the most commonly used solvents (e.g., water, 12.62 eV; acetonitrile, 12.20 eV; methanol, 10.84 eV; isopropanol, 10.17 eV). The ionization efficiency in a direct ionization mode is low, because solvent molecules deplete photons emitted by the discharge lamp and hamper the energy transfer to analyte molecules [16]. To resolve the difficulty, dopant, which acts as an intermediate between photon and analyte, is needed to increase the ionization efficiency for analyte [16]. Dopant molecules are first ionized by photons, then dopant ions ionize analyte molecules via charge exchange or proton transfer. As the intermediate, a suitable IE of dopant has to be lower than the energy of emitted photons from the lamp. Dopant photoions have a high recombination energy or low proton affinity (PA) because dopant ion should remain stable [23]. Kaupilla et al. used anisole as a dopant for identifying compounds with low proton affinity and low ionization energy [24]. A mixture of toluene and anisole was employed as a dopant to analyze polycyclic arenes (PCAs) [25]. Robb et al. compared the effect of some dopants on charge exchange ionization of non-polar PCAs using reversed-phase LC-APPI/MS [26]. However, to the best of our knowledge, the application of APPI in the analysis of organic species in coals and their derivatives has not been reported.

In this work, to obtain comprehensive structural information of coals, two ionization methods, ESI and APPI, were used for analyzing esterified extracts from the oxidation of Zhundong subbituminous coal. Molecular association and MM distribution in esterified extracts were studied. Toluene and the mixture of toluene and anisole (95/5 in vol.) were selected as dopants for APPI, which were compared in ionization process and the corresponding assisted-ionization mechanisms were discussed.

2. Experimental

2.1. Sample preparation

2.1.1. Raw coal sample

ZSBC was used in this work. The coal was pulverized to pass through a 150-mesh screen and dried at 80 °C for 10 h in vacuum. Proximate and ultimate analyses for ZSBC are shown in Table 1.

2.1.2. Reagents

Aqueous HCl (36%), aqueous H₂O₂ (30%), diethyl ether (DEE), ethyl acetate (EA), aqueous NaOCl (active chlorine content ≥ 6%, alkali content 7%–8%), NaOH, anhydrous MgSO₄, anhydrous Na₂SO₃, toluene and anisole are analytical reagents. All of the organic solvents were distilled prior to use. Methanol, water and isopropanol with chromatographic grade were also obtained commercially.

2.1.3. Pretreatment of ZSBC with aqueous H₂O₂

3 g ZSBC and 30 mL aqueous H₂O₂ were mixed and stirred for 4 h. The reaction mixture was filtrated to obtain the filtrate and pretreated ZSBC (PTZSBC), which was dried in vacuum at 80 °C for 24 h.

Table 1

Proximate and ultimate analyses (wt%) of ZSBC.

Proximate analysis			Ultimate analysis (daf)				
M _{ad}	A _d	VM _{daf}	C	H	N	S	O _{diff}
8.79	5.68	34.94	75.23	3.18	0.70	0.56	20.33

daf = dried and ash-free base; M_{ad} = moisture (air dried base); A_d = ash (dried base, i.e., moisture-free base); VM_{daf} = volatile matter (dried and ash-free base).

2.1.4. Oxidation of PTZSBC with aqueous NaOCl

As Fig. 1 shows, 1 g PTZSBC was added to 80 mL aqueous NaOCl and magnetically stirred at 30 °C for 10 h. Then anhydrous Na₂SO₃ was added to the mixture to decompose excess NaOCl followed by filtration through a 0.45 μm membrane to obtain filtrate 1 (F₁) and filter cake 1 (FC₁). The F₁ was acidified with aqueous HCl till pH < 2 and filtrated to acquire filter cake 2 (FC₂) and filtrate 2 (F₂). The F₂ was extracted with DEE for 5 times to acquire extract solution 1 (ES₁) and inextractable solution 1 (IES₁). The IES₁ was extracted with EA for 5 times to obtain extract solution 2 (ES₂) and inextractable solution 2 (IES₂). The ES₁ and ES₂ were dried over anhydrous MgSO₄ and filtrated to remove MgSO₄·nH₂O. Organic solvents and water in the ES₁, ES₂, and IES₂ were removed using a Büchi R-210 rotary evaporator to obtain extract 1 (E₁), extract 2 (E₂) and inextractable fraction (IEF), respectively. The E₁, E₂ and IEF were esterified with CH₂N₂/DEE solution at 30 °C for 8 h to acquire methyl esterified E₁ (MEE₁), E₂ (MEE₂) and IEF (MEIEF), respectively.

2.2. Analytical methods and instrumentation

The MEE₁, MEE₂ and MEIEF were analyzed using a Agilent 1200/6210 HPLC/time-of-flight mass spectrometry (TOF-MS) equipped

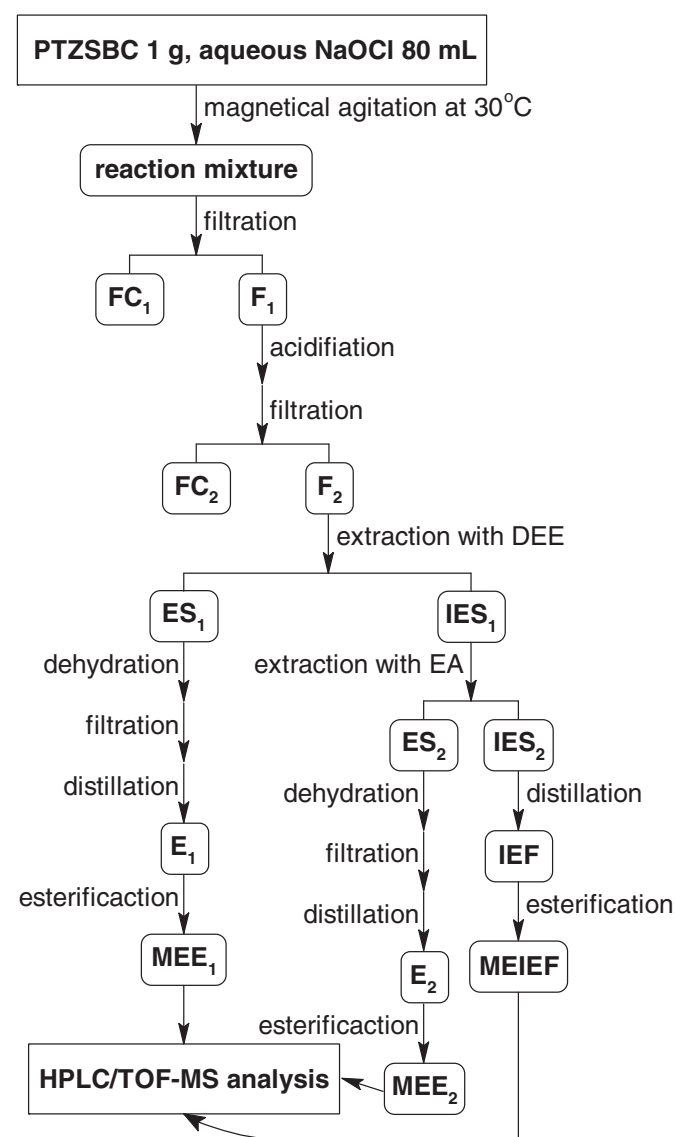


Fig. 1. Procedure for the preparation of MEE₁, MEE₂ and MEIEF.

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