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Methanolysis of extraction residue from Xianfeng lignite with NaOH and product characterizations with different spectrometries

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ABSTRACT

Extraction residue (ER) from Xianfeng lignite via ultrasonic extraction was subjected to methanolysis in the presence of NaOH at 300 °C for 2 h, and extracts 1–4 (E'_1-E'_4) from ER methanolysis were acquired by subsequent separation of the resulting soluble portion (SP). NaOH could promote ER methanolysis and hence increased the SP yield. Detailed molecular compositions (MCs) of E'_1-E'_4 were characterized with Fourier transform infrared spectrometer, gas chromatograph/mass spectrometer (GC/MS), direct analysis in real time ionization source coupled to ion-trap mass spectrometer (DARTIS/ITMS), and atmospheric solid analysis probe/time of flight-mass spectrometer (ASAP/TOF-MS). The results show that the SP is rich in aliphatic moieties, carbonyl and hydroxy groups, and has molecular mass distribution ranging from *m*/*z* 100 to 600. According to GC/MS analysis, phenols, especially polymethylphenols, were enriched in E'_1 and E'_2, whereas almost all the alkanoic acids, alkanedioic acids, benzoic acids, and phenyl-substituted alkanoic acids only appeared in E'_4. A series of polar and/or involatile organic species, which are difficult to be detected with GC/MS, were detected with DARTIS/ITMS and ASAP/ TOF-MS. NaOH could play an important role in cleaving ether bonds in ER during methanolysis and thereby enhanced the formation of oxygen-containing organic species. The use of multiple spectrometries provides a promising approach for understanding MC of the SP from coals.

1. Introduction

Lignites are abundant fossil resources in China with reserve more than 130 billion tons. However, they are considered as inferior fuels because of their low calorific value, high moisture content and ash yield. High moisture content (usually > 30%) in lignites militates against conventional use of lignites due to the high energy consumption for desiccation. On the other hand, lignites have great potential as feedstock for the production of chemicals, because they are rich in oxygen-containing organic compounds and most of them are value-added chemicals or specialty chemicals [1]. Therefore, developing efficient non-fuel utilization of lignites has deserves great attention.

Coal alkanolysis with alkali was first investigated by Makabe et al. [2–7] to evaluate the structural features of coals. The treated coals were almost soluble in pyridine. Structural features of the treated coals and reaction mechanism were deduced by analyzing the soluble portion (SP). Hydrolysis and rupture of the ether linkages were supposed to be the main reactions. Afterwards, Bimer et al. examined the effect of chemical pretreatment on the methanolysis of coals with NaOH at high temperature [8–11] and the effect of NaOH/methanol treatment on the formation of tar and gas during coal pyrolysis [12,13]. Lei et al. [14,15] investigated liquefaction of Shengli lignite with NaOH/methanol and found that the highest product yield was acquired at 300 °C with NaOH/lignite mass ratio of 1:1. Unfortunately, all the above investigations afforded little information on the molecular composition (MC) of the SP from coal alkanolysis limited by the analytical methods. Detailed characterization of the resulting SP using advanced analytical techniques is necessary.

For organic compounds from coals and their derivates the most commonly used analytical technique is gas chromatograph/mass spectrometer (GC/MS) due to its high sensitivity and good performance in separation [16]. However, GC/MS is usually suitable for analyzing relatively volatile, thermally stable, and less polar species. In addition, GC/MS has disadvantages such as long time-consumption and relatively complex sample pretreatment. Ambient ionization mass spectrometry, which has witnessed rapid development in recent years, is a useful analytical technique performed under ambient conditions [17]. It allows the direct and rapid analysis of a sample with minimal sample pretreatment, and can expand the detection range of GC/MS. Direct analysis in real-time (DART) [18–23] and atmospheric solid analysis probe (ASAP) [24–28] are two types of ambient ionization techniques which have been widely applied in many fields. Recently, DART ionization source coupled to ion-trap mass spectrometer (DARTIS/ITMS) was applied to characterize organic species from extraction [29] and oxidation [30] of coals, and ASAP/time of flight-mass spectrometer (ASAP/TOF-MS) was used to analyze coal-related model compounds [31,32].

