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# Recovery and Reuse of 1-Allyl-3-methylimidazolium Chloride in the Fractionation of *Pinus radiata* Wood

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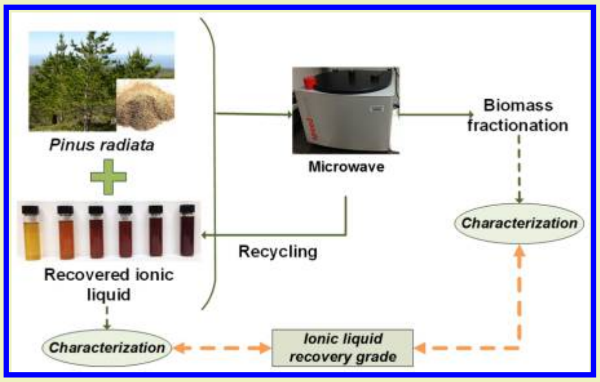
*Supporting Information*

**ABSTRACT:** Ionic liquids are expected to be potential solvents for biorefinery purposes. However, the high cost has limited widespread implementation, making their recycling essential to the process. Herein, the capacity to recover and reuse the ionic liquid 1-allyl-3-methylimidazolium chloride ([Amim][Cl]) in the fractionation of *Pinus radiata* wood using microwave heating was evaluated. In the proposed process, cellulose- and lignin-rich materials were obtained. The ionic liquid used was recovered and reused in the forthcoming cycles up to five times. Characterization of [Amim][Cl] recovered demonstrated that although the structure of the ionic liquid remained unaltered, some woody fractions were accumulated. As a consequence, a reduction of the fractionation yields was obtained, and variations of the composition and amorphicity of the fractions recovered were produced. Through a global mass balance, this study gives an overall approximation of the concentration of the main components and the characteristic streams involved in successive cycles.



**KEYWORDS:** *Ionic liquids, Recycling, Biomass fractionation, Pine wood, Microwave heating*

## ■ INTRODUCTION

Ionic liquids (ILs) are effective solvents for a variety of materials, including polymeric compounds.[1] Their negligible vapor pressure, nonflammability, and high chemical and thermal stability, among other features, make them potential solvents for a wide range of polymers.[2]

Lignocellulosic biomass is the most available plant material on our planet and the most sustainable feedstock for the production of biomass-based energy.[3] Biomass softwood resources are expected to be part of the biorefinery feedstock base. However, their high recalcitrance makes them difficult to fractionate compared to grass or hardwood biomass.[4] Fractionation and pretreatment technologies can account for up to 40% of the total processing costs of lignocellulosic biomass conversion.[5] Current implemented technologies are high energy input (liquid hot water pretreatments), excessive degradation of biomass releasing inhibitors (steam explosion), or a few effective treatments in softwoods (alkaline pretreatments).[5] Ionic liquids based biomass fractionation technologies have emerged as potential solvents in lignocellulosic biomass pretreatment processes. Although at commercial scale ILs are still a challenging task, their advantages have made them an alternative for the future of biorefineries.[6] In a fractionation approach, ILs reduce recalcitrance enabling deconstruction and disruption of the lignin and hemicellulose network.[7] In a pretreatment approach, the cellulose crystallinity reduction increases cellulose accessibility, which favors high conversions from cellulose to glucose.[5,8] Furthermore, their low volatilities make possible treatments of biomass at atmospheric pressure, with nonodorous and safer liquors.[9]

Several imidazolium ILs, such as [Emim][OAc], [Bmim][Cl], [Amim][Cl], or [Emim][DEP], among others, have been proven to dissolve cellulose and lignocellulosic biomass.[10,11] [Emim][OAc] is considered the most suitable IL for biomass fractionation to date, but also one of the most expensive.[12] Although most chloride salts are difficult to handle due to the high melting point and viscosity, [Amim][Cl] was found to be the most effective to dissolve wood chips. In particular, microwave heating has been effectively used as a method to accelerate dissolution in other chemical processes and has already been checked by Casas et al. as an efficient method to dissolve pine wood with [Amim][Cl].[13,14] Cellulose dissolution in lignocellulosic materials with [Amim][Cl] is due to the disruption of hydrogen bonding and the coordination of chloride ions with the hydroxyl groups of cellulose. In addition, the double bond in the side chain of [Amim][Cl] facilitates a reduction in viscosity and an increase in dissolution capacity compared to [Bmim][Cl].[15] Finally, [Amim][Cl] $T_{\mathrm{onset}}$ (273

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°C) is higher than [Emim][OAc] (216 °C), enabling higher working temperature conditions without thermal degradation.[16]

After biomass dissolution, an antisolvent is commonly employed to regenerate the biomass dissolved. Water, methanol, ethanol, or isopropanol are some commonly reported antisolvents studied to date.[17] Some former studies have already pointed out Kamleft–Taft and polarity scale ($E_T^N$) as adequate parameters to describe solvent properties (Table 1). Focusing on lignin solubility, Weerachanchai et al. observed that water does not precipitate lignin from an IL–lignin dissolution in contrast with alcohols such as methanol, ethanol, or isopropanol.[18] Regarding cellulose regeneration, a large $\beta$ value (>0.8) is recquired to effectively dissolve cellulose.[19] Methanol has higher values of $\alpha$ (hydrogen-bond acidity) and $E_T^N$ (normalized molar transition energies) than other alcohols, which indicates a high hydrogen bond donor, and a moderate polarity of the antisolvent interacting strongly with the IL and faster displacing the interactions between the IL and cellulose, leading to quick cellulose regeneration.[18,20]

