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

Özgür Sönmez[a,*], Özcan Yıldız[a], Mehmet Özden Çakır[a], Belgin Gözmen[a], E. Sultan Giray[b]

[a] Department of Chemistry, Faculty of Arts and Science, Mersin University, Ciftlikkoy Campus, Mersin, Turkey
[b] Department of Chemistry, Faculty of Arts and Science, Çukurova University, Adana, Turkey

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

* Corresponding author.
E-mail address: osonmez@mersin.edu.tr (Ö. Sönmez).

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
Available online 14 October 2017
0016-2361/ © 2017 Elsevier Ltd. All rights reserved.

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

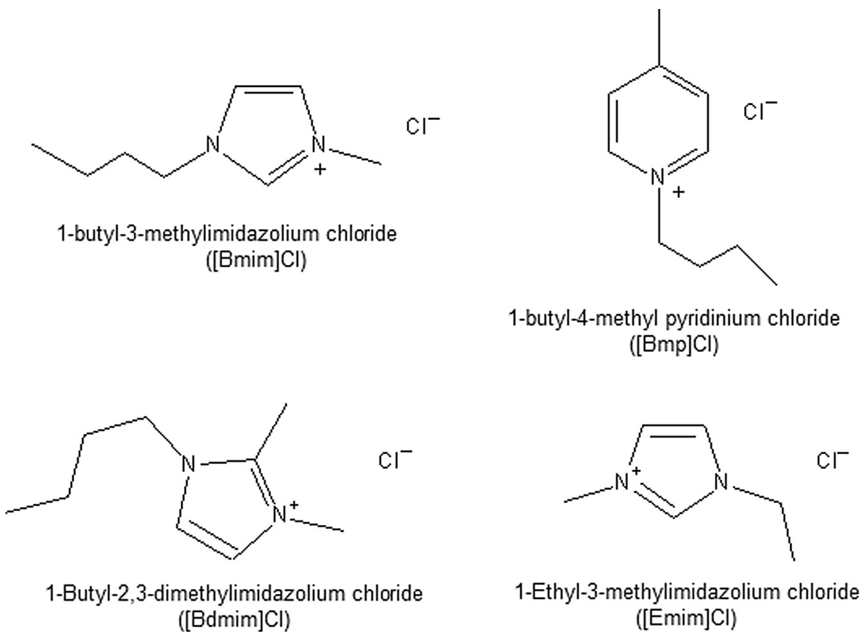

Fig. 1. Chemical structure, chemical name, and abbreviations of ILs used in this study.

between aromatic groups [10,34,36]. The low extraction yield of AE lignite in NMP is due to the lack of charge-transfer and pi-pi interactions. However, the high extraction yield of UZ coal in NMP indicates the presence of charge-transfer and pi-pi interactions. Consequently, when NMP is used as a single solvent, it does not break the noncovalent interactions in AE lignite, resulting in low extraction yield.

As discussed above, NMP is not strong enough to break the noncovalent interactions in AE lignite. Therefore, to enhance the extraction yield of both coal samples in NMP, some ILs was used as additive solvents. The results obtained are shown in Fig. 3. Compared with AE lignite, the ILs were not effective on the extraction of UZ coal in NMP. As expected, different extraction yields were obtained from coals of various rank. The reason for this may be due to the different oxygen contents of the both coal samples. Some studies have shown that the oxygen content of coal affects the extraction yield, especially in low-rank coals. For example, Koyana et al. [37] reported that polar solvents are required to obtain higher extraction yield for coals with a high oxygen content. Sakimoto et al. [38] also showed that the effectiveness of a polar solvent increased with increasing phenolic hydroxyl content in coal. ILs are also polar solvents and an increase in extraction yield for low-rank coal can be expected when they are used as extraction solvents.

The noncovalent interactions in coal significantly affect their extraction by solvents. ILs can break these noncovalent interactions and contribute to the extraction of the coal. Cui et al. [39] explained the interaction mechanism between ILs and coal using the electron-donor-acceptor theory. ILs cations and anions act as electron donors and acceptors and they break the noncovalent interactions, such as hydrogen bonds between the coal molecules. The breaking of these noncovalent interactions causes a structural loosening and increases the extraction yield. They also suggested that the cations and anions in ILs react with the oxygen and hydrogen atoms of the hydroxyl group in coal, respectively. Lei et al. [6,27] proposed that the extraction yield of low-rank coals such as lignites with ILs depends on the oxygen and carboxyl contents of the coal. They also showed that the extraction yield with ILs increased with an increasing number of carboxylic groups. The extraction of lignites in ILs is achieved by breaking the hydrogen bonds, which results in structural relaxation and an increase in extraction yield [16,40]. As shown Table 1, the oxygen content of AE lignite is higher than that of UZ coal, this indicates the presence oxygen-containing functional groups such as carboxylic acid, carbonyls and phenolic hydroxyls. ILs disrupt the hydrogen bonds among the oxygen-containing functional groups in AE lignite, resulting in higher extraction yields. In comparison, the extraction yield of UZ coal obtained by ILs addition is low. This indicates that the interactions between UZ coal and ILs are weak. This may be due to the low oxygen content of UZ coal, resulting

