New Ionic Liquid for the Dissolution of Lignin

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This work aims to develop a new ionic liquid, used as an aprotic green ä solvent, to dissolve kraft lignin from black liquor. The kraft lignin was extracted through precipitation with carbon dioxide at atmospheric pressure. 1,8-Diazabicyclo[5.4.0]undec-7-ene-based ionic liquids were obtained by quaternization of the nitrogen atom with a hydrogen atom or an alkyl chain. The yields of the synthesis of the ionic liquids varied between 76 and 80%. Dissolving experiments were carried out using the lignin isolated from the black liquor of a kraft process. Up to 20% (w/w) of the lignin can be dissolved in butyl-1,8 diazabicyclo[5.4.0] undec-7-enium chloride ($[DBUC_4]^+[Cl^-]$), hexyl-1,8 diazabicyclo[5.4.0] undec-7-enium chloride $[DBUC_6]^+[Cl^-]$, and octyl-1,8 diazabicyclo[5.4.0] undec-7-enium chloride $[DBUC_8]^+[Cl^-]$. The time it takes to dissolve the lignin in these three liquids shows that its solubility is influenced mostly by the nature of the cations. The lignin solubility was reduced in relation to the increased length of the grafted carbon chain. The thermogravimetric analysis (TGA) showed these liquids can be used as lignin solvents from room temperature up to 300 °C (onset of degradation). Steric exclusion chromatography showed a slight decrease (6%) in the molecular weight of the lignin dissolved in these ionic liquids.

INTRODUCTION

In the context of rarefaction of fossil-fuel resources and protection of the environment, special attention has been given over the past few years to the development of processes that are more nature-friendly and to the upgrading of renewable resources. Lignocellulosic polymers represent a seemingly inexhaustible source of biomass-issued matter. Mainly exploited in the paper industry, these polymers show interesting physicochemical properties and high potential for development. To broaden the application field of these bioresources, it is highly desirable to confer them with new properties by having them chemically or structurally modified or transformed into by-products. After cellulose, lignin is the most abundant polymer in nature. Lignin is a complex tridimensional polymer made up of phenylpropane units, composed of more than 50% carbon. This tridimensional polymer forms from three phenolic precursors: guaiacyl, syringyl, and p-hydroxyphenyl (Binder *et al*. 2009; Gandini *et al*. 2002). Lignin representative formulas vary according to the source, the age, and the accuracy of the determination. One of the accepted structures is the one proposed by Adler (1977). For the past several years, lignin has been used as a combustible in the paper industry. Indeed, the residue of wood delignification, called black liquor, is evaporated and then burnt to produce energy. In recent years, research projects have attempted to upgrade part

of the black liquor lignin without modifying the energy balance of the kraft mills. In fact, the lignin of this liquor has found very little use. An estimated 63×10^4 million tons/year of lignin are produced in the world (Mohan *et al*. 2006). Only a small portion of the lignin is marketed, which is a result of the uncertainties linked to its structure and high molecular weight.

The pre-treatment of biomass by ionic liquids is a green and viable option for its upgrading. Ionic liquids are organic salts having a melting point lower than 100°C and often lower than room temperature. They form a very important new class of solvents because of their low vapor pressure, high ionic conductivity, and exceptional chemical stability (Welton 1999). The role of ionic liquids as "green" solvents has become increasingly important for catalytic reactions in the field of polymerization and solubilization of natural macromolecules (Li *et al*. 2007, 2008; Sievers *et al*. 2009, Lee *et al*. 2009). The systems most commonly studied are binary mixtures of anions (Cl⁻, Br⁻, BF_4^-, $PF6^-$, and $CF_3SO_3^-$) and cations (imidazolium, pyridinium, phosphonium, and quaternary ammonium). A wise choice of anions and cations results in the desired properties. Ionic liquids (ILs) do not degrade at high temperatures. They are non-flammable, except for "energetic" ILs, which are made of nitrate or picrate anions. Because of their almost negligible vapor pressure, they present a great thermochemical stability. However, most of the research on the treatment of biomass in an ionic liquid medium is aimed at dissolving crystalline cellulose (Kadokawa *et al*. 2009; Liu *et al*. 2011; Kuang *et al*. 2008; Lin *et al*. 2009; Hua *et al*. 2009 ; Zhao *et al*, 2009), not on the forest biomass, which is a more complex matter. In their research, Sang *et al*. (2009) show that an ionic liquid can dissolve wood cellulose and lignin. The difficulty of correlating the dissolution of the cellulose, lignin, and wood was revealed by Sang *et al.* (2009) by comparing the dissolution of lignin and wood in methylsulfatedimethylimmidazolium [mmim]⁺[MeSO₄]⁻.