Table 1. Kamleft–Taft and Polarity Scale ($E_T^N$) Parameters[9,17,20,21]

| | Kamleft–Taft Parameters | | | |
|---|---|---|---|---|
| | $\alpha$ | $\beta$ | $\pi^*$ | $E_T^N$ |
| AmimCl | 0.46 | 0.83 | 1.17 | >0.5 |
| methanol | 0.98 | 0.66 | 0.60 | 0.76 |
| ethanol | 0.86 | 0.75 | 0.54 | 0.65 |
| isopropanol | 0.76 | 0.84 | 0.48 | 0.57 |
| water | 1.17 | 0.47 | 1.09 | 1.00 |

Despite the advantages of ILs, their high cost compared to the substrate processed, and their toxicity limit large-scale application. Techno-economical analysis suggests ionic liquid recycling as a mandatory requirement.[22]

Many methods are used to recover ILs. The conventional method consists of evaporating the antisolvent used under a vacuum with the subsequent intensive energy demand of the process.[22,23] Another alternative is the use of aqueous kosmotropic salt solutions to form a three-phase system, but high salt-rich fractions may cause environmental problems.[24] Recently, Lynam et al. have reported a membrane distillation method to separate water and the ionic liquid that could be used in biomass pretreatment processes.[25]

Several studies have demonstrated the feasibility of recovering [Emim][OAc] under vacuum distillation and reusing it several times.[26] One of the factors that should be assessed is the reactivity of the IL with the biomass, as Clough et al. observed the degradation of the hydroxyalkyl chain and the loss of formaldehyde units in the IL [Emim][OAc].[27] ILs that are not reactive with biomass are assessed to avoid limitations in their recycling.

In this work, the feasibility of the recovery and reuse of [Amim][Cl] used for *Pinus radiata* wood fractionation, to obtain a cellulose and a lignin rich material is studied. Solids yields for each cycle are studied. The recovered IL was analyzed and correlated with the biomass yields. Furthermore, the solids obtained in the fractionation process with fresh and recovered IL were analyzed to determine its chemical composition, crystallinity, and functional groups. The concentration of involved components in each stream was determined in a mass balance approach.

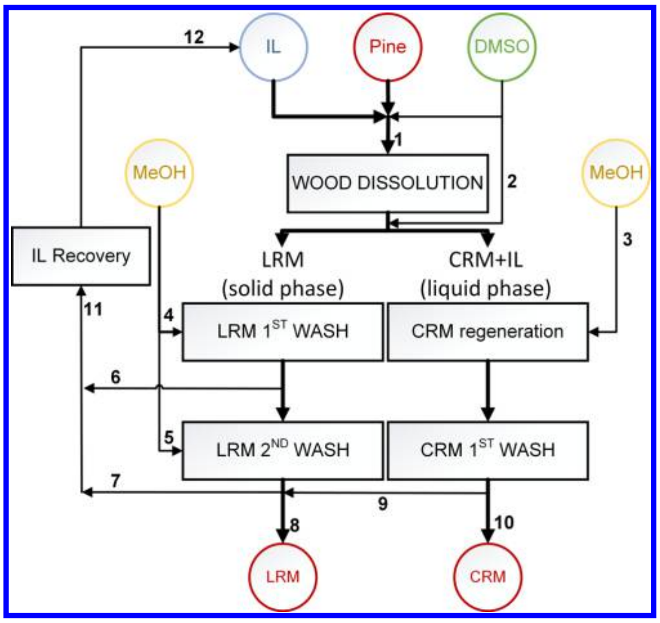
## EXPERIMENTAL SECTION

**Materials and Reagents.** The ionic liquid 1-allyl-3-methylimidazolium chloride ([Amim][Cl], >98%, Iolitec GmbH) was employed for wood dissolution. Previously, [Amim][Cl] was dried in a vacuum oven for 24 h at 60 °C. *Pinus radiata* chips were provided by the Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria (INIA). The biomass samples were characterized in terms of moisture content and chemical composition following the NREL methodology.[28] *Pinus radiata* chips were milled and sieved to obtain particle sizes <150 $\mu$m. Extractives were removed by extraction, first with acetone and then with water, in a Soxhlet extractor.

Dimethyl sulfoxide (DMSO, ≥ 99.9%, Panreac) and dry methanol (MeOH, max 0.005% water, Panreac) were employed as the cosolvent and antisolvent, respectively. In addition, microcrystalline cellulose (Avicel PH-101) was used as a reference material in the characterization of the regenerated cellulose. Organosolv lignin from *Pinus radiata* wood was also used as a reference material for the UV–vis measurements, obtained with a mixture of 60% (w/w) ethanol/water at 200 °C for 50 min (process developed in a Parr reactor model 4567). Sulfuric acid was used to precipitate the lignin from the mixture.

**Experimental Procedure.** The scheme of the experimental process is shown in Scheme 1. *Pinus radiata* wood (0.8 g) was mixed with 20 g of [Amim][Cl] and 2.6 g of DMSO (stream 1). Samples were heated under microwave radiation in a Berghof SpeedWave Four microwave oven, using a two-step program, following the procedure reported in a previous work.[13]

Scheme 1. Experimental Process



Once the dissolution step was finished, the cosolvent DMSO (25 mL) was added to the mixture (stream 2), and centrifuged at 6000 rpm for 10 min to separate the liquid phase formed by [Amim][Cl] and the dissolved wood, and the solid phase formed by the lignin rich material (LRM).

Afterward, methanol (200 mL) was added to the liquid phase to precipitate a cellulose-rich material (CRM) (stream 3). The solution was stirred for 10 min in a water bath at 40 °C. This solution was filtered under a vacuum to obtain the above-mentioned CRM (stream 10).