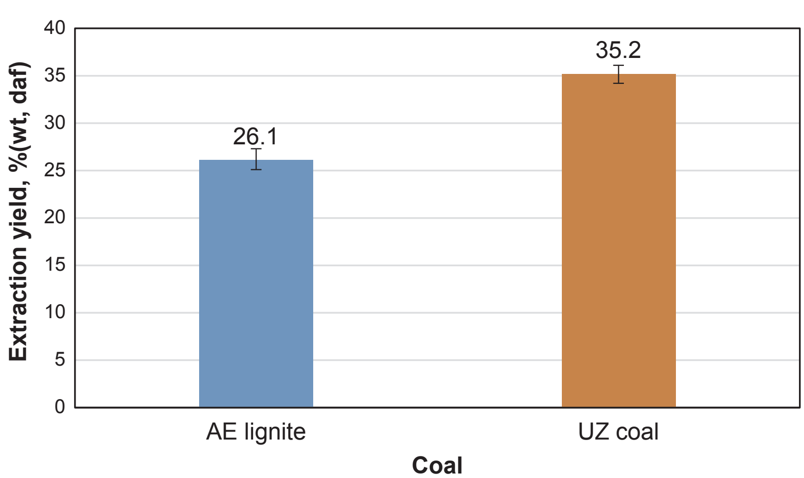

Fig. 2. The extraction yield of coal samples in NMP.

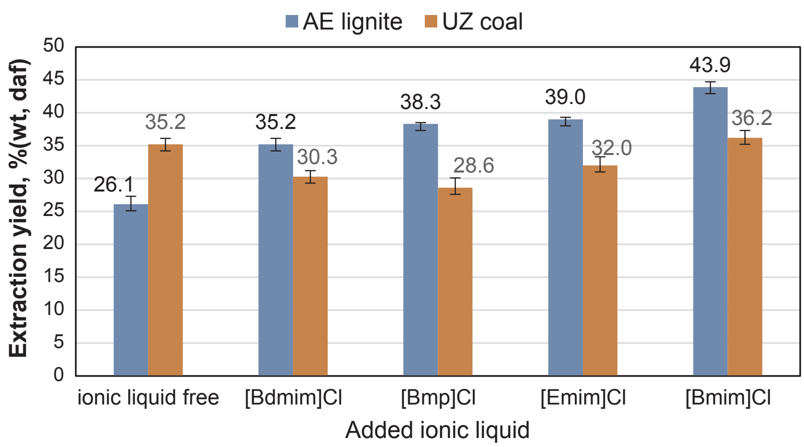

Fig. 3. Effect of different ionic liquids on extraction yield (ILs/coal ratio: 2.0 and extraction time is 1 h).

