Fuel Processing Technology 129 (2015) 222–226

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Dissolution performance of coals in ionic liquid 1-butyl-3-methyl-imidazolium chloride

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A R T I C L E I N F O

Article history:
Received 22 January 2014
Received in revised form 19 September 2014
Accepted 19 September 2014
Available online 7 October 2014

Keywords:
Coal type
Extraction
BMIC

A B S T R A C T

A series of coals with various ranks were extracted with ionic liquid (IL) 1-butyl-3-methyl-imidazolium chloride (BMIC), which was found to be a very effective solvent for the extraction of coals in a previous study. The relationship between the extract yield of coal with BMIC and the quantities of oxygen-containing functional groups in lignites was investigated. Also the mechanism of extraction of Xianfeng lignite (XL) with BMIC was investigated by the diffuse reflectance spectra (DRIFT) analysis. It was found that the extract yields of coals with BMIC varied with the ranks of coals. With the increase of the oxygen content and the decrease of carbon content, extract yield of coal with BMIC significantly increased. Extract yield of lignites with BMIC increases almost linearly with the increase of carboxyl content. The extraction with BMIC significantly changes the types and the distribution of hydrogen bonds in XL.

1. Introduction

An understanding of the solubility of coals is of both fundamental and practical importance. From the fundamental view, extraction and/or thermal dissolution of coal in organic solvents is one of traditional and useful methods to investigate the structure of coal. The nature of coal/solvent interactions and their effects on solubility of coal ordinarily provide important insights into the physical and chemical structures of coal. Iino and coworkers [1,2] found that a carbon disulfide-N-methyl-2-pyrrolidinone (CS_2/NMP) mixed solvent (1:1 by volume) gave more than 60% extract yield at room temperature for some bituminous coals, then they proposed that the main structure for these bituminous coals is an associated model. To obtain information on the main structure of coal, the coal must be extracted effectively. From the practical view, the thermal dissolution of coal with organic solvents is one of useful methods to produce ash-free coal called HyperCoal [3–6], which can be fired in gas turbines directly to achieve a higher net power output and be used in low temperature gasification [7,8] and as an additive in cokemaking [9]. But at mild extraction conditions the extract yield of low-rank coal with many conventional organic solvents is very low.

Painter et al. firstly reported that certain ILs (such as BMIC) can fragment, swell, partially solubilize, and disperse some coals. They found that the solubility of a Powder River Basin coal and an Illinois No. 6 coal in BMIC is higher than that of an Upper Freeport coal and thought that the strength and extent of the interactions between coals and ILs will vary with the structure of the coals [10]. Also our groups found that the solubility of the XL in BMIC is almost 4 times than that of a Shenmu–Fugu subbituminous coal [11]. This result also indicated that coal type significantly affects the extract yield of coal with BMIC. Recently Jin Won Kim et al. synthesized a new bis(imidazolium) cation-based IL and found that the lengths of alkyl ether chains between imidazolum rings in prepared ILs affect the dissolution performs and distribution of products [12]. Also Kalpit Shah et al. found that IL interacts differently with the different coal macerals [13]. However, the extraction behavior of coals with ILs is still unknown, especially that little information about coal type on extraction behaviors of coal with ILs and/or the interaction between coals and the ILs is available in literature based on our knowledge.

In the present paper, the extraction behaviors of a series of coal with different ranks with BMIC under microwave irradiation were investigated. The relationship between the nature of different rank coals and the extract yield with BMIC was correlated. The nature of different lignites was investigated by analyzing the number of oxygen containing functional groups. Also the mechanism of dissolution of lignite with BMIC was investigated by DRIFT analysis. The investigation facilitates the better understanding of the dissolution performance of coals in ILs.

2. Experimental

2.1. Properties of coals

Eight coals were used in this study, which as received were ground to sizes smaller than 200 mesh, stored under nitrogen atmosphere, and dried under vacuum at 80 °C overnight before use. The ultimate

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http://dx.doi.org/10.1016/j.fuproc.2014.09.021
0378-3820/

Table 1
Ultimate analysis of the coal samples.

Sample	Symbol	Ultimate analysis (wt/%, daf)				$S_{t,d}$	H/C atomic ratio
		C	H	O[a]	N		
Qinglongshan lean coal	QLC	92.35	4.96	>0.95	1.28	0.45	0.6445
Australia coking coal	ACC	91.94	5.47	>0.25	1.69	0.64	0.7139
Dongdu gas coal	DGC	84.71	6.15	>5.49	1.79	1.85	0.8712
Shanjialin rich coal	SRC	80.93	5.59	>10.24	1.35	1.89	0.8289
Shenmu–Fugu subbituminous coal	SFSBC	79.86	5.56	>12.99	1.23	0.36	0.8355
Xilinggele No. 6 lignite	XL6	68.45	6.35	>22.65	1.26	1.30	1.1132
Shengli lignite	SL	68.25	5.23	>24.34	1.12	1.05	0.9196
Xianfeng lignite	XL	64.75	5.81	>27.08	1.84	0.52	1.0768

[a] By difference; daf, dry and ash-free basis; and $S_{t,d}$, total sulfur (dry basis).

and proximate analyses of these coals were shown in Table 1. The IL used in this study was BMIC purchased from Shanghai Cheng Jie Chemical Co. LTD. and dried at 100 °C in a vacuum oven 48 h prior to the experiments.