A crucial step to guarantee the maximum [Amim][Cl] recovery yield and avoid [Amim][Cl] residues in the CRM and LRM is the washing step. Both solids, the CRM and the lignin rich material (LRM) were washed several times to ensure the [Amim][Cl] removal. The CRM was first washed with the 200 mL of methanol used in the regeneration step and then with 200 mL of water (not included in the scheme). The LRM was washed two consecutive times with methanol (50 mL per washing) (streams 4 and 5). LRM (stream 8) and CRM (stream 10) were dried in a vacuum oven at 60 °C. All the washing fractions containing [Amim][Cl], DMSO, and methanol were analyzed by HPLC.

The above process was repeated five times, using the IL recovered in the previous cycle. To ensure that the [Amim][Cl] used in all the cycles was completely derived from the previous cycle, the process was repeated 6, 5, 4, 3, and 2 times in the first, second, third, fourth, and fifth cycle, respectively.

The washing fractions (streams 6, 7, and 9) were collected (stream 11) and distilled in a vacuum rotary evaporator. Assuming that residual DMSO may remain in the IL-rich fraction, an [Amim][Cl]/DMSO ratio of 90/10 (wt %/wt %) in the recovered ionic liquid was fixed. Thus, the DMSO amount was added to maintain the [Amim][Cl]/DMSO ratio and reused in the next cycle (stream 12).

CRM and LRM yields were obtained according to eqs 1 and 2, respectively:

$$\text{yield CRM}_{\text{cycle}\,n}\,(\text{wt\%}) = \left(\frac{\sum_{i=1}^{n}\text{mass CRM}}{\sum_{i=1}^{n}\text{mass raw wood}}\right) \times 100 \tag{1}$$

$$\text{yield LRM}_{\text{cycle}\,n}\,(\text{wt\%}) = \left(\frac{\sum_{i=1}^{n}\text{mass LRM}}{\sum_{i=1}^{n}\text{mass raw wood}}\right) \times 100 \tag{2}$$

Additionally, nonlocated wood fractions will be defined according to eq 3:

$$\text{yield nonlocated (wt\%)} = 100 - \text{yield LRM} - \text{yield CRM} \tag{3}$$

**[Amim][Cl] Characterization.** An Agilent 1260 HPLC was used to determine the [Amim][Cl] concentration in the washing and distillate fractions. The analysis was developed using a Hi-Plex Ca column and an RI detector with a flow rate of 0.6 mL/min at 40 °C. Water was used as mobile phase, and samples were diluted at least 20 times before injecting.

Attenuated total reflectance Fourier Transform infrared (FTIR/ATR) spectra of the [Amim][Cl] samples were acquired using a Jasco 4700 spectrometer operating with a Golden Gate TM diamond accessory Specac 10542. FTIR/ATR spectra were measured between 3500 and 700 $\text{cm}^{-1}$ using 64 scans and a resolution of 4 $\text{cm}^{-1}$. The Spectra manager software was used for instrument management.

[Amim][Cl] was also studied by proton nuclear magnetic resonance ($^{1}$H NMR) in $H_2O$-$d_6$, which was performed in a Bruker DPX 300 MHz using 64 scans. For the analysis, 10−20 mg of each sample were diluted in 1 mL of solvent.

The lignin content in the recovered [Amim][Cl] was analyzed by UV/vis spectroscopy using a Varian Cary 50 scan UV/vis spectrophotometer. Due to the strong absorbance of [Amim][Cl] in the UV region, the samples were measured at 440 nm.[29] The recovered [Amim][Cl] was diluted 40 times with 0.1 N NaOH and filtered before measuring the absorbance.[30] The total dissolved lignin concentration was obtained from the reference curve of the Organosolv lignin samples prepared. The lignin content in the recovered [Amim][Cl] was calculated from eq 4.

$$\text{lignin in [Amim][Cl](wt\%)} = \left(\frac{\text{mass of lignin in IL}}{\text{total mass of IL}}\right) \times 100 \tag{4}$$

The thermal decomposition behavior of the reused [Amim][Cl] was studied and compared to a mixture of fresh [Amim][Cl]/DMSO 90/10 (wt %/wt %) using a TG/DSC1Mettler Toledo instrument. Each sample was heated from 40 to 105 °C to remove water and maintained for 30 min. Then, the sample was heated to 800 °C at a heating rate of 10 °C/min. Dry nitrogen was added at a flow rate of 50 mL/min and the experiments were performed in PCA/Sapphire crucibles (Mettler Toledo) of 70 $\mu$L. For each experiment, 7−9 mg of sample were used. The characteristic parameters of the TG and DTG curves were determined.

**CRM and LRM Characterization.** FTIR spectra of CRM and LRM were recorded in a Jasco 4700 spectrometer between 2000 and 600 $\text{cm}^{-1}$. Samples (1 mg) were mixed with 200 mg of KBr in an agate mortar; the resultant mixtures were pressed at 7 tonnes for 30 s and analyzed using 16 scans at 4 $\text{cm}^{-1}$ of resolution.

X-ray diffraction (XRD) patterns of the CRM were measured on an X'Pert Pro MPD System. The diffracted intensity of Cu K$\alpha$ radiation (45 kV and 40 mA) was analyzed in a 2$\theta$ range between 5° and 50° and a step size of 0.03. All spectra were subjected to baseline correction using X'Pert HighScore Plus software.

