Parallel Microwave-Assisted Synthesis of Ionic Liquids and Screening for Denitrogenation of Straight-Run Diesel Feed by Liquid-Liquid Extraction

Miguel A. Cerón, Diego J. Guzmán-Lucero, Jorge F. Palomeque and Rafael Martínez-Palou*

Programa de Ingeniería Molecular. Instituto Mexicano del Petróleo. Eje Central Lázaro Cárdenas 152, 07730, D.F. México

Abstract: Fifty-six ionic liquids were efficiently synthesized in parallel format under one-pot, solvent-free microwaveassisted synthesis. These compounds were evaluated as extracting agents of nitrogen-containing compounds from a real Diesel feed before being submitted to the hydrodesulfurization process to obtain ultralow sulfur Diesel. Our results showed that halogenated ionic liquids are an excellent alternative due to these ionic liquids are relatively inexpensive, presenting a high selectivity for the extraction of nitrogen-containing compounds and can be regenerated and recycled.

Keywords: Denitrogenation, diesel, ionic liquids, microwave, parallel synthesis.

1. INTRODUCTION

Combinatorial methodologies have dramatically changed the chemical research and discovery process, offering an unlimited source of new molecule entities to be screened for activity or application. In recent years, researchers have begun to employ microwave as a tool in order to diminish reaction time, avoid side products, increase yield and simplify the course of reactions for combinatorial chemistry [1].

Recently, a high emphasis has been placed on the deep desulphurization of oil products because hydrocarbon combustion releases SOx, which are responsible for acid rain, air contamination and ozone consumption. Environmental regulations have been modified to allow that lower levels of sulfured compounds to be ejected into the atmosphere. Industrially, the removal of organosulfur and organonitrogen compounds in fuel oils is carried out by means of a simultaneous hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) process at around 350 °C using catalysts based on CoMo or NiMo, which involves the C-S and C-N bond cleavage to produce H_2S and NH_3 , respectively [2].

It is well known that the selective removal of nitrogenated compounds from the feeds before HDS strongly enhances the further deep desulfurization and increases the catalyst time of life because nitrogen compounds in the fuel and NH_3 are poisonous to the catalysts of HDS; thus, the development of new approaches to reduce the nitrogen content in transportation fuel oils is needed in order to meet ultra-clean fuels for environmental protection and hydrogen production [3].

Ionic liquids are an excellent alternative to substitute volatile organic solvents in more environmental friendly technologies, also known as "green technologies" because of their very low vapor pressures, their thermal and chemical stability, their ability to act as catalyst, and their non-flammability and non-corrosive properties which decrease the risk of worker exposure and the loss of solvent to the atmosphere [4]. Ionic liquids can be synthesized in good yield under microwave irradiation [5].

Ionic liquids have shown to be good solvents for the extraction of contaminants of hydrocarbon feeds, such as sulfurated, nitrogenated and aromatic compounds by liquid-liquid extraction [6]. Particularly, the application of ionic liquids as extracting agents of *N*-containing compounds have been studied by several researchers. However, in these researches few ionic liquids have been probed and simulated samples of Diesel (model Diesel), generally containing one or two pure hydrocarbons and one or two pure N-heterocyclic compounds, have been employed to simplify the study.

Eβer *et al.* determined a high partition coefficient (K_N) of 340 mg(N) kg(IL)⁻¹/mg(N) kg(oil)⁻¹ for an experiment with model oil containing 1000 ppm of nitrogen as indole in *n*-dodecane using [BMIM][OcSO₄], but the K_N -value of the N-species piperidine and pyridine was "only" 0.7 and 2.9, respectively [7].

Zhang *et al.* evaluated the adsorption capacities of *N*-containing saturated and non-saturated heterocyclic compounds and probed the extractive removal of both organonitrogen and organosulfur compounds for a model fuel using [BMIM]BF₄. The amount removed from each model fuel is much less than the absorption capacity for the corresponding pure model compound by the ionic liquid, reflecting a partitioning of the model compounds in both the ionic liquid and the dodecane phases. The most effective extraction was the pyridine which is fully miscible in the ionic liquids [8].