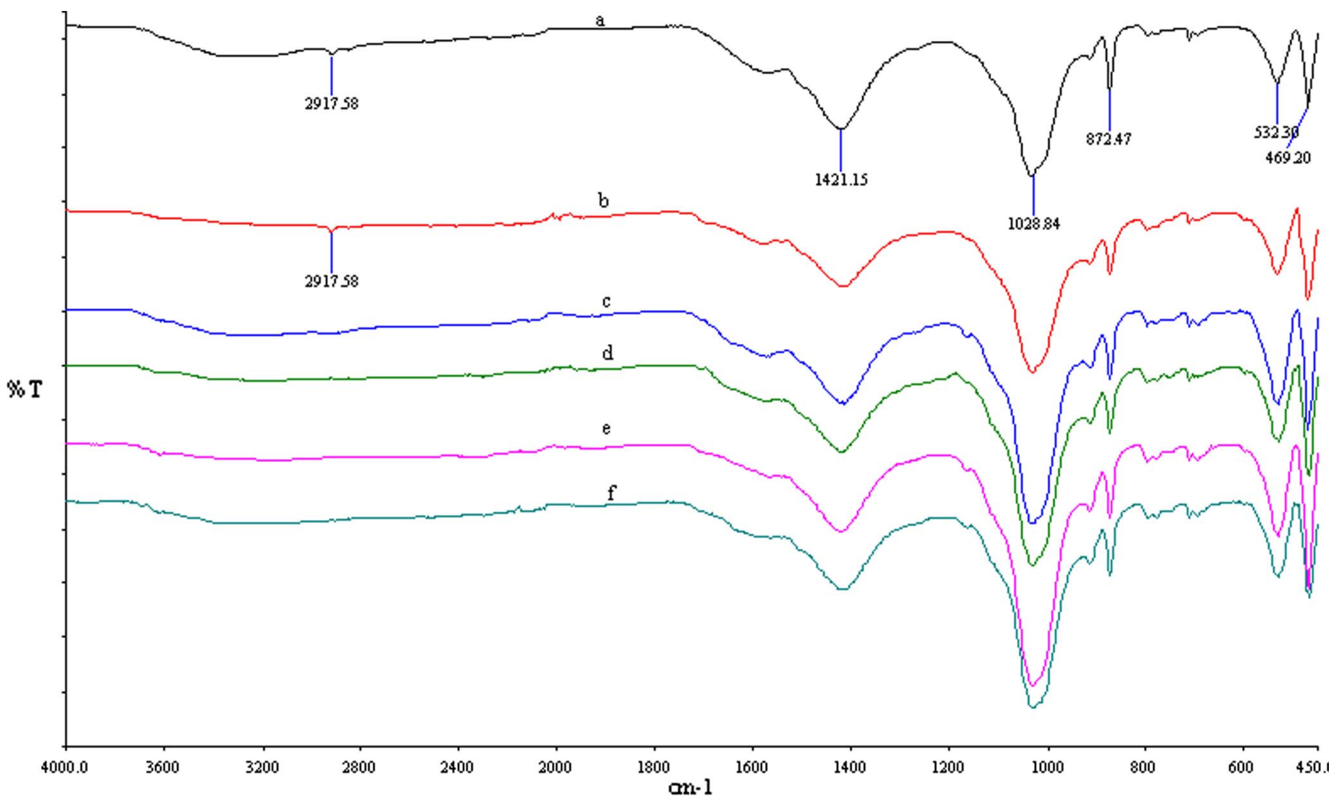

Fig. 4. FTIR spectra of AE lignite and the residues (R) obtained from its extraction (a: raw coal, b: R-NMP, c: R-[Bmim]Cl, d: R-[Bdmim]Cl, e: R-[Emim]Cl, f: R-[Bmp]Cl).

in a lower amount of hydrogen bonding. These results show that coal type affects the extraction yield of coal when ILs are added to NMP.

The increase in extraction yield of AE lignite is also evident from the FTIR spectra. Fig. 4 shows the FTIR spectra of AE lignite and its residues obtained from extraction. As shown, after extraction of AE lignite with NMP, there is no change in its FTIR spectrum. But the intensity of 2917 cm^{-1} (assigned to aliphatic C—H stretching) decreases and the intensities of 1028 cm^{-1}, 532 cm^{-1}, and 470 cm^{-1} (assigned to minerals) increases in the residues obtained from extractions by NMP/ILs. These results indicate that a great portion of the organic part of the coal has been dissolved. The increase in extraction yield with ILs addition supports this. On the other hand, when the UZ coal FTIR spectrum was analysed, there was a decrease in the peak intensity observed at 1594 cm^{-1} due to aromatic groups. This decrease may be due to a reduction in the number of aromatic rings in the coal after extraction with NMP [41]. As shown in Fig. 5, after extraction of UZ coal with NMP/ILs, a significant change in its FTIR spectrum was not observed.

3.2. Effects of ILs type on extraction yield

At this point it can be observed that the ILs used are not effective in the extraction of UZ coal. On the other hand, the extraction yield of AE lignite is significantly increased by the addition of a small amount of ionic liquid into NMP. In this study, both the imidazolium-based and pyridinium-based ILs used were found to be effective in the extraction of AE lignite and increases in extraction yields, ranging from 9.1% to 17.8%, were obtained. The imidazolium and pyridinium cations break the hydrogen bonds between oxygen-containing functional groups in coal, resulting in a relaxed coal structure. Of the ILs used, [Bmim]Cl was the most effective, while [Bdmim]Cl was the least effective. With the addition of [Bmim]Cl to NMP, the extraction yield increased by 17.8% from 26.1% to 43.9% for AE lignite. But, the addition of [Bdmim]Cl increased the extraction yield from 26.1% to 35.2%, an increase of 9.1%. As seen in Fig. 1, [Bdmim]Cl has one more alkyl group than the other three ILs. Therefore, it is considered that the interaction