The chemical composition of LRM was calculated based on the National Renewable Energy Laboratory methodology adapted to small quantities of samples.[31] LRM was treated in a two-step acid hydrolysis, resulting in an insoluble residue compound by acid-insoluble lignin and ashes and a liquid fraction containing soluble lignin and sugars. The acid insoluble lignin was gravimetrically measured after drying the residue at 105 °C for 12 h. The amount of acid-soluble lignin was determined from the UV absorbance of the hydrolysate at 240 nm and an absorptivity of 12 $\text{L·g}^{-1}\text{·cm}^{-1}$. Sugars in the hydrolysate were determined by HPLC using an RI detector. A Carbosep CHO-682 column was run at 80 °C with water as the mobile phase and a flow rate of 0.4 mL/min. The anhydrous correction to hexoses (162/180) and pentoses (132/150) were applied to each sugar concentration, respectively. Sugar recovery standards (SRS) correction was applied following the NREL/TP-510-42618 procedure.

## RESULTS AND DISCUSSION

This paper focuses on studying the ability of the [Amim][Cl] to be reused. The IL characterization and the evolution of the treatment efficiency along the reuse cycles is discussed. Furthermore, the properties of the solids obtained (CRM and LRM) as a consequence of the IL reuse grade are also examined.

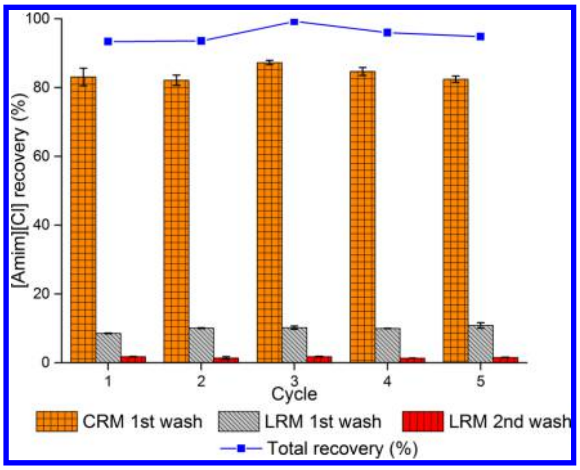


Figure 1. [Amim][Cl] recovery.

**Recovery of [Amim][Cl].** To determine the quantity of solvent required to wash each solid and recover the majority of the IL used in the two-step process, a washing methodology was used. Figure 1 shows that [Amim][Cl] remains in both solids (CRM and LRM). In the case of CRM, most of the [Amim][Cl] is removed in the wash with methanol (82−84% of the initial IL introduced). In the case of LRM, recovery of [Amim][Cl] is observed in both washings. Although most of the [Amim][Cl] impregned into the LRM is recovered in the first wash (9−11%), there is a small quantity of [Amim][Cl] (1.3−1.7%) that is recovered in the second wash. A sequential washing was also performed with [Bmim][Cl] and cellulose by Lozano et al, who also used HPLC analysis to determine the

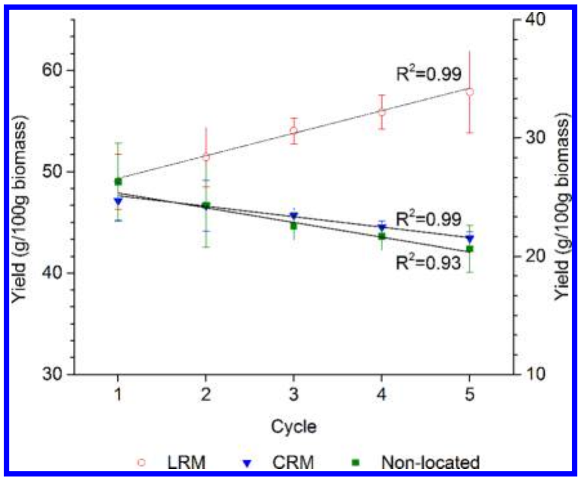


**Figure 2.** CRM, LRM, and nonlocated fractions yields.

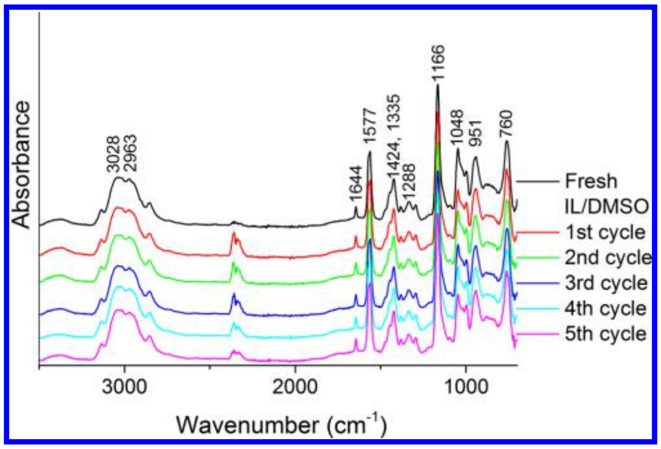


**Figure 3.** FTIR/ATR spectra of fresh and recovered [Amim][Cl].

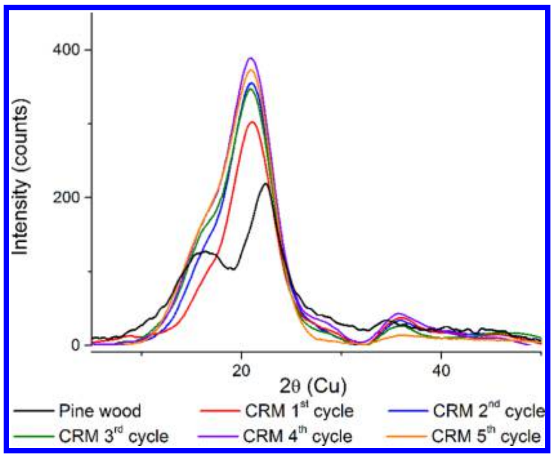


**Figure 4.** XRD patterns of CRM.

total [Bmim][Cl] recovered in the washing step, with IL recovery yields in the range of 95−99%.[32]

Previous FTIR analyses of CRM showed that, on some occasions, just a wash with methanol was not sufficient to completely remove the IL retained into the CRM.