In the present study, we developed and characterized three new ionic liquids. We studied the role of these ionic liquids used as solvents in the pre-treatment of lignin from kraft black liquor. Particular emphasis was placed on the green aspect and the neatness of the ionic liquids. Indeed, three liquids based on 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were synthesized without solvent. DBU is part of the amidine family. An amidine is the equivalent of an amide in which the carbonyl group (C=O) was replaced by an imine group (=NH). From a chemical standpoint, amidines are much more basic than amides and are part of the stronger neutral bases. In the literature there are many protic polar ionic liquids based on DBU that are able to dissolve lignin (D'Andola *et al*. 2008). However, the synthesis of DBU-based solvent-free aprotic ionic liquids is less widely reported.

EXPERIMENTAL

Materials

Samples of softwood kraft black liquor were supplied by the Kruger mill in Trois-Rivières, QC, Canada. The reagents used to synthesize the ionic liquids were purchased from Sigma Aldrich. We used the following: 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU, 98%), 1-chlorobutane (99,5%), 1-chlorohexane (99%), 1-chlorooctane (99%), and ethyl acetate (99%).

Methods

Extraction of lignin from kraft black liquor

Acid precipitation was carried out, basically as described in the literature (Garcia *et al*. 2009; Tejado *et al*. 2007; Axelsson *et al*. 2006). The CO_2 precipitation of the lignoboost process (Nagy *et al*. 2010) was adapted to atmospheric pressure.

Synthesis of $[DBUC_4]^+$ $[Cl^-]$, $[DBUC_6]^+$ $[Cl^-]$ and $[DBUC_8]^+$ $[Cl^-]$

1,8-Diazabicyclo[5.4.0]undec-7-ene-based ionic liquids were obtained by quarter-nization of the nitrogen atom with a hydrogen atom or an alkyl chain. During the synthesis of the aprotic ionic liquids, an equivalent of DBU (0.259 mol, *i.e*., 40 mL) with 1.2 equivalents of 1-chlorobutane (0.311 mol, *i.e*., 33.5 mL), 1-chlorohexane (0.311 mol, *i.e*., 43.1 mL), or 1-chlorooctane (0.311 mol, *i.e*., 52.8 mL) were poured into a 300-mL flask at 50 °C under agitation for about 48 h without solvent. This produced a viscous solution of $[DBUC_4]^+[Cl^-]$, $[DBUC_6]^+[Cl^-]$, or $[DBUC_8]^+[Cl^-]$. The excess reagents and impurities were removed with ethyl acetate. The latter were removed using a rotary evaporator at 50 °C for about 2 h. This produced a very hygroscopic orange solid. For safety reasons, we did not use $[DBUC_2]^+[Cl^-]$ or $[DBUC_3]^+[Cl^-]$ because chloroethane is in the gaseous state and the temperature of boiling chloropropane is quite low (34 to 36 °C).

Dissolving the lignin precipitated from the kraft black liquor in the ionic liquids

We added 0.5 g, 0.75 g, and 1 g of kraft lignin, respectively, in 4.5 g, 4.25 g, and 4 g of the ionic liquids, and the whole solution was placed in an oven at 105 °C. The lignin solution was then cooled to room temperature. The lignin was regenerated by adding distilled water to the solution under vigorous agitation for 2 h. The precipitated lignin was collected by centrifugation at 3400 RPM.

Analytical Methods

Spectroscopy NMR ^{31}P and ^1H

The NMR ^{31}P spectra for the lignin extracted with acid and CO_2 were obtained using 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) as a reagent of phosphorylation. All samples were dried under vacuum for 48 h, and then analyzed by NMR of ^{31}P in a blend of pyridine/$CDCl_3$ after phosphorylation. The quantification was done using cyclohexanol as internal standard. The acquisition conditions were as reported by Monteil-Rivera *et al*. (2012). The chemical shifts were referenced in relation to the signal of the water product with TMDP at 132.2 ppm.

