Fuel 212 (2018) 12–18

Contents lists available at ScienceDirect

Fuel

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

Influence of the addition of various ionic liquids on coal extraction with NMP

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ARTICLE INFO

Keywords:
Coal
Solvent extraction
NMP
Ionic liquids

ABSTRACT

In this work, two Turkish coals were extracted with N-methyl-2-pyrrolidone (NMP) and NMP containing a small amount of ionic liquids (ILs) under reflux conditions at atmospheric pressure. The effects of coal type, ionic liquid type, ionic liquid-to-coal ratio, and ultrasonic interactions on extraction yield were investigated. The ILs used were: 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-buty-4- methylpyridinium chloride ([Bmp]Cl), 1-ethyl-3-methylimidazolium chloride ([Emim]Cl), and 1-butyl-2,3-dimethylimidazolium chloride ([Bdmim]Cl). It was found that the extraction yield of coals using NMP/ILs varied with coal type, IL type and amount of IL. ILs were effective on the extraction of Afsin-Elbistan (AE) lignite, but not on the extraction of Üzülmez (UZ) coal. A significant increase in extraction yield for AE lignite was observed when a small amount of IL was added into NMP. It was determined that [Bmim]Cl was the most efficient IL used for the extraction of lignite compared to the others ILs used, and the extraction efficiency was found to increase by increasing the amount of ionic liquid added into NMP.

1. Introduction

With its population and economy growing, Turkey's demand for energy resources is increasing rapidly. Low-rank coals such as lignites are important energy resources for Turkey because of their enormous reserves. However, Turkish lignites are considered to be of poor quality due to their high moisture, mineral matter, and organic oxygen contents, resulting in low calorific value, and the large amount of pollution generated from their burning. However, besides these bad features, the abundance of valuable organic components, including aromatic and aliphatic chemicals, makes lignites an attractive raw materials for the production of value-added products, especially organic chemicals [1]. Therefore, the development of effective methods for efficient lignite use is required and many attempts have been made towards this. One of the effective ways for lignites utilization is achieved high value-added products from lignites. Solvent extraction of lignites with organic solvents is a useful method for producing high value-added products such as clean liquid fuels, hyper-coal (ash-free coal), and chemical feedstocks. Additionally, the solvent extraction technique is widely used to investigate the structure of coal [2–5]. Various organic solvents such as carbon disulphide, benzene, n-hexane, toluene, chloroform, tetrahydrofuran, NMP, pyridine, and methanol have been used in the solvent extraction of lignites [5]. During the solvent extraction of lignites, a high extraction yield is desirable to obtain useful information on the structure of coal and to produce high yields of the value-added products. But with many organic solvents, the extraction yield of lignites is very low at mild extraction conditions, such as below the pyrolysis temperature [6]. To increase the extraction yield, lignites have been extracted with mixed solvents. Iino and Matsuda [7] extracted two different coals with an alcohol-benzene mixture at room temperature and found that the extraction yields from mixtures were much greater than those from alcohols and benzene alone. They also found that a carbon disulphide (CS_2)-pyridine mixture (1:1 vol) was an efficient solvent for the extraction of bituminous coals at room temperature [8]. Takanohashi et al. [9] used single solvents and mixed solvents to extract Loy Yang lignite under ultrasonic interactions at room temperature. Of the solvents used, NMP and NMP/methanol mixed solvent (8:2 vol) gave the high yields, 14.3% and 15.3%, respectively. Iino et al. [10] found that a CS_2/NMP mixed solvent gave a high extraction yield for many bituminous coals at room temperature. They also showed that a small amount of various additives, such as tetracyanoethylene and p-phenylenediamine, significantly enhanced extraction yields [11]. Giray et al. [12] reported that the extraction yield of coal with NMP/CS_2 was markedly enhanced by adding small aromatic amines. Sun et al. [13] studied the extraction of some coals using a supercritical carbon dioxide ($scCO_2$)/NMP mixed solvent and found that the yield from low-rank

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http://dx.doi.org/10.1016/j.fuel.2017.10.017
Received 13 February 2017; Received in revised form 7 July 2017; Accepted 5 October 2017
0016-2361/

coals was higher than with CS_2/NMP. Takahashi et al. [14] studied the effect of lithium and tetrabutylammonium salts with the addition of various anions on the extraction yield of coal in a CS_2/NMP mixed solvent and found that the addition of LiX increased the extract yield for several coals. Li et al. [15] showed that addition of LiCl was effective on the dissolution of coal in NMP. These findings show that some salts can be used in the solvent extraction of coal, especially low-rank coal such as lignite [16]. As shown, using additional solvents or salts with NMP increases the extraction yield of lignite.