The recovery is divided into two steps. In the first step, methanol is completely removed. In the second step, conditions must be more severe to remove most of the DMSO added. After distillation, the final recovery indicates that around 92−96% of the [Amim][Cl] introduced in this step is recovered. The high viscosity of [Amim][Cl] (2090 mPa s at 25 °C) difficult higher recovery yields in the distillation stage.[33]

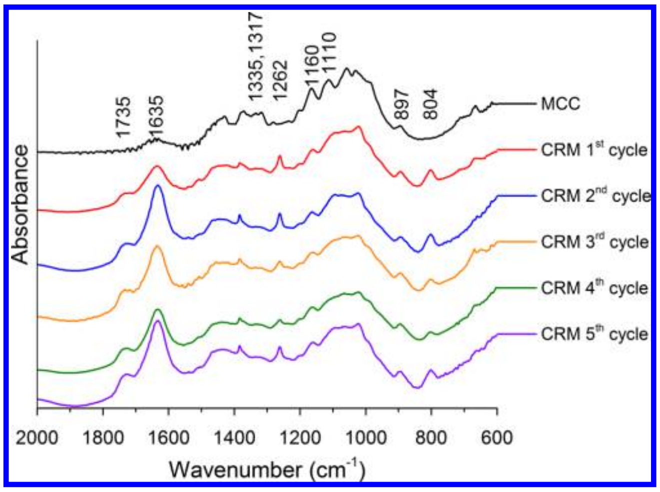


**Figure 5.** FTIR spectra of CRM.

The recovered IL analyzed by HPLC, did not show the presence of glucose, indicating that no cellulose to glucose degradation was produced during the pretreatment. To verify the negligible vapor pressure of [Amim][Cl], distilled fractions were analyzed by HPLC, showing no evidence of the presence of [Amim][Cl] in the distilled fractions.

**Efficiency of Recovered [Amim][Cl] in Biomass Fractionation.** The relation between CRM, LRM, and nonlocated yields calculated according to eqs 1, 2, and 3, and the reuse grade is shown in Figure 2.

There is a clear linear correlation between the CRM, LRM, and nonlocated fractions yields and the IL reuse grade. The LRM results show an incremental loss of the IL dissolving efficacy in consecutive cycles; the efficiency to dissolve pine wood decreases approximately 34% from the first to the fifth cycle. As a consequence of a decrease of the dissolution capacity, the decrease of the CRM yield indicates that regeneration rate is smaller. Nonlocated fractions represent 20−26% of the initial biomass introduced in the process, indicating that not all of the dissolved components are regenerated, and they presumably are being accumulated into the IL, as described below.

**Chemical Structure of Recovered [Amim][Cl].** The FTIR spectra of fresh and recovered [Amim][Cl] in successive cycles between 3500 and 700 cm$^{-1}$ is shown in Figure 3. In the case of fresh [Amim][Cl], DMSO in a ratio of 90/10 (wt %/wt %) was added to maintain the proportion.

Some bands variations were detected in the range of 3500−3200 cm$^{-1}$, indicating traces of water were accumulated in [Amim][Cl] after the recovery process.[34] Typical cation bands appear at 3028 cm$^{-1}$ (shoulder corresponding to the CH stretching vibration), 2963 cm$^{-1}$ ($CH_2HCH$ asymmetric stretching), 1644 cm$^{-1}$ (CC stretching vibration in allyl), 1577 cm$^{-1}$ (asymmetric $CH_3(N)CN$), 1424 cm$^{-1}$ ($CH_2/CH$ bending vibration in side chain), 1335 cm$^{-1}$ (CN stretching vibration), 1288 cm$^{-1}$ (CH rocking vibration), 1166 cm$^{-1}$ CH (bending vibration in imidazole ring), and 1048 cm$^{-1}$ ($CH_3N$ stretching).[35−37] A chloride anion vibration band appears at 760 cm$^{-1}$.[38] No relative differences were observed in these bands, which apparently indicates no thermal degradation of the ionic liquid occurred after the dissolution and recovery

Table 2. LRM Composition (mg/100 mg dry pine wood)

| | Lignin Rich Material | | | | | |
|---|---|---|---|---|---|---|
| | lignin | glucan | xylan | galactan | arabinan | mannan |
| pine wood | 34.5 ± 1.5 | 42.2 ± 0.9 | 3.9 ± 0.1 | 1.7 ± 0.2 | 0.6 ± 0.0 | 13.3 ± 1.4 |
| 1st cycle | 53.3 ± 1.2 | 16.0 ± 1.5 | 7.3 ± 0.3 | 5.1 ± 0.5 | 0.4 ± 0.1 | 15.3 ± 1.5 |
| 2nd cycle | 43.1 ± 0.1 | 28.1 ± 0.4 | 6.4 ± 0.1 | 3.8 ± 0.1 | 0.5 ± 0.0 | 12.5 ± 0.7 |
| 3rd cycle | 41.4 ± 2.0 | 27.8 ± 0.2 | 7.8 ± 0.0 | 3.9 ± 0.1 | 0.6 ± 0.1 | 12.9 ± 0.7 |
| 4th cycle | 42.7 ± 0.8 | 28.5 ± 0.2 | 7.1 ± 0.4 | 3.3 ± 0.2 | 0.6 ± 0.0 | 13.3 ± 0.1 |
| 5th cycle | 40.8 ± 0.2 | 28.4 ± 0.2 | 7.1 ± 0.6 | 3.3 ± 0.2 | 0.7 ± 0.1 | 13.3 ± 1.4 |