The content of hydroxyl groups was obtained by integration of the following spectral regions: aliphatic hydroxyls (149.4–145.5 ppm), syringyl (S) phenolic hydroxyls (143.3–141.9 ppm), condensed phenolic units (difference between 144.3–141.3 ppm and 143.3–141.9 ppm as previously done by Cateto *et al.* (2008)), guaiacyl (G) phenolic hydroxyls (140.5–138.3 ppm), p-hydroxyphenyl (H) phenolic hydroxyls (138.3–137.4 ppm), and carboxylic acids (136.0–134.0 ppm). The structures of the ionic liquids and the acetylated lignin were determined by NMR ^1H with a Mercury 200 MHz instrument.

Spectroscopy FT-IR

FTIR spectra were obtained with a Perkin Elmer instrument, System 2000, using pellets of lignin mixed with KBr (lignin content of 1%). Spectra were recorded between 400 and 4000 cm^{-1} with a resolution of 2 cm^{-1}.

Thermogravimetry and DSC

The thermal stabilities of kraft lignin and ionic liquids were analyzed by thermogravimetric analysis (TGA) with a Mettler Toledo (TGA / SDTA851e) and scanning calorimetry (DSC) with a Mettler Toledo DSC822e. Scans were registered between 25 and 500 °C in a dynamic mode with a heating rate of 10 °C/min, under a N_2 blanket (50 mL/min). For each experiment, about 4 mg of each sample was used.

Karl Fischer

A Karl Fischer volumetric titrator was used to determine the water content of the ionic liquids. The samples were first solubilized in anhydrous methanol (Hydranal methanol dry) buffered with benzoic acid, with the titrant being the Hydranal composite 5.

GPC analysis

The distributions of the molecular weights of the lignin dissolved in the $[DBUC_4]^+[Cl^-]$ and of the kraft lignin were determined by gel-permeation chromate-graphy (GPC) using a multiple detection system Viscotek (Houston) equipped with a GPCmax including an integrated pump, an automatic sampler, and a deaerator. All samples were dissolved in THF (15 mg/10 mL), filtered, and analyzed by GPC based on the conditions described by Monteil-Rivera *et al*. (2012). All samples were acetylated according to the method described by Zhao and Liu, (2010). The samples were acetylated and dissolved in THF (15 mg/10 mL), filtered, and analyzed by GPC according to the conditions reported by Monteil-Rivera *et al*. (2012).

RESULTS AND DISCUSSION

Extraction of the Lignin of the Kraft Black Liquor

The black liquor lignin was extracted using two methods. Results are presented in Fig. 1. The FT-IR analysis revealed lignin characteristic spectra that are in agreement with the literature (Zhao and Liu 2010; Ewa *et al*. 2009; Lisperguer *et al*. 2009; Boeriu *et al*. 2004).

The alcohol functions corresponded to an absorption band at 3450 cm^{-1}, and the band corresponding to the C-H vibrations was at 2940 cm^{-1}. An absorption band for the non-conjugated carboxyl groups was observed at 1716 cm^{-1} and the aromatic backbone vibrations were observed at 1610, 1521 cm^{-1} and 1415 cm^{-1}. The C-H related to the deformation and vibration of the aromatic rings at 1458 cm^{-1} and the phenolic OH groups at 1376 cm^{-1} were also present. Bands corresponding to the C-H of deformation in the syringyl and the guaiacyl units were observed at 1108 and 1040 cm^{-1}, respectively.
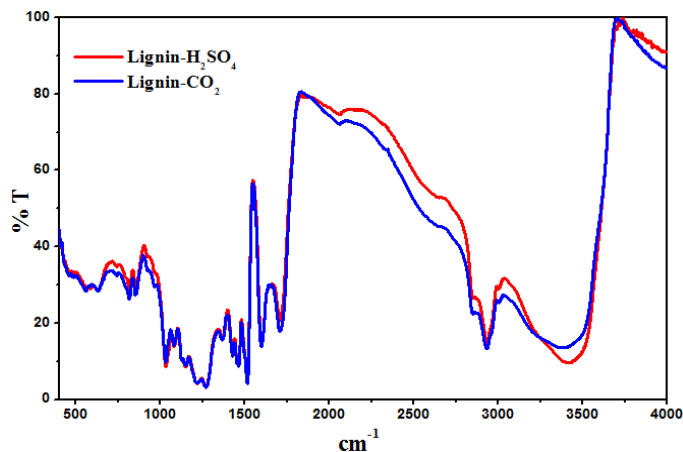
Fig. 1. FT-IR spectra for the lignin-H_2SO_4 and lignin-CO_2