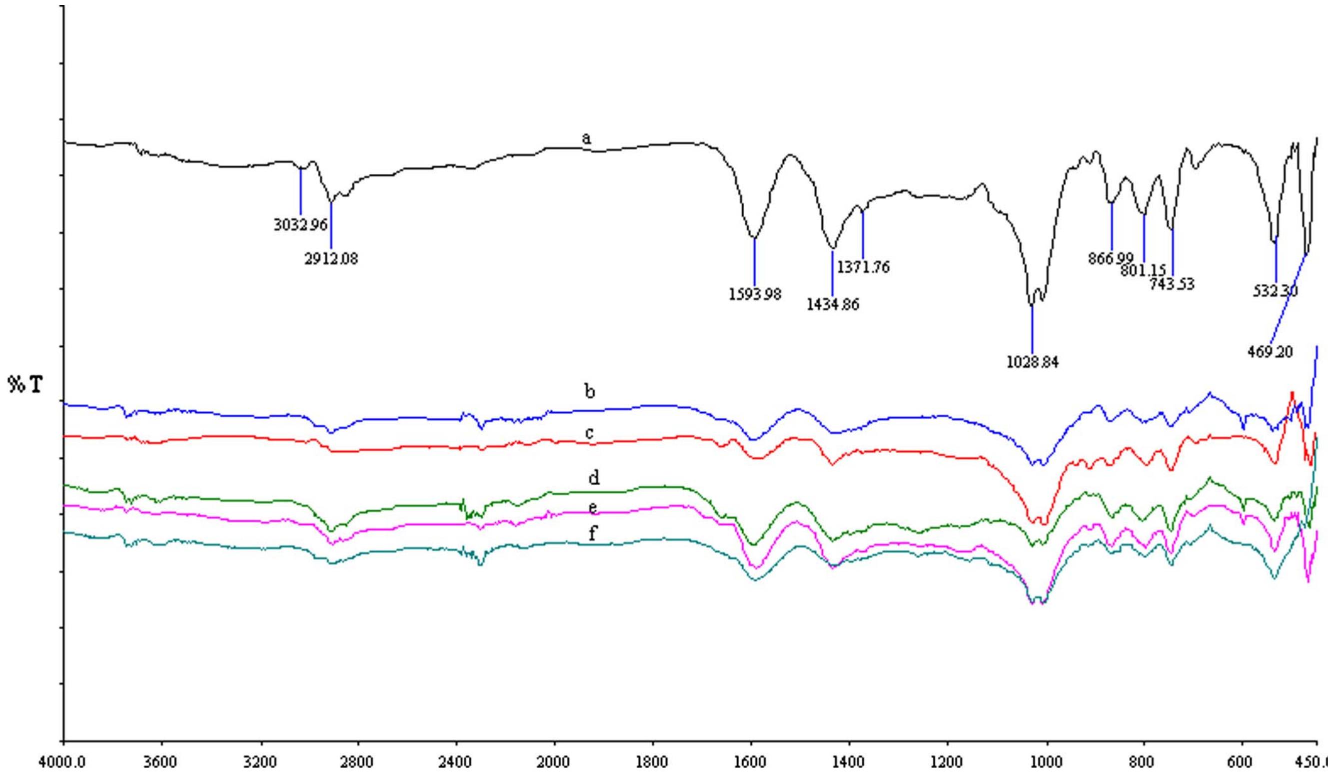

Fig. 5. FTIR spectra of UZ coal and the residues (R) obtained from the its extraction (a: raw coal, b: R-NMP, c: R-[Bmim]Cl, d: R-[Bdmim]Cl, e: R-[Emim]Cl, f: R-[Bmp]Cl).

of [Bdmim]Cl with coal is weaker than with the other ILs used, resulting in relatively less increase in extraction yield.

Some researchers suggest that the anions in ILs have a significant influence on extraction yield. For example, Huang et al. [42] used [Bmim] with different anions such as BF_4^- and PF_6^- in the extraction of coal-tar pitch. They found that [Bmim] with a single Cl^- showed the best performance. Lei et al. [25] studied the thermal dissolution of Xianfeng lignite in a series of ILs at 200 °C. They showed that the anions in the imidazolium-based ionic liquids significantly affected the extraction yield and that an IL with chlorine ions was more effective than with other anions. Painter et al. [24,43] proposed that the remarkable effect of chlorine ions on the dissolution of coal in ILs may result from the larger charge density of chlorine ions compare to other ions, which can enhance its ability to disrupt associations between polar entities in coal. The ILs used in this study contained only chlorine ions, thus the effect of anion type on extraction yield was eliminated.

