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N-methyl-2-pyrrolidone/CS_2 extraction induced changes in surface and bulk structures of a lignite

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ABSTRACT

Investigation on the changes in detailed surface and bulk structures during *N*-methyl-2-pyrrolidone/CS_2 mixed solvent extraction is crucial to improve and develop the technology of clean and value-added utilization of coals. The surface and bulk structures of Longkou lignite (LL) were investigated before and after ultrasonic-assisted extraction with mixed solvent by multiple direct tools, including, Fourier transform infrared (FTIR) spectrometer, X-ray photoelectron spectrometer (XPS), scanning electron microscope (SEM), and solid-state ^{13}C nuclear magnetic resonance (NMR). The results show that phenols, alcohols, and ethers are the main C–O bond containing species in LL, which is further confirmed by ^{13}C NMR and XPS analyses. The average ring number in each aromatic cluster and substituents in each aromatic ring are 4 and 2–3, respectively. XPS analysis shows that pyrrolic nitrogen is the main nitrogen occurrence and sulfur is mainly present in sulfoxide and sulfone in LL. ^{13}C NMR and FTIR analyses all reveal that aromaticity and aromatic cluster size for LL decreased, while the length and the number of substituents on aromatics increased after extraction. C–O and multi-substituted aliphatic carbons are not easy to dissolve and concentrate in extract residue. It is the basic pyridine-N rather than pyrrolic-N species that are easy to extract with mixed solvent. The content of thiophene-S increased significantly, while other organic sulfur species decreased after extraction, especially for thiophenol and sulfone. Furthermore, solvent extraction leads to the reduction of particle size and increase of surface roughness of LL.

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1. Introduction

Coal has always attracted interest as an energy source due to its wide geographical distribution and low mining cost. However, the conventional coal utilization processes like thermal chemical conversion need high temperature and pressure which consume enormous energies and lead to environmental problems, such as, excessive emission of CO_2. In addition, more than 50% of current coal reserves are categorized as low-rank coal, including sub-bituminous coal and lignite. Developing approaches that can use low-rank coals while address these problems is therefore essential. Clean and highly efficient value-added chemical harvesting from coals is one way in which they could become an environment-friendly source. Employing extraction methods, such as, supercritical gas extraction [1], supercritical fluid extraction [2], thermal dissolution [3], and mild solvent extraction [4] to capture useful components from lignite is thus a feasible approach.

Among these methods, mild solvent extraction using low boiling point solvents under the boiling point temperature or high boiling point solvents near room temperature as the extraction medium is an effective and suitable method for obtaining value-added chemicals from low-rank coals because of its convenient manipulation and low investment cost [5]. In addition, mild solvent extraction is also one of the most important approaches to obtain valuable information on coal structure through characterization of the extract and residue [6]. Particularly, *N*-methyl-2-pyrrolidone/CS_2 (NMP/CS_2) mixed solvent is a popular solvent system and has an extreme high extraction ability for many bituminous coals. Detailed investigations on the structural changes and the relationship between the coal structure and

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Table 1
Proximate and ultimate analyses of the LL, ER, and *E*.

Sample	Proximate analysis (wt%)			Ultimate analysis (wt%, daf)					
	M_{ad}	A_d	V_{daf}	C	H	O[a]	N	S	H/C
LL	8.26	31.85	42.34	68.26	2.97	26.83	1.37	0.57	0.52
ER	6.43	32.06	46.92	66.78	2.91	28.21	1.47	0.63	0.52
E	0.13	0.26	45.30	64.52	5.35	26.50	2.07	1.56	0.99

[a] By difference.

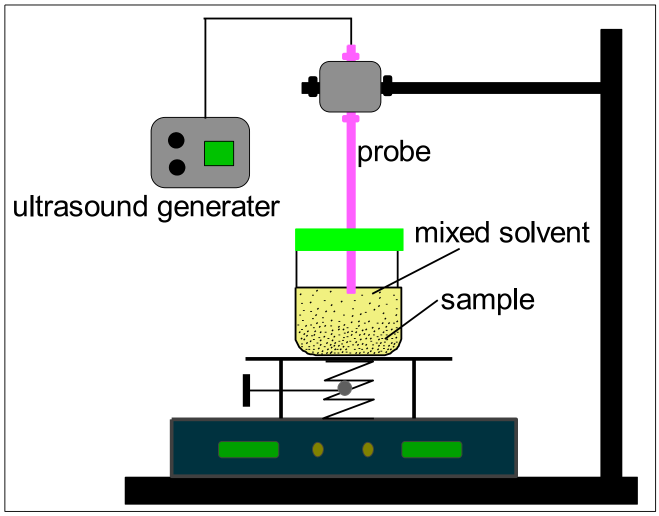

Fig. 1. Illustration of the ultrasonic-assisted extraction with mixed solvent.

extractable substance during mixed solvent extraction are crucial to understand the extraction mechanism and provide useful information for technology development.

So far, various studies have focused on extraction process of mixed solvent for some aspects. Iino et al.'s work showed that the residues from mixed solvent extraction of five bituminous coals had similar or slightly less volatile matter than the raw coals while contents of hydroxyl groups, C—O bonds, and radicals in coals increased after extraction [7]. In addition, it was believed that the swelling ratio of coals could increase obviously but the caking property of the coals reduced largely after the soluble fractions were removed using NMP/CS_2 mixed solvent [8]. The network structure (aggregates of coal molecules) in coal could be irreversibly changed as same as a heat treatment by the dissolution of non-covalent bonds with the mixed solvent which led to disappearance of the endothermic peak at 350 °C [9]. Besides these studies, it was found that fusinite and vitrinite fractions were mainly concentrated in the residues from mixed solvent extraction with yields below 30 wt%, but even at 74.1 wt% extraction yield, some vitrinite components still remained in the residues [10]. Structure changes of coals were evaluated intensively at various aspects as reviewed above, however, changes of the detailed surface structures, such as, surface functional groups, surface element composition, and surface morphology, for lignite caused by mixed solvent extraction were rarely explored and investigated. Furthermore, it is considered that surface compositions of coal determined by X-ray photoelectron spectrometer (XPS) and Fourier transform infrared (FTIR) spectrometer may be different from those bulk composition from solid-state ^{13}C nuclear magnetic resonance (SS ^{13}C NMR) spectroscopy which give rise to inconsistency of the results between the two type analytical tools [11].

In this work, the surface structures and compositions of Longkou lignite (LL) were characterized before and after ultrasonic-assisted extraction (UAE) with NMP/CS_2 mixed solvent by multiple tools, including XPS, FTIR spectrometer, and scanning electron microscope (SEM). Then SS ^{13}C NMR was employed to evaluate bulk structural compositions of LL and the changes during extraction to verify the results from surface analytical tools. The probably mechanism during mixed solvent extraction of LL was inferred based on the experimental data. The goal of this study is to determine detailed structural compositions of LL and changes during mixed solvent extraction, which is important for the efficient and environment-friendly utilization of coal by extraction approach and understanding the dissolution mechanism.

2. Experimental section

2.1. Materials

Longkou lignite (LL) was obtained from Longkou coal mine in Shandong province, China. The lump coal was ground to pass through the 200 mesh sieve, and the pulverized coal was vacuum-dried at 80 °C for 6 h prior to use. The properties of the raw coal are listed in Table 1. *N*-methyl-2-pyrrolidone, CS_2, and acetone used in the experiments were purchased from Sinopharm Chemical Reagent Co., Ltd., China and all the organic solvents are analytical-pure reagents, which were distilled before use.

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