The aliphatic, phenolic, and carboxylic hydroxyl concentrations of the lignin-H_2SO_4 and lignin-CO_2 were determined by a quantitative NMR analysis of ^{31}P after phosphorylation with 2-chloro-4,4,5,5-tetramethyl-1, and 2,3-dioxaphospholane (Fig. 2, Table 1). As in the case of the FTIR data, both ^{31}P NMR spectra were similar. The distribution of these lignin alcohols showed that the proportion of phenolic alcohols was larger than the other alcohols. These results conform to those found in the literature (Nagy *et al*. 2010).
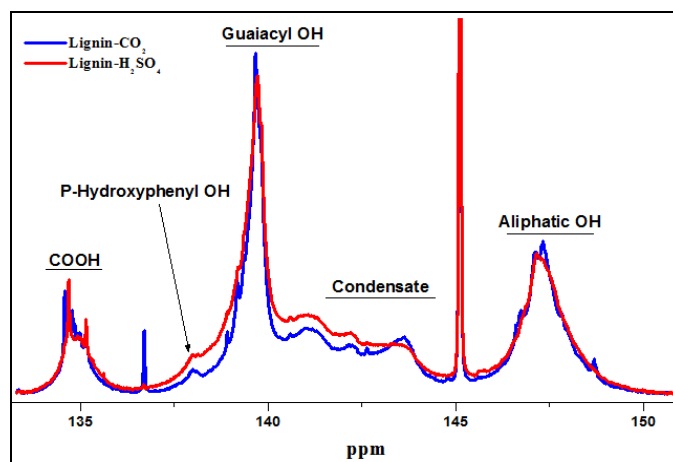

Fig. 2. NMR ^{31}P spectra of samples of lignin extracted with sulfuric acid and CO_2 after phosphorylation with TMDP (solvent: pyridine/$CDCl_3$)

Table 1. Concentration of Aliphatic OH, Phenolic OH, and COOH Groups Present in the Samples of Lignin-H_2SO_4 and Lignin-CO_2 by NMR [31]P

Sample	OH (mmol.g^{-1})						
	Total COOH	Phenolic H[a]	Phenolic G[a]	Phenolic S[a]	Condensed Phenolic	Total Phenolic	Total Aliphatic
Lignin (H_2SO_4)	0.33	0.14	1.53	0.00	1.22	2.89	1.17
Lignin(CO_2)	0.37	0.07	1.42	0.00	1.15	2.64	1.27
Phenolic OH groups : (H) p-Hydroxyphenyl; (G) Guaiacyl; (S) Syringyl							

Synthesis and Properties of Ionic Liquids

The yields of the synthesis of the ionic liquids varied between 76 and 80%. The structures of the resulting compounds were determined by NMR ^{1}H and described below in Figs. 3, 4, and 5.
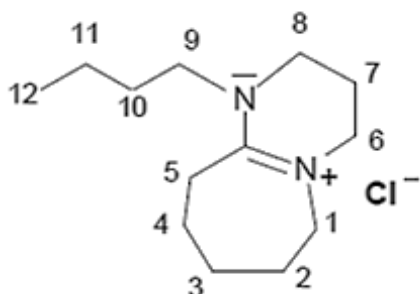

Fig. 3. Structure of $[DBUC_4]^+[Cl^-]$

Yield: 80%

Melting Temperature: **60 °C**

NMR 1H: δ = 3.4-3.6 (m, 2H1), 1.7-1.9 (m, 2H2), 1.6-1.7 (m, 2H3), 1.6-1.7 (q, 2H4), 2.9 (m, 2H5), 3.5-3.6 (t, 2H6), 1.7-1.9 (q, 2H7), 3.5-3.8 (m, 2H8), 3.7 (m, 2H9), 2.1 (q, 2H10), 1.4 (m, 2H11), 1.0 (t, 3H12).
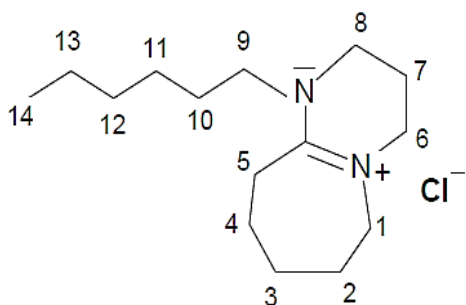