In 2008, Xie *et al.* synthesized and evaluated four kinds of ionic liquids with different carbon chain length and saturation of *N*-substituent groups: 1-butyl-3-methylimidazolium chloride (BMImCl), 1-allyl-3-methylimidazolium chloride (AlMlmCl), 1-benzyl-3-methylimidazolium chloride (BzMImCl) and 1-octyl-3-methylimidazolium chloride (OcMImCl). The distribution coefficient of carbazole (CAR) and dibenzothiophene (DBT) between the ILs phase and the

^{*}Address correspondence to this author at the Programa de Ingeniería Molecular. Instituto Mexicano del Petróleo. Eje Central Lázaro Cárdenas 152, 07730, D.F. México; Tel. + 52 55 91757846; Fax + 52 55 9156380; E-mail: rpalou@imp.mx

model fuel phase in BMImCl and AlMImCl were 46 and 14, and the selectivity of CAR/DBT were 125 and 38, respectively [9].

Huh *et al.* reported on the use of Zn-containing imidazolium-based ionic liquids bearing an alkylsulfate anion for the extraction of nitrogen compounds present in hydrocarbon mixtures at room temperature, using a model oil. The performance of dialkylimidazolium alkyl sulfate ionic liquid for the extraction of basic nitrogenated compounds, such as quinoline and acridine, was significantly improved up to more than 2 times by the co-presence of Lewis acidic ZnCl₂ [10].

In this work, 56 ionic liquids were synthesized in parallel under the microwave irradiation and evaluated as extracting agents for the denitrogenation of a real sample of straightrun Diesel feed before being submitted to the HDS process. The experiments were conducted at 60°C using a ratio ionic liquid/Diesel of 1:5. According to our results, Lewis acid ionic liquids are the best extract agents, however, "first generation" ionic liquid containing a halogen as anion also removes the nitrogenated compounds efficiently which are an excellent alternatives as extracting agents.

2. EXPERIMENTAL

2.1. Materials and Equipments

All Aldrich reagents were used without previous purification, except 1-methylimidazole and pyridine which were vacuum-distilled from CaH₂ prior to use. Melting points were measured in a Fisher Scientific apparatus with a 300°C thermometer. ¹H NMR (300 MHz) and ¹³C NMR (75.4 MHz) spectra were obtained with a Jeol Eclipse-300 equipment using TMS as internal standard and using CDCl₃ as solvent at room temperature. Total nitrogen and sulfur were determined in an Antex 9000S series equipped with autosampler. Microwave reactions were conducted using a commercially available monomode microwave unit (CEM Discover) [11].

2.2. Sampling

Sample of straight-run Diesel was obtained from a Mexican petroleum refinery. Samples from the storage tanks were taken according to ASTM procedure D 4057–95.

2.3. Sample Characterization

Samples were characterized by the following methods in brackets: Especific weight 20/4°C (ASTM D-1232), Atmospheric distillation (ASTM D-86-05), Cetane index (ASTM D-976), Cinematic viscosity (ASTM D-445), Aniline temperature (ASTM D-611), Total sulfur (ASTM D-5453), Total nitrogen (ASTM D-4629), Basic nitrogen (ASTM UOP-313) and Aromatic distribution (ASTM D-5186).