3.3. Influence of ILs/coal ratio on extraction yields

Fig. 6 shows the effect of ILs/coal ratio on the extraction yields of two coal samples. [Bmim]Cl was chosen as the additive ionic liquid because of its best performance for the extraction of AE lignite among the ILs used. As seen in Fig. 5, addition of [Bmim]Cl is not effective for UZ coal. Whereas, as the amount of [Bmim]Cl added into NMP increases, the extraction yield increases for AE lignite. The extraction yield of AE lignite without adding [Bmim]Cl was found to be 26.1%, and as the amount of [Bmim]Cl increased, the extraction yield increased. When [Bmim]Cl]/coal ratios were 0.1, 0.5, 1.0, and 2.0, the extraction yields were 31.4%, 35.2%, 37.1%, and 43.9%, respectively. This corresponds to an increase of approximately 5–18% in extraction yield. This may be due to the fact that more hydrogen bonds in the lignite are broken with an increasing amount of ionic liquid, resulting in increased extraction yield. As AE lignite has a high oxygen content, this may be in excess of the number of hydrogen bonds due to the excess of oxygen-containing functional groups. Therefore, more of the ionic liquid required to break these hydrogen bonds. These results show that the ILs/coal ratio has a significant influence on the extraction process.

3.4. Effect of ultrasonic irradiation

At this stage of study, the effect of ultrasonic irradiation on the extraction yield of coal was investigated. Ultrasonic irradiation causes cavitation by passing high intensity acoustic waves through a liquid, resulting in the formation of many microbubbles, whose collapse creates local high temperatures and pressures [44]. The cavitation and collapse of generated microbubbles in liquid medium cause a micromixing effect [45]. Ultrasonic irradiation has been used in the extraction of coal at the mild conditions and has been shown to enhance extraction yield [46–48]. Hence, we thought that better results could be obtained under ultrasonic irradiation at the mild conditions. [Bmim]Cl was selected as the additive ionic liquid and the [Bmim]Cl/coal ratio was 2. Extractions were carried out under ultrasonic (40 kHz) irradiation at 75 °C for 30 min. The results are shown in Table 2.

As seen in Table 2, the extraction yields of UZ coal are fairly low with or without ultrasonic irradiation. The solvent extraction of coal takes place with the relaxation of the organic part of coal. Relaxation of organic part of coal molecule proceeds in two ways: solvent-induced and thermal-induced relaxation [49–51]. In the case of weak interactions between coal and solvent, noncovalent interactions are not broken with solvent-induced relaxation, resulting in low extraction yield. Although NMP is a polar solvent, it cannot break the noncovalent interactions under ultrasonic irradiation at 75 °C. Hence, quite low extraction yields were obtained for UZ coal. Conversely, relatively higher extraction yields were obtained for AE lignite with ultrasonic irradiation. As seen in Table 2, the extraction yield of AE lignite was increased by adding [Bmim]Cl from 18.5 to 24.6 wt% in the presence ultrasonic irradiation, which was slightly higher than that in its absence, i.e. 16.7–21.1 wt%. When using [Bmim]Cl with NMP in the presence of ultrasonic interaction, an extraction yield of 24.6% was obtained, corresponding to an increase of approximately 8%. As seen, ultrasonic

