

Technoeconomic Assessment of a Biomass Pretreatment + Ionic Liquid Recovery Process with Aprotic and Choline Derived Ionic Liquids

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ABSTRACT: Ionic liquids have shown promising results in biomass pretreatment; however, an extensive water washing step is necessary. This fact increases not only the processing costs but also those associated with the ionic liquid recovery step. In this work, *Eucalyptus globulus* wood pretreated with two acetate-based ionic liquids, namely 1-ethyl-3-methylimidazolium acetate and choline acetate, has been washed with increasing volumes of water in order to analyze the influence of the amount of washing water used on the subsequent enzymatic hydrolysis stage and on the IL recovery costs. Vapor–liquid equilibria data of recovered ionic liquid/water mixtures have been determined to simulate the IL recovery step with Aspen Plus, calculating the operating costs using the Aspen Plus Economics Analyzer afterward. [Emim][OAc] was more efficiently washed and more effective toward wood pretreatment than [Ch][OAc]. Both IL/water systems were successfully modeled, and simulation studies showed that incremental volumes of water led to higher operating costs in the IL recovery step that are compensated with less IL makeup costs. Therefore, this work offers a technoeconomical analysis of the IL recovery step in a real biorefinery pretreatment process as a function of the volume of water used in the pretreated wood washing stage.

KEYWORDS: Water washing step, Saccharification, Vapor–liquid equilibria, Thermodynamic modeling, Ionic liquid recovery simulation, Cost estimation

INTRODUCTION

Lignocellulosic biomass can be considered as one of the main alternatives to fossil fuels.¹ Among the different biomasses that can be found, hardwood, and concretely *Eucalyptus globulus*, is a promising material due to its fast growth, adaptability, and availability.^{2,3} A pretreatment step that can disrupt the biomass network is needed in order to exploit different woody fractions since the wood structure is one of the main impediments for the development of an efficient technology.⁴ Different pretreatment technologies have been proposed, such as autohydrolysis, steam explosion, alkali pretreatment, etc.^{5,6} Among them, pretreatment with ionic liquids (ILs) emerged in the past decade as a promising alternative due to their viability to replace conventional organic solvents.⁷ ILs are melted salts at temperatures below 100 °C and have been used in different fields, such as extraction of biocompounds from microalgae, separation technologies, and biomass pretreatment and fractionation.^{8–11} They are capable of dissolving biopolymers, such as cellulose, reducing its crystallinity and enhancing enzymatic accessibility.^{12–14} In addition, ILs have been

reported to be easily recovered due to their nonvolatility and thermal stability.¹⁵

Imidazolium-based ILs, which have been widely studied, are petroleum-derived; thus, presenting some drawbacks, such as low biodegradability, cytotoxicity, and high costs.¹⁶ The most used imidazolium-based IL in biomass pretreatment is the 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]). Nevertheless, the toxicity of this IL makes it necessary to remove it from pretreated biomass by an extensive water-washing step.^{17–19} Choline acetate ([Ch][OAc]) has called attention as an alternative to imidazolium-based ILs in the past decade.^{15,16} [Ch][OAc] is easily synthesized by acid–base reaction of choline hydroxide and acetic acid, which makes this IL cheaper and more environmentally friendly than the

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conventional ones.²⁰ In addition, [Ch][OAc] is a completely bioderived IL, being more biodegradable and biocompatible than imidazolium-based ILs.^{15,21} Nevertheless, its viscosity is more than 5-fold higher than that for the [Emim][OAc], a fact that could cause stirring, mass transport, or temperature control problems.^{22,23} In this study, both acetate-based ILs ([Emim][OAc], selected as reference IL, and [Ch][OAc]) are used to pretreat *Eucalyptus globulus* wood.

The pretreated wood needs to be washed to eliminate the impregnated IL since it deactivates the enzymes, worsening the enzymatic digestibility in a subsequent enzymatic hydrolysis step.²⁴ The high amount of water employed in the water-washing step constitutes a limiting aspect in a potential scale-up process.²⁵ In addition, it represents an environmental issue that needs to be overcome. Elgharabawy et al.²⁶ proposed that different contents of IL impregnated in the pretreated biomass would deactivate the enzymes to a different extent. In this line, the volume of water employed in the washing step could be optimized, studying the effect of the impregnated IL on the enzymatic step.