2.4. Ionic Liquids Synthesis

Ionic liquids were synthesized in a one-pot, closed-vessel and solvent-free microwave-assisted synthesis according to the following general procedure:

In a microwave tube (10 mL) provided with a magnetical stirrer, 4 mmol of imidazole derivative (1-methyl-, 1,2dimethyl-,1-vynyl- or 1-butyl-imadazole) or pyridinium derivatives and the equimolar quantity of the corresponding alkyl halide and metal salt (MeY, Me = Li or K) were mixed. The tube was caped and heated at 150°C during 30 minutes (for imidazolium) and 45 minutes (for pyridinium derivatives) at 150 W of max. power, under pressure and with simultaneous cooling. The ionic liquids obtained were washed with ethyl acetate (2 x 20 mL) and ether (2 x 20 mL) and dried under vacuum during 8 hours. Products were characterized by ¹H and ¹³C NMR. Spectrums were essentially identical as described before [12]. In the cases of metathesis reactions, the MeCl_n was added at the reaction tube after the halogenated ionic liquids were formed. The addition was carried out with vigorous stirring at room temperature until the complete dissolution of the salt and until it resulted in a single phase.

2.5. Denitrogenation Procedure by Liquid-Liquid Extraction

10 mL of the straight-run Diesel were mixed with 2 mL of each ionic liquids in a glass vessel (50 mL) containing a magnetic stirring bar. The vessels were closed and the mixture was stirred (600 rpm) for 15 minutes at 60°C with an IKA magnetic stirrer equipped with a thermocouple thermometer. Then the stirring was stopped and the mixture was allowed to stand during 15 minutes for phase separation, and then a sample of Diesel (upper layer) was taken for analysis. The degree of denitrogenation (DD, %) was determined for each extraction with respect to the original content of total nitrogen in the Diesel sample (466 ppm) according to eq. 1.

$$DD(\%) = \frac{Ci - Cf}{Ci} \times 100 \tag{1}$$

where C_i and C_f are the total nitrogen content in the straightrun Diesel before and after the extraction.

3. RESULTS AND DISCUSSION

3.1. Diesel Composition

Physical and chemical characterization of the Diesel sample are presented in Table 1. As it is observed in Table 1, the composition of our sample is in accordance with the characteristics of a typical Diesel feed, however, sulfur and nitrogen level contents are very high. The concentration of aromatics is in the relatively expected concentration.

3.2. Parallel Synthesis of Ionic Liquids Under Microwave Irradiation

Parallel synthesis of combinatorial libraries is a synthetic sequence where the assembly of library is performed using an ordered array of spatially separated reaction vessels under the same reaction conditions.

In contrast to the traditional polymer-supported reagents (and catalyst) synthesis for combinatorial chemistry, microwave-assisted synthesis without polymer-supported reagents produces compounds that are immediately available for any specific application screening.

ids Combinatorial Chemistry & High Throughput Screening, 2012, Vol. 15, No. 5 429

 Table 1.
 Physical and Chemical Characterization of the Diesel Sample Used in this Work

Analytical Test (Units)	Content	
Atmospheric distillation (Initial Bp – Final Bp, °C)	172.7 - 376.7	
Especific weight 20/4°C	0.8652	
Cetane index	49.3	
Cinematic viscosity (mm ² /s, 40°C)	5.6	
Aniline temperature (°C)	72.8	
API Gravity (°)	81.80	
Saybolt Color	>+30	
Total sulfur (ppm)	13000	
Total nitrogen (ppm)	466	
Basic nitrogen (ppm)	111	
Aromatic distribution (% w):		
Monoaromatics	18.4	
Diaromatics	12.7	
Polyaromatics	2.6	
Total Aromatics	33.7	

Recently, some examples of the one-pot microwave and microwave/ultrasound-assisted syntheses of "second generation" ionic liquids were published [12]. In this work ionic liquids were synthesized under microwave irradiation in solvent-free and one-pot closed vessel conditions with simultaneous cooling. For time-efficiency, all the reactions were carried out under the same microwave conditions (time = 30 minutes, temperature = 150° C) in one-pot closed vessel solvent-free parallel synthesis (Fig. 1).