2.2. Extraction of coal samples with BMIC

The dissolution experiments of coals with BMIC or fresh NMP were carried out in a microwave apparatus (XH-100B, Beijing Xiang Hu Science and Technology Development Co., Ltd.) with temperature measurement, time controlling and stirring. In each run, coal (1.0 g) and BMIC (10 g) or NMP were charged into Teflon tube to be extracted at 200 °C for 30 min at microwave oven. Afterward the reaction mixtures were cooled to room temperature and washed out by NMP. Then reaction mixtures were separated by filter membrane paper with a pore size of 0.45 μm after centrifugation for 50 min at 14,000 rpm. The residue was exhaustively extracted with fresh NMP many times in the same way until the filtrate became almost colorless. Then, the residue was washed successively with water many times and dried under vacuum at 80 °C for 24 h. Each extract yield was calculated as the weight ratio of the residue to the coal sample on dry and ash-free base. NMP was removed through rotary evaporation, and the extracts in filtrate were precipitated by adding some water.

2.3. Sample characterization

FTIR spectra of the coal samples, extracts, and residues were measured on a Nicolet 6700 spectrometer using the KBr-pellet technique.

Quantitative measurement of oxygen-containing group in coal: Total acid and carboxyl in coal were measured by titrimetric method based on the following reactions:

$$Ba(OH)_2 + 2HA = BaA_2 + 2H_2O\ (\text{total acid})$$

$$2(-COOH) + Ca(CH_3COO)_2 = -COO-Ca-OOC- + 2CH_3COOH$$

$$CH_3COOH + NaOH = CH_3COONa + H_2O\ (\text{carboxyl})$$

Phenolic hydroxyl was obtained by subtraction of total acid and carboxyl.

DRIFT of samples were measured on a Nicolet 6700 spectrometer with the high temperature/high-pressure accessory of Thermo Spectra-Tech using ZnSe windows. The detector was liquid nitrogen cooled MCT (mercury cadmium telluride). DRIFT spectra were collected when the samples were heated from room temperature to 200 °C in 100 ml/min Ar to eliminate the influence of moisture.

3. Results and discussion

3.1. Extraction behaviors of coals with BMIC

Eight coals (from 64.75% C to 92.35% C) were used to determine the dependence of extract yields of coals with BMIC on coal rank. As shown in Fig. 1, the extract yield of coal with BMIC is significantly dependent on the coal rank. Among the eight coals studied, the XL, a kind of Chinese lignite with 64.75% C, gives the highest extract yield of 74.0%. However, QLC, a kind of Chinese nonanthractic coal with 92.35% C, gives the lowest extract yield of 1.2%. SFSBC, a kind of Chinese sub-bituminous coal with 79.86% C, gives 37.1% extract yield. Overall, extract yield of coals with BMIC follows the order: lignite > bituminous coal > nonanthractic coal. The extract yield of coal with ILs is probably related to the disruption of crosslinking structure of the coal network. Also Painter et al. found that the solubility of two coals, a Powder River Basin coal and ILLinois No. 6 coal, in BMIC was higher than that of Upper Freepore coal [10]. This finding suggests that the strength and extent of the interactions between coals and ILs vary with the structure of coals. The above result clearly indicates that the mainly aggregated structure of XL can be effective fragmented in ILs, suggesting that BMIC is an effective solvent to explore the structure of lignite or to produce HyperCoal from lignite.

3.2. Relationship between the extract yield of raw coal with BMIC and the coal parameters

Base on above the result, it can be observed that the extract yield of coal with BMIC depends on coal rank. It is of value to examine the coal parameters that are correlated with the extract yield of coal with BMIC. As shown in Fig. 2(a), in addition to XL6 (a kind of Chinese Xilinggele No.6 lignite), on the whole, the extract yield of coals with BMIC decreases with the increase of carbon content up from 64.75% C to 92.35% C. It has been postulated that the non-covalent interactions, such as hydrogen bonding, van der Waals, charge transfer, and aromatic π–π interaction, govern the associated molecular structure of coal and play an important role in the physical and chemical properties of coal. Different coals may have different non-covalent interactions. Ordinarily solvent extraction may disrupt some non-covalent interactions. Bituminous coals are thought to form mainly aggregated structures through π–π interaction, whereas low-rank coals form crosslinking structures through interactions among functional groups containing heteroatomics

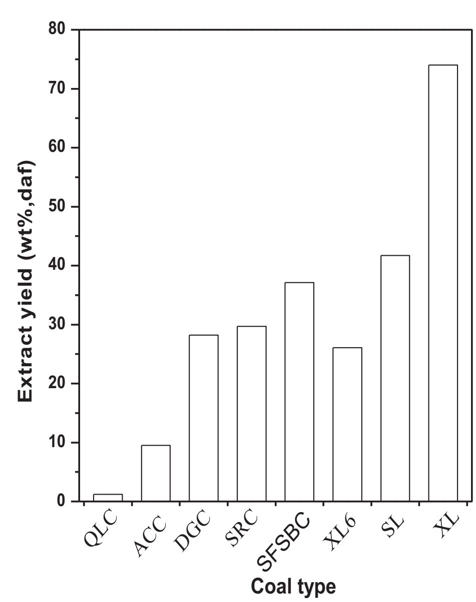

Fig. 1. Extract yields with BMIC for coals.