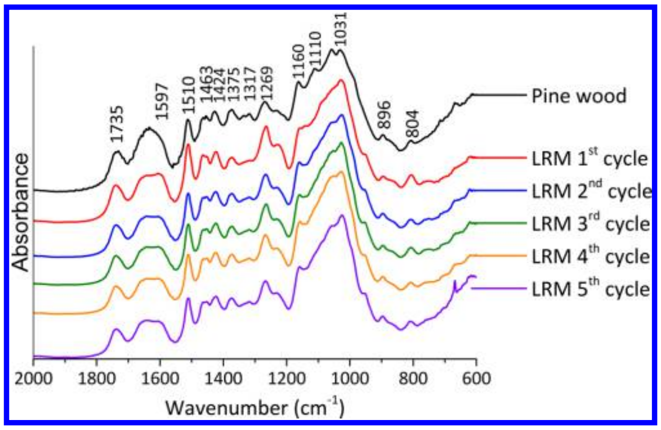


**Figure 6.** FTIR spectra of LRM.

treatments. This assumption was also observed by Chin et al, using [Amim][Cl] in homogeneous cellulose acetylation.[39] A typical DMSO band is observed at 951 $cm^{-1}$ for all the spectra. Height is similar for all the samples, verifying the proportion of 90/10 (wt %/wt %) [Amim][Cl]/DMSO used in the process.

$^1H$ NMR spectra of fresh and recovered IL are shown in Figure S1. It is observed how peaks at chemical shifts of 8.65, 7.40, 5.91, 5.38, 4.75, and 3.82 correspond to the hydrogen atoms of cation position nos. 7 (1H), 6 and 5 (1H), 2 (1H), 1 (2H), 3 (1H), and 4 (3H), respectively. Peak at chemical shift of 2.65 corresponds to hydrogen atoms of DMSO position nos. 8 and 9 (3H). No other additional peaks are observed in any of the spectra, confirming no degradation of the IL. These results are in accordance with those obtained by Xu et al.[11] In this case the presence of water is not observed.[11]

**Biomass Accumulation.** UV–vis analysis was performed to determine the lignin concentration in the recovered [Amim][Cl]. Portions of 0.02, 0.04, 0.07, 0.10, and 0.14 g of lignin per 100 g of IL are accumulated in the first, second, third, fourth, and fifth cycles, respectively. Lignin accumulated in the first cycle remains, and additional quantities are summed in consecutive cycles. This pattern has also been observed with other ionic liquids used for biomass pretreatment such us [Emim][OAc], or [BMIM][$MeSO_4$].[30,40] The addition of sulfuric acid solution to the recovered [Amim][Cl], following the strategy used to separate black liquor derived from the pulping process, results in dark particles precipitation (Figure S2a from the Supporting Information).[41,42] Moreover, the addition of water results in clearer particles precipitation (Figure S2b from Supporting Information) similar to the polysaccharides precipitated in the regeneration step, visually confirming that biomass accumulation in the IL is being produced.

TG characteristic parameters are shown in Table S1 (from the Supporting Information). $T_{onset}$ is 255.5 °C for fresh [Amim][Cl], which is lower than reported (273 °C) due to the DMSO content.[43,44] In all cases, temperatures are slightly lower in the first cycle and increase gradually up to the fifth cycle. Weerachanchai et al. already observed this behavior in the recovery of [Emim][OAc], attributing the change of degradation temperature to lignin accumulation.[30] In this case, the linear correlation observed for all TG characteristic parameters with nonlocated fractions yields ($R^2$ = 0.98–0.99), elucidate that not only lignin is the cause of higher degradation temperatures, but also carbohydrates. The $T_{50\%}$ for organosolv lignin and $T_{onset}$ for Avicel PH-101, both used as reference materials, are 376.5 and 311 °C, both higher than those obtained in the IL.

**Characterization of CRM.** The process developed to obtain a CRM was already detailed by Casas et al., who deeply characterized the regenerated solid to confirm that this is composed by polysaccharides.[13]

XRD diffraction reveals the amorphicity of all CRM solids (Figure 4). According to Seagal's method, the crystallinity index must be calculated as a ratio between amorphous cellulose at approximately $2\theta = 16.6°$ and crystalline cellulose at approximately $2\theta = 22°$.[45] However, both characteristic peaks of cellulose I and the reflection peak at $2\theta = 34.5°$ only appear in the untreated pine wood. In all CRM samples, a shift in the crystalline cellulose peak is produced from $2\theta \approx 22$ to 20. This new peak is typical of cellulose II.[46,47] The width of this amorphous peak at half-height is higher when the reuse grade increases (from the first to the fifth cycle, fwhm values are 5.79°, 6.49°, 7.08°, 7.04°, and 7.25°, respectively). The peak at $2\theta = 34.5°$ shifts to $2\theta = 35.8°$. The XRD data reveals that CRM amorphicity is higher, when the [Amim][Cl] reuse grade increases.[48] This tendency may be a consequence of both dissolution and the regeneration efficiency step, involving the regeneration of more amorphous CRM when the dissolving efficacy decreases (increase of the reuse grade).