In the case of ionic liquids containing a halogen as anion (A = X = Cl or Br), known as "first generation ionic liquids", only the imidazole derivative and the corresponding alkyl halide were employed as reagents (neither MeY nor MeCl_n were required). For ionic liquids obtained for ionic exchange with MeY, where Me = Li, Na or K and A = Y = PF₆, BF₄, acetate, benzoate or triflate, the reactions were carried out by employing an equimolar quantity of the reagents and in spite of the reactions was not optimized, all ionic liquids were obtained in yields and purities higher than 85% (estimated by proton NMR) after purification process by washes with ethyl acetate and ethyl ether (2 x 20 mL).

Ionic liquids obtained by the metathesis reaction with $A = MeCl_{n+1}$ where Me = Al, Fe, Cu and Mo were prepared using different molar ratios IL:MeCl_n 1:0.8 (Lewis basic ionic liquids), 1:1 (neutral) and 1:1.3 (Lewis acid ionic liquid) by the addition of the salt at room temperature after the halogenated ionic liquid precursor was formed.

For a wider screening, a series of pyridinium type ionic liquids (II) were also synthesized in a one-pot, closed-vessel and solvent-free microwave-assisted synthesis in similar conditions except that the reaction time was 45 minutes (Fig. 2).

Following this parallel protocols 56 ionic liquids were obtained (see Table 2).

3.2. Evaluation of Ionic Liquids for Denitrogenation of a Straight-Run Diesel Feed by Liquid-Liquid Extraction

The ionic liquids synthesized were evaluated as extracting agents for denitrogenation of Diesel by the liquidliquid extraction procedure. A ratio of 1:5 of IL:Diesel was employed during 10 minutes of stirring at 60°C. After 15 minutes of phase separation, an aliquot of Diesel phase was separated for nitrogen content determination.

60°C was selected as the temperature of the extraction because this is the typical temperature of Diesel charge before feeding HDS and also, at this temperature, all the studied ionic liquids are low viscosity liquids.

The total nitrogen concentrations were analyzed by chemiluminiscence in an Antex 9000 analyzer equipped with a robotic liquid autosampler which permits a quick and automatic series of analysis. The degree of denitrogenation (DD, %) was determined for each extraction with respect to the original content of total nitrogen in the Diesel sample (466 ppm).

According to the results obtained in our screening the following observations can be summarized:

Effect of the substituent (R_1) at N1 in imidazolium type ionic liquids: Ionic liquids containing methyl substituent at N1 are presumably more efficient than those containing vinyl and butyl substituents (see for example entry 14 vs 23 and 24).

Effect of the substituent (R_3) at N3 in imidazolium type ionic liquids: The extraction efficiency increases from C4 to C8, maybe because imidazolium containing C8 presents lower viscosity (see entry 2 vs 15).



Fig. (2). One-pot parallel synthesis of pyridinium type ionic liquids under solvent-free conditions.