Fig. 4. Structure of $[DBUC_6]^+[Cl^-]$

Yield: 78%

Melting Temperature: **45 °C**

NMR [1]H: δ = 3.4-3.6 (m, $2H_1$), 1.4-1.9 (m, $2H_2$, $2H_3$, $2H_4$), 2.9 (m, $2H_5$), 3.5-3.6 (t, $2H_6$), 1.7-1.9 (q, $2H_7$), 3.5-3.8 (m, $2H_8$), 3.7 (m, $2H_9$), 2.6 (m, $2H_{10}$), 2.1 (q, $2H_{11}$), 1.5 (q, $2H_{12}$), 1.2 (m, $2H_{13}$), 0.8 (t, $3H_{14}$).
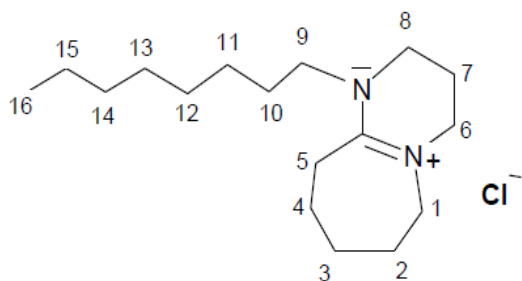

Fig. 5. Structure of $[DBUC_8]^+[Cl^-]$

Yield: 76%

Melting Temperature: **30 °C**

NMR [1]H: δ = 3.4-3.6 (m, $2H_1$), 1.3-1.6 (m, $2H_2$, $2H_3$, $2H_4$), 2.7 (m, $2H_5$), 3.5-3.6 (m, $2H_6$), 1.8 (q, $2H_7$), 3.5-3.8 (m, $2H_8$), 3.7 (t, $2H_9$), 3.4 (m, $2H_{10}$), 2.5 (m, $2H_{11}$), 2.2 (q, $2H_{12}$), 2.1 (q, $2H_{13}$), 1.9 (q, $3H_{14}$), 1.0 (m, $2H_{15}$), 0.6 (t, $3H_{15}$).

The heat stabilities of all three ionic liquids are presented in Fig. 6 (DTG). The TG analyses indicated that the thermal degradation of the three liquid samples occurred at about 300 °C. The DTG curves indicate the rate of weight loss, while DTGmax represents the maximum rate of degradation and can be used to compare the heat stability of the samples. The lowest DTGmax was 354 °C, corresponding to $[DBUC_8]^+[Cl^-]$. This value was slightly different of the DTGmax of $[DBUC_4]^+[Cl^-]$ (368 °C) and $[DBUC_6]^+[Cl^-]$ (362 °C). It should be noted that in spite of this slight difference in the DTGmax, there was a tendency for a reduction of the heat stability that depended on the size of the cation. Indeed, the large organic cation of the ionic liquids generated few

interactions and gave a low melting point and a low heat resistance. If the length or the volume of the alkyl chain grafted on the DBU backbone increased, this phenomenon was amplified. According to Larsen *et al*. (2000), the decrease of the ionic liquid heat resistance comes mostly from their incapacity to organize themselves into a compact network.

The DSC analysis of $[DBUC_4]^+[Cl^-]$, $[DBUC_6]^+[Cl^-]$, and $[DBUC_8]^+[Cl^-]$ showed three endothermic absorption bands at 130 °C, 162 °C, and 158 °C, respectively, which corresponded to the evaporation of water in the liquids. The band corresponding to $[DBUC_4]^+[Cl^-]$ was more pronounced than the bands corresponding to the other liquids (Fig. 7). The evaporation of the water contained in an ionic liquid temperature depends on the nature of the ions and the viscosity of the liquid. According to the literature (Cammarata *et al*. 2001), the ionic liquid anions develop hydrogen bonds with the water. On the other hand, the size of the cation influences the evaporation of water (Bonhôte *et al*. (1996), with a constant anion, the viscosity increases as the side chain of the cation increases. This observation is in agreement with our results. Trapped water in liquids $[DBUC_6]^+[Cl^-]$ and $[DBUC_8]^+[Cl^-]$ are more difficult to remove because they are more viscous than $[DBUC_4]^+[Cl^-]$. This observation explains the difference in evaporation temperature of water in different ionic liquids.