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Lignites contain more or less SP that can be extracted. To avoid the disturbance of the compounds from the inherent SP for analyzing SP from methanolysis, in the present study, extraction residue (ER) from Xianfeng lignite (XL) was used to investigate the methanolysis reaction in the presence of NaOH. Fourier transform infrared (FTIR) spectrometer, GC/MS, DARTIS/ITMS, and ASAP/TOF-MS were used to characterize MC of the SP from ER methanolysis, aiming at facilitating the utilization of the SP and understanding the structural features of lignites.

2. Materials and methods

2.1. Materials

XL was collected from Xianfeng Coal Mine. It was pulverized to pass through a 200-mesh sieve (particle size of <74 μm) and dried in a vacuum at 80 °C for 24 h before use. All the organic solvents, including methanol, petroleum ether (PE), carbon disulfide (CDS), and diethyl ether (DEE), used in the experiments are analytical reagents and distilled prior to use. According to our recent study [33], XL was sequentially extracted under ultrasonication with five solvents to afford extracts 1–5 (E_1-E_5) and isometric CDS/acetone mixed solvent (IMCDSAMS)-inextractable portion, i.e., ER. As listed in Table 1, ER has lower nitrogen content but higher sulfur content than XL.

2.2. ER Methanolysis and subsequent treatments

As Fig. 1 shows, 1 g ER, 20 mL methanol, and 1 g NaOH were put into a 100 mL stainless-steel, magnetically stirred autoclave. The air inside the autoclave was purged with N_2. Then the autoclave was heated to 300 °C and maintained at 300 °C for 2 hfollowed by cooling to room temperature in a water bath. The reaction mixture was taken out from the autoclave and filtrated to afford filtrate 1 (F_1) and filter cake 1 (FC_1). FC_1 was washed with IMCDSAMS several times. The rinse solution was incorporated into the filtrate followed by rotary evaporation to obtain SP, which was extracted with PE under ultrasonication to obtain extract 1 (E'_1) and PE-inextractable portion (PEIEP), followed by extraction of PEIEP with CDS to obtain extract 2 (E'_2) and CDS-inextractable portion (CDSIEP). CDSIEP was acidized with hydrochloric acid to pH < 2 and filtrated to obtain filter cake 2 (FC_2) and filtrate 2 (F_2). FC_2 and F_2 were extracted with PE and DEE to afford extracts 3 and 4 (E'_3 and E'_4), respectively. All the yields were calculated on ash-free mass of XL.

2.3. Analytical methods

ER, E_1-E_5, and E'_1-E'_4 were analyzed with a Nicolet Magna IR-560 FTIR spectrometer by collecting 32 scans at a resolution of 4 cm^{-1} in reflectance mode with measuring regions of 4000–400 cm^{-1}. E_1 -E_5 and E'_1-E'_4 were analyzed with an Agilent 7890/5975 GC/MS. It is equipped with a capillary column coated with HP-5 (cross-link 5% PH ME siloxane, 60 m length, 0.25 mm inner diameter, and 0.25 μm film thickness) and a quadrupole analyzer with m/z range from 33 to 500 and operated in electron impact (70 eV) mode. Data were processed using MSD ChemStation software. Compounds were confirmed by comparing mass spectrawith NIST05a library data.

Table 1
Proximate and ultimate analyses (wt.%) of XL and ER.

Sample	Proximate analysis			Ultimate analysis (daf)				$S_{t,d}$	H/C
	M_{ad}	A_d	V_{daf}	C	H	N	O_{diff}		
XL	25.67	18.45	36.52	63.07	6.01	1.79	>28.73	0.40	1.1356
ER				62.77	6.01	1.61	>29.15	0.46	1.1414

diff: by difference; 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).