Table 2. Removal of Nitrogenated Compounds from Diesel by Ionic Liquids

Entry	Cation Type	Rı	R ₂	R ₃	Anion (A)	DD (%)
1	Ι	Methyl (Me)	Н	Butyl (Bu)	Br	65
2	Ι	Me	Н	Bu	Cl	70
3	Ι	Me	Н	Bu	PhCOO	59
4	Ι	Me	Н	Bu	CH ₃ COO	69
5	I	Me	Н	Bu	PF ₆	58
6	I	Me	Н	Bu	BF_4	52
7	Ι	Me	Н	Bu	Tf	56
8	I	Me	Н	Bu	BrFeCl ₃ (1:0.8)	65
9	Ι	Me	Н	Bu	BrFeCl ₃ (1:1.0)	84
10	Ι	Me	Н	Bu	$BrFeCl_{3}$ (1:1.5)	89
11	I	Me	Н	Bu	ClFeCl ₃ (1:0.8)	69
12	I	Me	Н	Bu	ClFeCl ₃ (1:1.0)	89
13	I	Me	Н	Bu	ClFeCl ₃ (1:1.5)	95
14	I	Me	Н	Octyl (Oct)	Br	70
15	l	Me	Н	Oct	Cl	75
16	l	Me	Н	Oct	CH ₃ COO	55
17	l	Me	Н	Oct	$CIAICI_3 (1:1.5)$	94
18	I	Me	Н	Oct	$CIFeCI_3$ (1:1.0)	90
19	I	Me	Н	Oct	$CIFeCI_3$ (1:1.5)	95
20	I	Me	Н	Benzyl (Bz)		65
21	I	Me	Н	BZ Vyznil (Vyz)	PhCOO	49 57
22	I	Bu	Н	v yiii (v y)	Dr Dr	57
23	I	Du Du	п	V y Oot	DI Dr	45
24	I	Bu	п	Bu	Br	53
25	I	Bu	н	Bu	Cl	58
20	I	Bu	н	Bu	BE	30
27	I	Me	Н	Allyl	Br Br	52
28	I	Me	Me	Bu	Br	53
30	I	Me	Me	Bu	Cl	55
31	I	Me	Me	Oct	$ClFeCl_2(1.1.0)$	83
32	I	Me	Me	Oct	$ClFeCl_3(1:1.5)$	87
33	II	Н	Н	Bu	Br	90
34	II	Н	Н	Bu	Cl	76
35	II	Н	Н	Bu	BF ₄	69
36	II	Н	Н	Bu	PF ₆	65
37	II	Н	Н	Bu	PhCOO	50
38	II	Н	Н	Bu	Tf	48
39	II	Н	Н	Bu	CH ₃ COO	51
40	II	Н	Н	Bu	ClFeCl ₃ (1:0.8)	63
41	II	Н	Н	Bu	ClFeCl ₃ (1:1.0)	88
42	II	Н	Н	Bu	ClFeCl ₃ (1:1.5)	86
43	II	Н	Н	Bu	ClAlCl ₃ (1:1.5)	91
44	II	Н	Me	Bu	Br	40
45	II	Н	Me	Bu	BF ₄	36
46	II	Me	Me	Bu	Br	39
47	II	Me	Me	Bu	PF ₆	39
48	II	Me	Me	Bu	Tf	34
49	II	Н	Н	Oct	Br	85
50	II	Н	Н	Oct	Cl	66
51	II	Н	Н	Oct	ClFeCl ₃ (1:1.5)	87
52	II	Н	Н	Oct	ClMoCl ₃ (1:1.5)	80
53	II	Н	Н	Oct	ClCuCl (1:1.5)	29
54	II	Н	Me	Bu	ClFeCl ₃ (1:1.5)	88
55	II	Me	Me	Oct	Cl	50
56	II	Me	Me	Oct	ClFeCl ₃ (1:1.5)	83

Effect of the substituent R_2 at C2 in imidazolium type ionic liquids: Ionic liquids with $R_2 = H$ are more efficient extracting agents than those with $R_2 = Me$; perhaps the methyl substituent at R2 promoted a steric effect that made the interaction of nitrogenated compounds diffcult in ionic liquids (1 vs 29; 2 vs 30; 17 vs 32 and 18 vs 31).

Effect of the halogen type (Cl vs Br) for the "first generation" ionic liquids: In general, halogenated ionic liquids are efficient extractants of nitrogenated compounds and Cl containing anions are slightly more efficient than Br for imidazolium type cation, while Br are more efficient for pyridinium type cations. However, ionic liquids containing Br are obtained quickly and with higher yield. These first generation ionic liquids are cheaper than ionic liquids containing other anions because additional reagents are required in their synthesis and the yield is lower. Halogencontaining ionic liquids are also moisture stables and can be recuperated and reused in several reaction cycles (see entries 1 vs 2, 14 vs 15, 33 vs 34 and 49 vs 50).