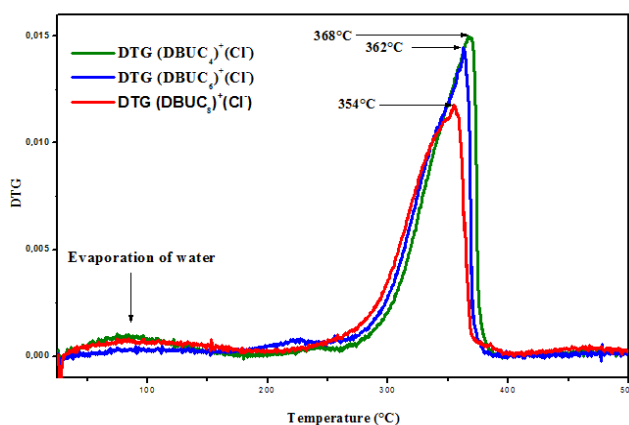**Fig. 6.** Curves of the first derivatives (DTG) of the thermograms of $[DBUC_4]^+[Cl^-]$, $[DBUC_6]^+[Cl^-]$, and $[DBUC_8]^+[Cl^-]$
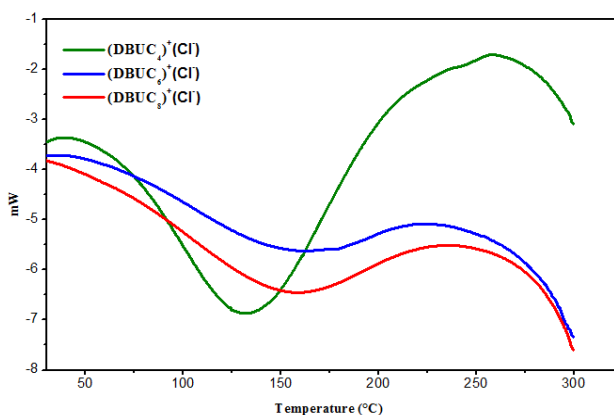
Fig. 7. DSC Analysis of the ionic liquids $[DBUC_4]^+[Cl^-]$, $[DBUC_6][Cl^-]$, and $[DBUC_8][Cl^-]$

The Karl Fisher analysis of the ionic liquids (Table 2) showed that the longer the chain was on the DBU, the less hygroscopic was the liquid. These results confirmed the DSC analysis.

Table 2. Water Content of the Ionic Liquids $[DBUC_4]^+[Cl^-]$, $[DBUC_6]^+[Cl^-]$, and $[DBUC_8]^+[Cl^-]$

Ionic Liquid	Water Content
$[DBUC_4][Cl^-]$	5.34 ± 0.046%
$[DBUC_6][Cl^-]$	3.98 ± 0.053%
$[DBUC_8][Cl^-]$	2.47 ± 0.058%

Dissolving the Lignin-CO_2 in $[DBUC_4]^+[Cl^-]$, $[DBUC_6]^+[Cl^-]$, and $[DBUC_8]^+[Cl^-]$

As explained previously, CO_2 precipitation is more environmentally friendly than acid extraction. Consequently, the lignin-CO_2 system was used for all the dissolution tests. Lignin-CO_2 samples were added to the ionic liquids without pre-treatment and heated to 105 °C. The dissolving times for the lignin in each ionic liquid are given in Table 3, and dissolution is represented in Fig. 8. The solubility was checked by ultrasound. After sonication, if the solution remained transparent without deposit, then the dissolution was regarded as complete.

Table 3. Dissolving Lignin-CO_2 in $[bmim]^+[Cl^-]$

Ionic Liquid	Dissolved Lignin (%)	Dissolving Temperature (°C)	Dissolution	Dissolving Time (hour:mn)	Water Content (%)
$[bmim]^+[Cl^-]^a$	13.9 g/L[a]	75	Undefined	Undefined	Undefined
$[bmim]^+[Cl^-]^b$	1.4[b]	75	Undefined	Undefined	Undefined
$[bmim]^+[Cl^-]^c$	2	105	Total	7:00	Undefined
$[DBUC_4]^+[Cl^-]$	5	105	Total	2:50	5
	10	105	Total	6:30	
	15	105	Total	9:00	
	20	105	Partial	9:00	
	20	105	Total	29:00	
$[DBUC_6]^+[Cl-]$	5	105	Total	4:00	3.98%
	10	105	Total	8:15	
	15	105	Total	11:00	
	20	105	Partial	11:00	
	20	105	Total	30:00	
$[DBUC_8]^+[Cl-]$	5	105	Total	4:40	2.47
	10	105	Total	8:30	
	15	105	Total	13:00	
	20	105	Partial	13:00	
	20	105	Total	30:00	
$[bmim]^+[Cl^-]$ = 1-butyl-3-methylimidazolium					
a: (Pu *et al.* 2007) b: (Simmons *et al.* 2011) c: Our synthesis					