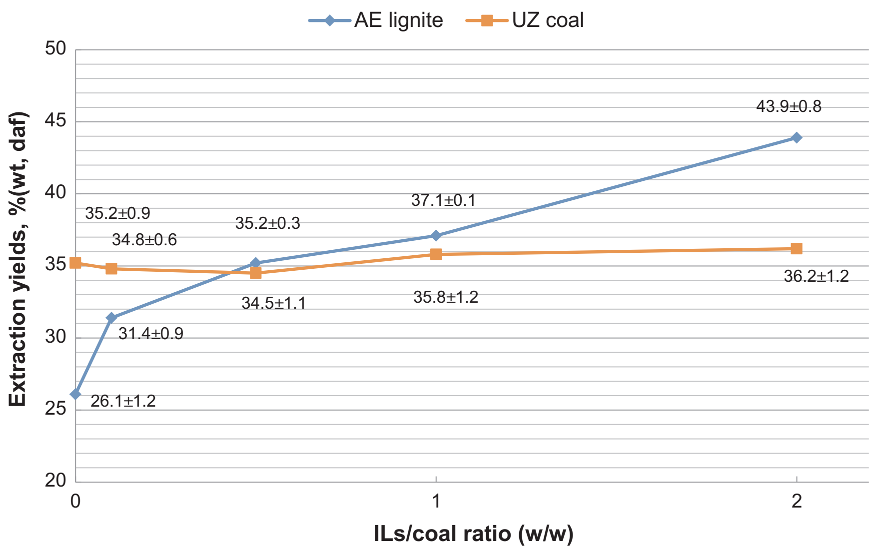

Fig. 6. Effect of the ratio of [Bmim]Cl/coal on extraction yield (extraction time is 1 h).

Table 2
Effect of ultrasonic irradiation on the extraction yield of coal.

	Extraction yields, (wt%, daf)			
	AE lignite		UZ coal	
	NMP	NMP/[Bmim]Cl	NMP	NMP/[Bmim]Cl
Without ultrasonic irradiation	16.7 ± 0.9	21.1 ± 0.5	3.5 ± 0.2	3.2 ± 0.5
With ultrasonic irradiation	18.5 ± 0.5	24.6 ± 0.4	3.2 ± 0.2	3.1 ± 0.4

irradiation increased the extraction yield of AE lignite. Ultrasonic irradiation accelerates the interactions between coal and solvent, and the ILs and ultrasound together relax the organic part of the coal and allow diffusion of extractable material from the coal [52].

4. Conclusions

In this study, a small amount of various ILs was added to NMP to increase the extraction efficiency of two different ranked coals at mild conditions. The effect of the ILs varied depending on the type of coal. Adding ILs to NMP resulted in high performance extraction of AE lignite, but no extraction ability for UZ coal. It was determined that the most effective ionic liquid was [Bmim]Cl, and its extraction efficiency was found increase by increasing the amount of ionic liquid added to NMP. For AE lignite, the extraction yield increased by 17.8% from 26.1% to 43.9% when a small amount of [(Bmim)Cl] was added to NMP. The ultrasonic extraction technique was shown to be effective in the extraction of AE lignite at low temperature with an NMP/ILs mixture, and an increase of approximately 8% in extraction yield was obtained. But, neither IL addition nor ultrasonic interaction caused an increase in extraction efficiency at 75 °C for UZ coal. The results obtained from this research show that ILs can be effective in processes such as extraction and liquefaction, especially in low-quality lignites.

Acknowledgment

The authors are grateful to the TUBITAK (Scientific and Technical Research Council of Turkey, Project Reference 114M878) for the financial support.