The FTIR spectra of the CRM solids are displayed in Figure 5. Characteristic cellulose bands are present in all CRMs. Bands at 1335 and 1317 $cm^{-1}$ (corresponding to the OH in plane deformation and $CH_2$ rocking vibration) are affected by the crystallinity decrease and hydrogen bonds breakage during the dissolution process.[49]

The band at 1160 $cm^{-1}$ (COC stretching asymmetry) shows the cellulose vibrational energy changes as a consequence of the wood dissolution process.[13] Bands at 1110 $cm^{-1}$ (ring asymmetric stretching) and 897 $cm^{-1}$ (ring stretching) confirm the crystallinity decrease and amorphicity increase already exposed with the XRD results. Furthermore, an intense band at 1635 $cm^{-1}$, characteristic of the OH of water absorbed from cellulose, is also observed in the CRM solids.[13,50] There are three bands that are not present in MCC. The band at 1735 $cm^{-1}$ corresponds to C=O esters, characteristic of hemicelluloses. The band at 1262 $cm^{-1}$ is a CO stretching band

Table 3. Mass Balance (mg/1000 mg of [Amim][Cl])

| stream | 1 | 2 | 3 + 4 + 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|
| description | initial | DMSO | methanol | LRM 1st wash | LRM 2nd wash | LRM | CRM wash | CRM | washing fractions | recovered IL |
| **First Cycle** | | | | | | | | | | |
| IL | 1000.0 | 0.0 | 0.0 | 85.4 | 17.7 | 0.0 | 830.9 | 0.0 | 933.9 | 880.2 |
| DMSO | 111.1 | 1375.0 | 0.0 | 98.8 | 33.8 | 0.0 | 1242.7 | 0.0 | 1375.3 | 1356.1 |
| methanol | 0.0 | 0.0 | 19800.0 | 1403.8 | 1666.1 | 0.0 | 13080.0 | 0.0 | 16150.0 | 0.0 |
| carbohydrates | 25.6 | 0.0 | 0.0 | | | 8.9 | | 9.9 | | |
| lignin | 14.3 | 0.0 | 0.0 | | | 10.7 | | 0.0 | | 0.2 |
| **Second Cycle** | | | | | | | | | | |
| IL | 1000.0 | 0.0 | 0.0 | 100.5 | 13.9 | 0.0 | 772.2 | 0.0 | 886.6 | 862.4 |
| DMSO | 111.1 | 1375.0 | 0.0 | 94.0 | 11.0 | 0.0 | 884.6 | 0.0 | 989.6 | 320.4 |
| methanol | 0.0 | 0.0 | 19800.0 | 1708.9 | 1730.5 | 0.0 | 13126.4 | 0.0 | 16565.7 | 0.0 |
| carbohydrates | 25.7 | 0.0 | 0.0 | | | 11.8 | | 9.5 | | |
| lignin | 14.5 | 0.0 | 0.0 | | | 9.8 | | 0.0 | | 0.4 |
| **Third Cycle** | | | | | | | | | | |
| IL | 1000.0 | 0.0 | 0.0 | 102.0 | 17.9 | 0.0 | 872.9 | 0.0 | 992.8 | 870.5 |
| DMSO | 111.1 | 1375.0 | 0.0 | 110.5 | 15.7 | 0.0 | 1075.3 | 0.0 | 1201.5 | 308.8 |
| methanol | 0.0 | 0.0 | 19800.0 | 1919.9 | 2075.4 | 0.0 | 15716.8 | 0.0 | 19712.2 | 0.0 |
| carbohydrates | 25.7 | 0.0 | 0.0 | | | 13.3 | | 8.7 | | |
| lignin | 14.7 | 0.0 | 0.0 | | | 10.4 | | 0.0 | | 0.7 |
| **Fourth Cycle** | | | | | | | | | | |
| IL | 1000.0 | 0.0 | 0.0 | 99.8 | 13.6 | 0.0 | 846.7 | 0.0 | 960.1 | 911.1 |
| DMSO | 111.1 | 1375.0 | 0.0 | 116.1 | 14.2 | 0.0 | 1015.4 | 0.0 | 1145.7 | 459.7 |
| methanol | 0.0 | 0.0 | 19800.0 | 2194.4 | 2368.9 | 0.0 | 16293.1 | 0.0 | 20856.4 | 0.0 |
| carbohydrates | 25.7 | 0.0 | 0.0 | | | 0.0 | | 7.8 | | |
| lignin | 14.4 | 0.0 | 0.0 | | | 0.0 | | 0.0 | | 1.0 |
| **Fifth Cycle** | | | | | | | | | | |
| IL | 1000.0 | 0.0 | 0.0 | 108.4 | 15.5 | 0.0 | 824.3 | 0.0 | 948.2 | 913.1 |
| DMSO | 111.1 | 1375.0 | 0.0 | 123.8 | 17.0 | 0.0 | 1087.8 | 0.0 | 1228.6 | 539.2 |
| methanol | 0.0 | 0.0 | 19800.0 | 2264.6 | 2607.4 | 0.0 | 16854.7 | 0.0 | 21726.7 | 0.0 |
| carbohydrates | 25.7 | 0.0 | 0.0 | | | 14.9 | | 7.1 | | |
| lignin | 14.4 | 0.0 | 0.0 | | | 11.5 | | 0.0 | | 1.4 |

derived from arabino-4-*O*-methylglucuronoxylans, predominant in pine wood, and the band at 804 cm$^{-1}$ is due to glucomannan.[50,51] These bands confirm the presence of hemicelluloses in the CRM. No characteristic lignin bands have been found. Additionally, there is no presence of [Amim][Cl], indicating that the washing step has removed the ionic liquid in the CRM solid.

**Characterization of LRM.** The composition of LRM is determined according to the NREL methodology and exhibited in Table 2.