The results of the lignin-CO_2 dissolution showed that its solubility was a function of the size of the ionic liquid cation. The larger the cation is, the less soluble it is. For the same percentage of lignin, the dissolution time increased with the size of the cation. For example: the time for dissolution 5% lignin in $[DBUC_4]^+[Cl^-]$, $[DBUC_6]^+[Cl^-]$, and $[DBUC_8]^+[Cl^-]$ were, respectively, 2 h, 50 min; 4 h, 00 min; and 4 h, 40 min. The

solubilization was essentially due to the development of ionic and hydrogen bonds between the entities of the ionic liquid and the polymeric chains (Fig. 9).
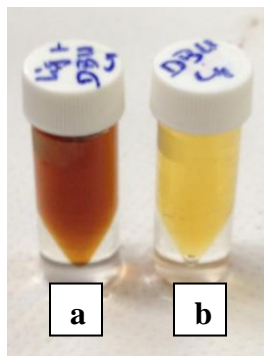

Fig. 8. (a) 4% of Lignin-CO_2 solubilized in $[DBUC_4]^+[Cl^-]$; (b): Ionic Liquid ($[DBUC_4]^+[Cl^-]$) alone
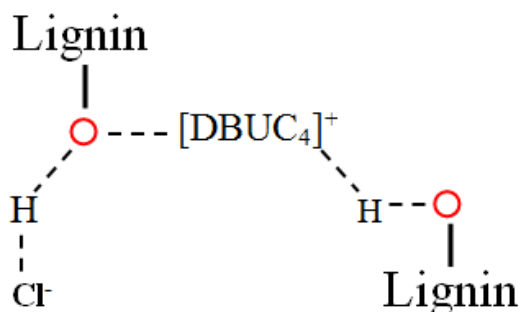

Fig. 9. Interactions between ionic liquid and lignin-CO_2

The results that follow show the combined influence of ionic liquid treatment and water precipitation. It is difficult to study only the effect of the ionic liquid on lignin because one cannot have a lignin precipitated with water only. Lignin from kraft black liquor is precipitated with an acid solution or with CO_2.

Thermogravimetric analysis is widely used to study how organic polymers decompose. TG curves reveal the weight loss of substances in relation to the temperature of thermal degradation, while the first derivative of that curve (DTG) shows the corresponding rate of weight loss. Results corresponding to the two lignins are shown in Fig. 10. The thermogram of kraft lignin-CO_2 treated with ionic liquid was shifted to lower temperatures. This suggests that the treated lignin degraded faster than the untreated kraft lignin-CO2.

The first derivative of the weight loss curve of kraft lignin-CO_2 treated with the ionic liquid showed two peaks, at 265 and 366 °C (Fig. 10). Kraft lignin-CO_2 gave a DTGmax of 381 °C. Temperatures of 366 °C and 381 °C were assigned to the respective degradation of lignin treated with ionic liquid and kraft lignin (Toledano *et al*. 2010; Toshihiro *et al*. 2009). This difference in degradation temperature could be explained by a loss of mass of the kraft lignin-CO_2 after dissolution in the ionic liquid. A temperature of 265 °C could be attributed to condensation or the degradation of a small fragment of lignin mass. A peak representing weight loss was observed around 90 °C, which corresponded to the absorbed water evaporation.
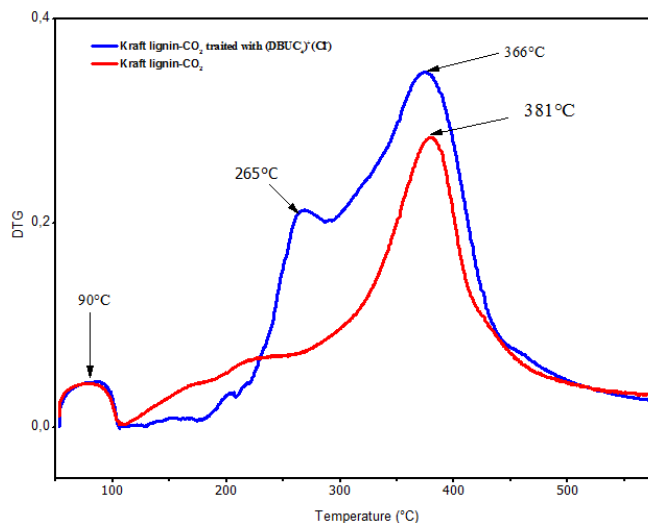
Fig. 10. DTG of kraft lignin-CO_2 and kraft lignin-CO_2 dissolved in $[DBUC_4]^+[Cl^-]$ and then regenerated