References

[1] Tian D, Liu X, Ding M. CS_2 extraction and FTIR & GC/MS analysis of a Chinese brown coal. Min Sci Technol 2010;20:562–5.
[2] Tahmasebi A, Jiang Y, Yu J, Li X, Lucas J. Solvent extraction of Chinese lignite and chemical structure changes of the residue during H_2O_2 oxidation. Fuel Process Technol 2015;129:213–21.
[3] Zhao YP, Tian YJ, Ding M, Dou YQ, Wei XY, Fan X, et al. Difference in molecular composition of soluble organic species from two Chinese lignites with different geologic ages. Fuel 2015;148:120–6.
[4] Rahman M, Samanta A, Gupta R. Production and characterization of ash-free coal from low-rank Canadian coal by solvent extraction. Fuel Process Technol 2013;115:88–98.
[5] Li ZK, Wei XY, Yan HL, Wang YG, Kong J, Zong ZM. Advances in lignite extraction and conversion under mild conditions. Energy Fuels 2015;29:6869–86.
[6] Lei ZP, Cheng LL, Zhang SF, Shui HF, Ren SB, Kang SG, et al. Dissolution of lignite in ionic liquid 1-ethyl-3-methylimidazolium acetate. Fuel Process Technol 2015;135:47–51.
[7] Iino M, Matsuda M. Synergistic effect of alcohol-benzene mixtures for coal extraction. Bull Chem Soc Jpn 1984;57:3290–4.
[8] Lino M, Matsuda M. Carbon disulphide-pyridine mixture, a new efficient extraction solvent for coal. Fuel 1983;62:744–6.
[9] Takanohashi T, Yanagida T, Iino M, Mainwaring DE. Extraction and swelling of low-rank coals with various solvents at room temperature. Energy Fuels 1996;10:1128–32.
[10] Iino M, Takanohashi T, Ohsuga H, Toda K. Extraction of coals with CS2-N-methyl-2-pyrrolidinone mixed solvent at room temperature. Fuel 1988;67:1639–47.
[11] Liu HT, Ishizuka T, Takanohashi T, Iino M. Effect of TCNE addition on the extraction of coals and solubility of coal extracts. Energy Fuels 1993;7:1108–11.
[12] Giray ESV, Chen C, Takanohashi T, Iino M. Increase of the extraction yields of coals by the addition of aromatic amines. Fuel 2000;79:1533–8.
[13] Sun Y, Wang X, Feng T, Yu G, Wang F. Evaluation of coal extraction with supercritical carbon dioxide/1-methyl-2-pyrrolidone mixed solvent. Energy Fuels 2014;28:816–24.
[14] Takahashi K, Norinaga K, Masui Y, Iino M. Effect of addition of various salts on coal extraction with carbon disulfide/N-methyl-2-pyrrolidinone mixed solvent. Energy Fuels 2001;15:141–6.
[15] Li C, Takanohashi T, Saito I, Iino M. Coal dissolution by heat treatment at temperatures up to 300 & #xB0;C in N-methyl-2-pyrrolidinone with addition of lithium halide. 1. Effects of heat treatment conditions on the dissolution yield. Energy Fuels 2003;17:762–7.
[16] Lei Z, Wu L, Zhang Y, Shui H, Wang Z, Pan C, et al. Microwave-assisted extraction of Xianfeng lignite in 1-butyl-3-methyl-imidazolium chloride. Fuel 2012;95:630–3.
[17] Lee YR, Row KH. Comparison of ionic liquids and deep eutectic solvents as additives for the ultrasonic extraction of astaxanthin from marine plants. J Ind Eng Chem 2016;39:87–92.
[18] Keskin S, Kayrak-Talay D, Akman U, Hortaçsu Ö. A review of ionic liquids towards supercritical fluid applications. J Supercrit Fluids 2007;43:150–80.
[19] Xu JJ, Yang R, Ye LH, Cao J, Cao W, Hu SS, et al. Application of ionic liquids for elution of bioactive flavonoid glycosides from lime fruit by miniaturized matrix solid-phase dispersion. Food Chem 2016;204:167–75.
[20] Prado R, Erdocia X, Labidi J. Study of the influence of reutilization ionic liquid on lignin extraction. J Clean Prod 2016;111:125–32.
[21] Li Y, Zhang X, Dong H, Wang X, Nie Y, Zhang S, et al. Efficient extraction of direct coal liquefaction residue with the [bmim]Cl/NMP mixed solvent. RSC Adv 2011;1:1579–84.
[22] Wang J, Yao H, Nie Y, Bai L, Zhang X, Li J. Application of iron-containing magnetic