Effect of the cation type: As can be observed in Table 2, the cation effect is less significant than that of anion, however, a slightly higher extraction is observed for pyridinium type (II) cations with respect to imidazolium type cations containing the same anion (see entries 1 vs 33, 2 vs 34, 4 vs 39, 13 vs 54, 14 vs 49 and 15 vs 50). This results can be attributed to a major structural similarity between pyridonium cation (five member one N atom heterocycles) and nitrogenated compounds present in the Diesel feed.

Effect of the anion type: The anion plays a very important role in the extraction ability of nitrogenated compounds. Anions like halogens (Cl and Br), XFeCl₃ and XAlCl₃ (X = Cl and Br) show a good ability to remove nitrogenated compounds, while other than CH₃COO, PhCOO, BF₄, PF₆, and Tf showed relatively low efficiency of extraction (see entries 2-7, 45 and 47 in Table **2**); however, the anion effect is more significant for the extraction of sulfurated compounds [13].

Substitutent effect in pyridinium type ionic liquids: Pyridinium cation (II with R_1 and $R_2 = H$) was the most appropriate for the extraction of nitrogenated compounds and their performances decrease when Me substituents are included in their structure as in the case of 2methylpyridinium and 2.6-dimethylpyridinium (lutidinium) as shown in entries 44 and 45.

Selective extraction of nitrogenated compounds vs sulfur compounds: Selective extraction of nitrogenated compounds is very important, especially in this kind of predesulfurized feed containing a very high content of sulfur-containing compounds, because these compounds can be transformed during HDS in valuable hydrocarbon feed and significant separation of these compounds from the feed can be translated in a considerable volumetric loss of hydrocarbons. In our case, halogenated ionic liquids showed a high selectivity for nitrogen-containing compounds, the desulfurization degree with [BuPy]Br, [OMOM]Cl and [OctPy]Br was less than 2%.

Effect of the ratio halogenated $IL/MeCl_n$ for ionic liquid obtained by metathesis: As can be observed in Table 1, the best results were obtained for Lewis acidic ionic liquids (ratio IL:MeCl_n = 1:1.5), especially from those

containing Fe or Al as metal and n = 3 (see entries: 8-13, 17-19, 31 and 32, 40-43 and 51, 54 and 56). Being fundamentally basic nitrogenated compounds, the results obtained with Lewis acid ionic liquid could be expected, as the consequence of the low viscosity obtained for ionic liquids containing IL:MeCl_n = 1:1.5. Lewis acid ionic liquids containing only one halogen in the structure (i.e. CIFeCl₃) of the anion are more efficient extractanting agents than the analogues containing Br and Cl (i.e. BrFeCl₃, see entry 10 *vs* 13 and 8 *vs* 11). For these kinds of ionic liquids, the imidazolium cation showed better performance than the pyridinium analog (see entries 32 *vs* 56). The effect of the type of metal was discussed by us before in relation with the desulfurization process, and the same analysis can be applied for denitrogenation [13].

Lewis acid ionic liquids remove the basic nitrogenated compounds presumably by means of chemisorptions by the interaction of N^{$\cdot\cdot$}Metal through Dewar-Chatt-Duncanson-like mechanism of electron donation-backdonation among electron rich nitrogenated compounds and transition metal centers of Me₂Cl₇⁻ anions in the ionic liquid [14].

However, these kinds of liquids suffer from being moisture sensitive and decomposing after being used, while the ionic liquids containing Br and Cl as anion are chemically stables and cheaper. The latest can be recuperated and reused in several cycles of extractions [9]. On the other hand, it is well known that Lewis acid ionic liquids can be an alternative for removing the sulfurated compounds [4].