All samples were acetylated according to the method described by Zhao and Liu (2010). The samples were acetylated and dissolved in THF (15 mg/10 mL), filtered, and analyzed by GPC according to the conditions reported by Monteil-Riviera *et al*. (2012).

The molecular weight distributions are shown in Fig. 11, while the corresponding values of Mn, Mw, and Mw/Mn are given in Table 4.
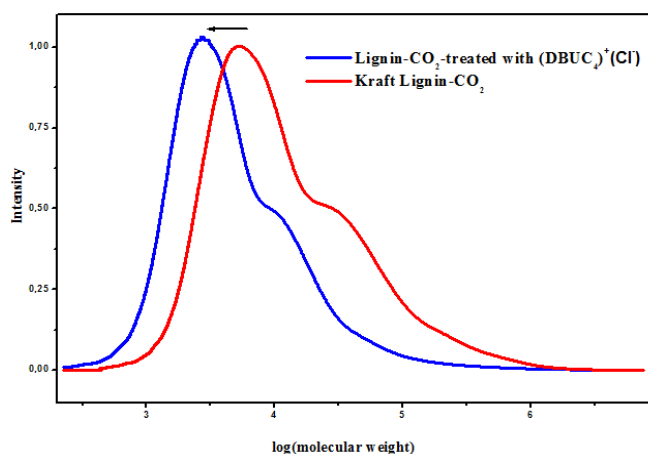

Fig. 11. Distribution of the molecular weight of the reference lignin and the reference lignin dissolved in $[DBUC_4]^+[Cl^-]$ and then regenerated

Table 4. Comparison of the Distribution of the Molecular Weight of the Reference Lignin and the Reference Lignin Dissolved in $[DBUC_4]^+[Cl^-]$ and then Regenerated

Sample	M_n (g.mol^{-1})	M_w (g.mol^{-1})	M_w/M_n
Lignin-CO_2	3,081	15,651	5,08
Treated Lignin-CO_2	2,907	14,629	5,03

The masses found are consistent with the literature (Gosselink *et al*. 2004; Sun and Tomkinson 2002). It should be noted that masses M_n and M_w of the regenerated lignin were slightly lower than those of the reference lignin, after dissolving in

$[DBUC_4]^+[Cl^-]$. This is in line with the degradation observed with our thermogravimetric analysis.

CONCLUSIONS

1. This work showed that the kraft lignin of black liquor can be precipitated with CO_2 at atmospheric pressure. This is a viable, clean method that gives the same lignin that is obtained with the acid method.

2. Aprotic ionic liquids based on 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were successfully prepared with high yields. $[DBUC_4]^+[Cl^-]$, $[DBUC_6]^+[Cl^-]$, and $[DBUC_8]^+[Cl^-]$ were synthesized without solvents with yields of 80, 78, and 76%, respectively. This approach consisted of reacting the DBU with an excess of chloroalkane, which yielded aprotic ionic liquids pure at almost 99%. The NMR ^{1}H of these ILs showed some impurity traces that were easily eliminated, as the impurities were made with an excess of reagents (chloroalkane) and water only.

3. Trials to optimize the temperature of the reaction have allowed us to demonstrate that this approach required temperatures that were 20 °C lower than for the synthesis of ionic liquids such as immidazolium, which requires a reaction temperature of about 70 °C.

4. This approach to the synthesis allowed a reduction in the use of greenhouse products (volatile solvents), and the pre-treatment gave lignin with promising properties, such as a reduced molecular weight. In our case, the heat treatment of kraft lignin at 105 °C in the $[DBUC_4]^+[Cl^-]$ gave 6% lower molecular weight.

5. These ionic liquids were viable solutions for the treatment of lignin at relatively high temperatures.

6. The work also demonstrated that it is possible to carry out the dissolution of the precipitated kraft lignin. Kraft lignin could be solubilized in these liquids at 105 °C at proportions of 20%.

ACKNOWLEDGMENTS

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