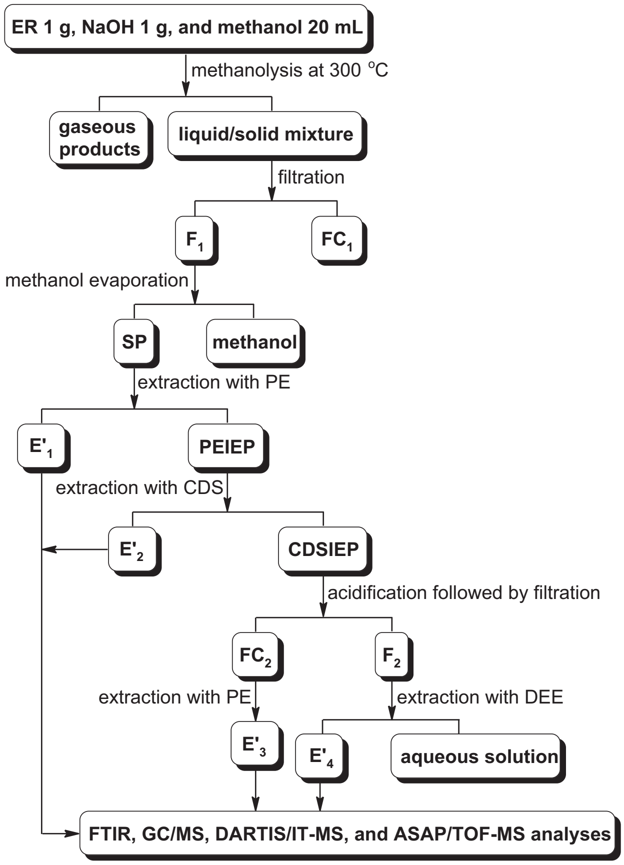

Fig. 1. Procedure for ER methanolysis, subsequent treatments and analyses.

E'_1-E'_4 were also analyzed with an IonSense DARTIS/Agilent XCT ITMS, and an IonSense ASAP/AP/Agilent 6210 TOF-MS to expand the detection range of GC/MS and afford more information on the SP. The DARTIS is interfaced to the ITMS using He as the discharge gas and N_2 as the alternative gas with a flow rate of 2 L min^{-1} and operated at 450 °C. The DARTIS/ITMS was run in positive ionization mode (PIM) with *a m/z* range from 50 to 1000 and processed using LC/MSD Trap software. The ASAP/TOF-MS is equipped with an atmosphere pressure chemical ionization ion source. A capillary with 25 mm length and 1.7 mm outer diameter was mounted on the center of an ASAP. The corona discharge current and capillary voltage were set to 4.0 μA and 4000 V, respectively. The temperatures of the desolvation gas and drying gas were 250 and 350 °C, respectively. The ASAP/TOF-MS was operated in PIM with a m/z range from 100 to 1000, and mass spectral data were processed using Agilent MassHunter WorkStation software.

3. Results and discussion

3.1. Group components in E_1-E_5

As illustrated in Fig. S1, the organic compounds identified in E_1-E_5 can be grouped into alkanes, cyclanes, alkenes, arenes, alkanols, phenols, aldehydes, ketones, carboxylic acids (CAs), alkyl alkanoates (AAs), dialkyl phthalates (DAPs), and nitrogen-containing species (NCSs) according to GC/MS analysis. Alkanes are the main group component in E_1-E_5, and the total relative content (RC) of alkanes in each extract is higher than 50%. As Fig. S2 displays, the absorbances of aliphatic moieties (AMs) at 2919, 2850, 1457, and 1380 cm^{-1} indicate that AM-rich species (AMRSs) in XL were easily extracted, which is consistent with the high relative content of alkanes in E_1-E_5. The absorbance at 1700 cm^{-1} assigned to carbonyl group may result from aldehydes, ketones, CAs, AAs, and DAPs, as shown in Fig. S1.