In summary, we found that ionic liquids are good alternatives for denitrogenation of straight-run Diesel feed. Several types of ionic liquids showed a good performance for the selective extraction of nitrogenated compounds by liquid-liquid extraction. In particular, the halogenated ionic liquids are excellent alternatives due to these compounds are relatively inexpensive, presenting a high selectivity for the extraction of nitrogen-containing compounds and can be regenerated and recycled. All ionic liquids probed were synthesized in parallel under solvent-free, one-pot microwave-assisted synthesis.

ACKNOWLEDGEMENT

We would like to thank to Instituto Mexicano del Petróleo (IMP) for both granting permission to publish results and for their financial support (IMP project D.00412).

CONFLICT OF INTEREST

Declared none.

REFERENCES

- Martínez-Palou, R. Advances in microwave-assisted combinatorial chemistry without polymer-supported reagents. *Mol. Divers.*, 2006, 10, 435-462.
- [2] Caeiro, G.; Costa, A.F.; Cerqueira, H.S.; Magnoux, P.; Lopes, J. M.; Matias, P.; Ribeiro, F. R. Nitrogen poisoning effect on the catalytic cracking of gasoil. *Appl. Catal. A*, 2007, 320, 8-15.
- [3] Stanislaus, A.; Marafi, A.; Rana M.S. Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production. *Catal. Today*, **2010**, *153*, 1-68.
- [4] Wassercheid, P.; Welton, T. *Ionic Liquids in Synthesis.* Willey-VCH, Weinheim, 2003.

- Rogers, R. D. & Seddon, K. R., Eds. *Ionic Liquids as Green Solvent: Progress and Prospects*. ACS: Boston, **2003**.
- [6] Martínez-Palou, R.; Flores, P. Ionic Liquids Applications for Clean Oilfield Technologies, in: *Ionic Liquids. Theory, Properties, New Approaches.* INTECH, Rijeka, Croatia, 2011, p. 567-629.
- [7] Eßer, J.; Wasserscheid. P.; Jess, A. Deep desulfurization of oil refinery streams by extraction with ionic liquids. *Green Chem.*, 2004, 6, 316-322.
- [8] Zhang, S.G.; Zhang, Q.L.; Zhang, Z.C. Extractive desulfurization and denitrogenation of fuels using ionic liquids. *Ind. Eng. Chem. Res.*, 2004, 43, 614-622.
- [9] Xie, L.-L.; Favre-Reguillon, A.; Wang, X-X.; Fu, X.; Pellet-Rostaing, S.; Toussaint, G.; Geantet, C.; Vrinat, M.; Lemaire, M. Selective extraction of neutral nitrogen compounds found in diesel feed by 1-butyl-3-methyl-imidazolium chloride. *Green Chem.*, 2008, 10, 524-531.

Received: September 22, 2011

[5]

Revised: December 19, 2011

Accepted: December 20, 2011

- [10] Huh, E. S.; Zazybin, A.; Palgunadi, J.; Ahn, S.; Hong, J. Zncontaining ionic liquids for the extractive denitrogenation of a model oil: A mechanistic consideration. *Energy Fuels*, **2009**, *23*, 3032-3038.
- [11] http://www.cem.com
- [12] Cravotto, G.;Gaudino, E.C.; Boffa, L.; Leveque, J.-M.; Estager, J.; Bonrath, W. Preparation of second generation ionic liquids by efficient solvent-free alkylation of N-heterocycles with chloroalkanes. *Molecules*, **2008**, *13*, 149-156.
- [13] Likhanova, N.; Guzmán, D., Flores, E.; Palomeque, J.; Domínguez, M.A.; García, P.; Martínez-Palou, R. Ionic liquids screening for desulfurization of natural gasoline by liquid-liquid extraction. *Mol. Divers.*, 2010, 14, 777-789.
- [14] Martínez-Magadán, J. M.; Oviedo-Roa, R.; García, P.; Martínez-Palou, R. DFT study of the interaction between ethanothiol and Fecontaining ionic liquids for desulfurization of natural gasoline. *Fuel Process. Technol.*, 2012, 97, 24-29..

Cerón et al.