ionic liquids in extraction process of coal direct liquefaction residues. Ind Eng Chem Res 2012;51:3776–82.
[23] Nie Y, Bai L, Dong H, Zhang X, Zhang S. Extraction of asphaltenes from direct coal liquefaction residue by dialkylphosphate ionic liquids. Sep Sci Technol 2012;47:386–91.
[24] Painter P, Pulati N, Cetiner R, Sobkowiak M, Mitchell G, Mathews J. Dissolution and dispersion of coal in ionic liquids. Energy Fuels 2010;24:1848–53.
[25] Lei Z, Zhang Y, Wu L, Shui H, Wang Z, Ren S. The dissolution of lignite in ionic liquids. RSC Adv 2013;3:2385–9.
[26] Lei Z, Wu L, Zhang Y, Shui H, Wang Z, Ren S. Effect of noncovalent bonds on the successive sequential extraction of Xianfeng lignite. Fuel Process Technol 2013;111:118–22.
[27] Lei ZP, Cheng LL, Zhang SF, Zhang YQ, Shui HF, Ren SB, et al. Dissolution performance of coals in ionic liquid 1-butyl-3-methyl-imidazolium chloride. Fuel Process Technol 2015;129:222–6.
[28] Giri CC, Sharma DK. Mass-transfer studies of solvent extraction of coals in N-methyl-2-pyrrolidone. Fuel 2000;79:577–85.
[29] Kim DS, Woo KJ, Jeong SK, Rhim YJ, Lee SH. Production of low ash coal by thermal extraction with N-methyl-2- pyrrolidinone. Korean J Chem Eng 2008;25:758–63.
[30] Renganathan K, Zondlo JW, Mintz EA, Kneisl P, Stiller AH. Preparation of an ultra-low ash coal extract under mild conditions. Fuel Process Technol 1988;18:273–8.
[31] Pande S, Sharma DK. Ethylenediamine-assisted solvent extraction of coal in N -methyl-2-pyrrolidone: synergistic effect of ethylenediamine on extraction of coal in N -methyl-2-pyrrolidone. Energy Fuels 2002;16:194–204.
[32] Pande S, Sharma DK. Studies of kinetics of diffusion of N-methyl-2-pyrrolidone (NMP), ethylenediamine (EDA), and NMP + EDA (1: 1, vol/vol) mixed solvent system in Chinakuri coal by solvent swelling techniques. Energy Fuels 2001:1063–8.
[33] Zhang HX. Determination of aromatic structures of bituminous coal using sequential oxidation. Ind Eng Chem Res 2016;55:2798–805.
[34] Chen C, Gao J, Yan Y. Role of noncovalent bonding in swelling of coal. Energy Fuels 1998:1328–34.
[35] Onal Y, Akol S. Influence of pretreatment on solvent-swelling and extraction of some Turkish lignites. Fuel 2003;82:1297–304.
[36] Shui H, Wang Z, Wang G. Effect of hydrothermal treatment on the extraction of coal in the CS_2/NMP mixed solvent. Fuel 2006;85:1798–802.
[37] Koyano K, Takanohashi T, Saito I. Estimation of the extraction yield of coals by a simple analysis. Energy Fuels 2011;25:2565–71.
[38] Sakimoto N, Koyano K, Takanohashi T. Relationship between extraction yield of coal by polar solvent and oxygen functionalities in coals. Energy Fuels 2013;27:6594–7.
[39] Cui C, Jiang S, Kou L, Wang L, Zhang W, Wu Z, et al. Effect of ionic liquids on the pyrolysis of coal. Electron J Geotech Eng 2016;21:5203–16.
[40] Liu S, Zhou W, Tang F, Guo B, Zhang Y, Yin R. Pretreatment of coal by ionic liquids towards coal electrolysis liquefaction. Fuel 2015;160:495–501.
[41] Cummings J, Tremain P, Shah K, Heldt E, Moghtaderi B, Atkin R, et al. Modification of lignites via low temperature ionic liquid treatment. Fuel Process Technol 2017;155:51–8.
[42] Huang J, Li C, Bai L, Nie Y, Wang E, He Y, et al. Extraction of coal-tar pitch using NMP/ILs mixed solvents. Sci China Chem 2014;57:1760–5.
[43] Pulati N, Sobkowiak M, Mathews JP, Painter P. Low-temperature treatment of Illinois No. 6 coal in ionic liquids. Energy Fuels 2012;26:3548–52.
[44] Safa M, Mokhtarani B, Mortaheb HR, Tabar Heidar K. Oxidative desulfurization of model diesel using ionic liquid 1-octyl-3-methylimidazolium hydrogen sulfate: an investigation of the ultrasonic irradiation effect on performance. Energy Fuels 2016;30:10909–16.
[45] Aldahri T, Behin J, Kazemian H, Rohani S. Synthesis of zeolite Na-P from coal fly ash by thermo-sonochemical treatment. Fuel 2016;182:494–501.
[46] Krzesinska M. The use of ultrasonic wave propagation parameters in the characterization of extracts from coals. Fuel 1998;77:649–53.
[47] Li Y, Li BQ. Study on the ultrasonic irradiation of coal water slurry. Fuel 2000;79:235–41.
[48] Zhong X, Wang M, Dou G, Wang D, Chen Y, Mo Y, et al. Structural characterization and oxidation study of a Chinese lignite with the aid of ultrasonic extraction. J Energy Inst 2015;88:398–405.
[49] Takanohashi T, Kawashima H, Yoshida T, Iino M. The nature of aggregated structure of Upper Freeport coal. Energy Fuels 2002;16:6–11.
[50] Yoshida T, Li C, Takanohashi T, Matsumura A, Sato S, Saito I. Effect of extraction condition on "HyperCoal" production (2) - Effect of polar solvents under hot filtration. Fuel Process Technol 2004;86:61–72.
[51] Wijaya N, Zhang L. A critical review of coal demineralization and its implication on understanding the speciation of organically bound metals and submicrometer mineral grains in coal. Energy Fuels 2011;25:1–16.
[52] Cooke NE, Fuller OM, Gaikwad RP. Ultrasonic extraction of coal. Fuel 1989;68:1227–33.