Glucan content decreases significantly, revealing the efficacy of [Amim][Cl] as cellulose solvent.[16] Note that the glucan content increases considerably from the first to the second cycle. In the first cycle (process developed with fresh [Amim][Cl]), there is only 16.0 mg of glucan/100 mg dry pine wood, whereas in successive cycles, this quantity increase to approximately 28 mg of glucan/100 mg of pine wood. The largest difference produced between the first and the second cycle shows the loss of efficacy with the reused [Amim][Cl]. However, there is still a notable difference between this solid composition and the untreated pine wood (42.2 mg of glucan/100 mg dry pine wood). This behavior has not been observed before, as most of the IL recycling processes are focused on biomass pretreatment prior to enzymatic hydrolysis. Separation between soluble and not soluble biomass in the IL has not been deeply studied. Lignin content increases considerably indicating that although the cellulose is dissolved, lignin remains. There is a notable difference between the untreated pine wood lignin content, the first cycle lignin content, and the second cycle lignin content (34.5, 53.3, and 43.1 mg of lignin/100 mg of dry pine wood).

Pentoses differences between untreated and treated wood are observed mainly in the xylan, probably due to a decrease in glucan content that causes an increase in other components. Xylan content varies between 7.3 and 6.4 mg of xylan/100 mg dry pine wood without an appreciable tendency. Galactan content increases from the untreated wood (1.7 mg of galactan/100 mg dry pine wood) to the first cycle treated wood (5.1 mg galactan/100 mg dry pine wood). After the first cycle the content decreses slightly, probably as a consequence of glucose total content increase. The mannan concentration in pine wood is also relevant (13.3 mg of mannan/100 mg dry pine wood). The use of fresh and recovered [Amim][Cl] in mannan has a similar tendency to galactan.

FTIR spectra have been developed in all LRM samples (Figure 6), confirming lignin, cellulose, and hemicellulose content. A fast comparison shows that all bands of the untreated pine wood are present in the LRM FTIR spectra.

Bands at 1597 cm$^{-1}$, corresponding to the aromatic skeletal vibration with C=O stretching, and at 1424 cm$^{-1}$, characteristic of aromatic skeletal vibrations combined with CH in plane deformation, have approximately the same intensity in all the samples.[52]

The band at 1510 cm$^{-1}$, characteristic of aromatic skeletal vibration guaiacyl > syringyl, seems to be more intense after the first cycle LRM sample and decreases in the subsequent LRM samples, becoming less intense in the untreated pine wood sample. This change verifies the overall lignin concentration obtained in each sample already explained in Table 2.

Finally, the guaiacyl ring breathing with the carbonyl stretching band at 1269 cm$^{-1}$ also increases in the LRM first cycle sample, decreasing in the following cycles as a consequence of the difficulty of dissolving guaiacyl units characteristics of softwoods.[52,53] The band at 1735 cm$^{-1}$ typical of hemicellulose remains almost unaltered in all spectra, and the band at 1262 cm$^{-1}$ is not observed.[50,51] However, the band at 804 cm$^{-1}$ characteristic of glucomannan, one of the most common hemicelluloses in pine, is observed to slightly decrease.[54] Regarding cellulose bands, the diminution of the intensity at 1160 cm$^{-1}$ confirms the reduction of cellulose content in LRM. No presence of the ionic liquid characteristic bands was observed (e.g., at 1577 cm$^{-1}$).

**Global Mass Balance.** Mass balance of the main components used in the overall process is shown in Table 3. Streams numbers are indicated in Scheme. 1. Pine wood fractions have been divided into two main components: lignin and polysaccharides (formed by cellulose and hemicellulose). Table 3 summarizes the calculations developed in the whole process with chromatographic, gravimetric, and NREL analysis techniques. In the whole mass balance, the differences between the initial wood introduced and the biomass obtained after the treatment demonstrate the considerable loss of carbohydrates as well as lignin that have not been located into the process and that presumably are being accumulated in the IL as some analytical techniques have confirmed. In the first cycle, losses for carbohydrates are around 26% and decrease significantly in the subsequent cycles (loss of approximately 14−16%). The accumulation of woody fractions is gradual and will reach a point that the removal of impurities will be necessary to continue the fractionation process. The addition of an antisolvent after certain number of IL reuse cycles may regenerate the IL and increase again its fractionation efficiency.

## ■ CONCLUSIONS

Fresh and recycled [Amim][Cl] used in the fractionation of *Pinus radiata* wood have been evaluated. The [Amim][Cl] employed along the process has been recovered, obtaining yields of up to 96%. From the first to the fifth [Amim][Cl] recovery cycle, a gradual decrease of the [Amim][Cl] capacity to dissolve pine wood has been observed. As a result, the LRM composition reveals differences, mainly produced between the solids obtained after the first (fresh IL) and the second IL recovery cycle, with 42.2 and 16.0 g of glucan/100 g of dry pine wood, respectively. CRM regeneration yields have also been reduced, while solids amorphicity is increased in successive IL recovery cycles. Note that gradual accumulation of lignin, and presumably carbohydrates are the causes of the decrease in pine wood fractionation yields. Despite of this reduction, the [Amim][Cl] chemical structure is not altered in the overall process.

In future work, the addition of an antisolvent after a certain number of cycles to regenerate the ionic liquid, remove biomass impurities, and clean the recovered ionic liquid should be studied.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b02723.

Figures S1 and 2 and Table S1 as mentioned in the text (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ ABBREVIATIONS

CRM, cellulose rich material; LRM, lignin rich material; IL, ionic liquid; [Amim][Cl], 1-allyl-3-methylimidazolium chloride

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