Recently, the amount of literature regarding applications of ionic liquids (ILs) has increased. This is due to their useful properties such as low vapour pressure, high thermal stability, low combustibility, environment-friendly and unique solvating properties for many polar and non-polar compounds [17,18]. ILs are pure salts composed of organic cations and organic or inorganic anions [19]. Their properties can be adjusted by varying both the cation and anion contents [20]. For these reasons, ILs have been used in the field of coal chemistry as an alternative green solvent. Some researchers have used ILs to extract valuable organic components and asphaltenes fractions from direct coal liquefaction residue [21–23]. These results showed that ILs can break the hydrogen bonds in coal effectively. Painter at al. [24] demonstrated that certain ILs were able to disperse, swell and fragment some coals. Lei et al. [25,26] studied the extraction of Xianfeng lignite in a series of ILs at 200 °C. They found that ILs affect the extraction of lignite and [Bmim]Cl showed good performance on the dissolution of Xianfeng lignite. In another study, coals of various rank were extracted with [Bmim]Cl, which proved to be very effective for the extraction of lignite [27]. Lei et al. [6] also studied the extraction behaviour of three lignites with 1-ethyl-3-methylimidazolium acetate ([Emim]Ac) and found it to be a more efficient solvent for the extraction of lignites than [Bmim]Cl.

In the present work, the effect of the addition of various ILs to NMP on the extraction of two different types of coal was investigated. The effects of coal type, ionic liquid type, and ionic liquid-to-coal ratio on extract yield were also investigated. These experiments were carried out under ultrasonic interactions and the effect of ultrasonic interactions on the extraction of coal with NMP/ILs mixed solvents was also investigated.

2. Experimental section

2.1. Coal samples

We used two coals of different rank for this investigation: Afsin-Elbistan (AE) lignite from southeast-Anatolia and bituminous Üzülmez (UZ) coal from the Western Black Sea region. The samples were ground in a ball mill and sized to < 60 mesh, dried at 80 °C for 12 h in a vacuum, and stored in a desiccator before use. Table 1 presents the proximate and ultimate analyses, determined according to ASTM standards (ASTM D3172-74 and ASTM 5373).

Table 1
Proximate and ultimate analyses of the coal samples used in this study.

Proximate analysis (wt%, db)	AE lignite	UZ coal
Ash	34.2	6.2
Volatile matter	46.6	28.9
Fixed carbon	19.2	64.9
Ultimate analysis (wt%, daf)		
C	57.3	91.8
H	6.5	3.9
N	2.1	1.3
S	3.5	0.7
O[a]	30.6	2.3

[a] By difference.

2.2. Extraction solvents

NMP was used as the main solvent and four different ILs were used as additives. The ILs were all purchased from Sigma-Aldrich and used as-received. Fig. 1 shows the chemical structures and abbreviations of these ILs. All solvents used were commercial pure chemical reagents without further purification.

2.3. Solvent extraction experiment

Extraction was carried out in a glass round-bottomed flask equipped with a reflux condenser, at the boiling point of the solvent (202 °C) and at atmospheric pressure. NMP was used as the extraction solvent and four ILs as additives. In brief, the flask was charged with coal (2 g), ILs and, NMP (30 mL), then heated for 1 h. To determine the effect of ILs/coal ratio (w/w), a 2 g coal sample was used and the ILs/coal ratios were 0.1, 0.5, 1.0, and 2.0. After extraction, the solid residue and the liquid phase were separated by filtration. The residue was washed with deionised water, methanol and acetone, then dried in vacuum at 80 °C for 12 h. The extraction yield is defined as follows:

$$Extraction\ Yield\ (wt\%,daf) = \left[\left(1-\frac{M_r}{M_c}\right)/\left(1-\frac{A_c}{100}\right)\right] \times 100 \quad (1)$$

All the experiments were repeated three times and the errors in extraction yield were < 1.3%.where, Mc (g), Mr. (g), and Ac (wt%, db) are the initial mass of the coal, the mass of the residue, and the ash content of the initial coal, respectively.

2.4. FT-IR measurement

The FTIR spectra were measured using a Perkin-Elmer Spectrum 100 with an attenuated total reflectance attachment. Each sample was scanned 32 times over a wave number range from 450 to 4000 cm^{-1} and at a spectral resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Effect of coal type on the extraction yield

The extraction of coal at mild conditions occurs by a solvent breaking up the noncovalent interactions between the coal molecules. During the extraction of coals using an organic solvent, the solvent breaks the noncovalent interactions between coal molecules such as the hydrogen bonds, London forces, charge-transfer interactions, pi-pi interactions and, ionic forces and extracts the coal [10,28]. If these interactions are easily broken, the extraction yield is higher. Some noncovalent interactions are so strong that they cannot be disrupted by conventional solvents, therefore the extraction yields are low. Various studies have found that NMP is one of the most effective solvent for coal extraction [29–32]. NMP is a polar solvent that cleaves the noncovalent interactions between coal molecules and thus increases extraction yield. In this study, bituminous UZ coal and AE lignite were extracted with NMP under reflux conditions at atmospheric pressure. The results are presented in Fig. 2. It was found that UZ coal gave a relatively higher extraction yield than AE lignite. Therefore, NMP is effective for UZ coal but not for AE lignite. The lower extraction yield of AE lignite is probably related to the difference in the noncovalent interactions between the coals. The aromatic structure of coal increases with increasing carbon content of coal [33]. The carbon content of UZ coal is higher than that of AE lignite, as shown in Table 1. Therefore, pi-pi interactions are dominant in the UZ coal. Conversely, in AE lignite, ionic forces and hydrogen bonds are dominant because of the presence of polar functional groups such as hydroxyls, carboxyls and carbonyls [34,35]. NMP contains a pyrrlodinone ring that interacts strongly with aromatic rings and destroys the charge-transfer and pi-pi interactions