Washing with different volumes of water affects the enzymatic digestibility and the IL recovery step. The IL regeneration represents a limiting role regarding the ionic liquid-based processes proposed in the literature.²⁷ Although several solute recovery and IL regeneration approaches have been evaluated through simulation with Aspen Plus, e.g., stripping with hot gas, distillation columns, re-extraction with supercritical fluids, among others,^{28,29} a series of flash distillation drums at vacuum conditions has been the most used technique to regenerate the ionic liquid for different processes involving ILs.³⁰ Nevertheless, this work is the first time that an IL recovery simulation is performed in biorefinery streams, using the recovered IL from the pretreatment step to study the system and model it, allowing the analysis of the variables that affect the most to the process economy. It is well-known that the IL cost and the capacity of recovering as much as possible of it after pretreatment represent the main costs in the whole economy of the process.^{31–33} Thus, the search for cheaper ILs that can be recovered at lower costs is crucial in order to get a competitive IL-based biorefinery. IL reutilization is another factor to take into account to develop suitable biorefinery processes. In this sense, the selected ILs have been successfully reused up to 5 cycles in the past.^{34,35}

In this work, a technoeconomical assessment of the downstream IL recovery process of a lignocellulosic biomass pretreatment, as a function of the water washing volume employed, is performed. As an initial asset of the process viability, enzymatic digestibility of wood pretreated with [Emim][OAc] and [Ch][OAc] ILs is measured. Once acceptable digestibility is confirmed, the technical and economic feasibility of the IL recovery is studied. For the first time, experimental vapor–liquid equilibria data of recovered IL from a pretreatment process stream are acquired, and the thermodynamic modeling is carried out. Thus, IL separation process simulation using Aspen Plus is proposed, and IL recovery costs (operating + IL makeup costs) are calculated to evaluate the feasibility to recover the employed ILs, [Emim][OAc] and [Ch][OAc], in a eucalyptus pretreatment process.

EXPERIMENTAL SECTION

Materials. 1-Ethyl-3-methylimidazolium acetate ([Emim][OAc]) and cholinium acetate ([Ch][OAc]) ILs were both supplied by Iolitec

GmbH with purities of 95 and 98%, respectively. *Eucalyptus globulus* wood was supplied by CIFOR-INIA (“Centro de Investigación Forestal-Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria”, in Spain). Eucalyptus wood was subjected to a Soxhlet extraction process to remove extractives and then sieved to obtain particle sizes <150 μm . The enzymatic cocktail Accellerase 1500 used in the enzymatic hydrolysis step was kindly donated by DuPont Industrial BioSciences.

Technoeconomic Assessment Scheme. Figure 1 shows a scheme of the methodology and calculation processes followed in this work.

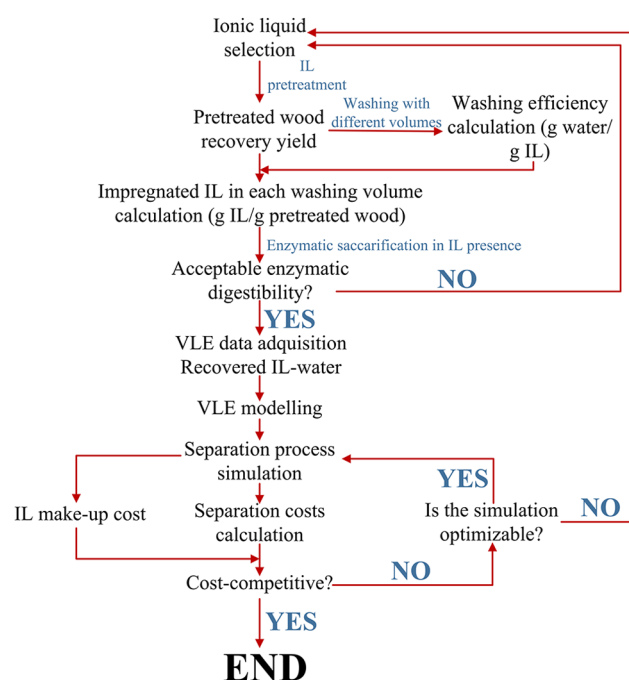


Figure 1. Scheme of the methodology and calculation processes followed to determine the technoeconomic viability of the IL pretreatment of wood and IL recovery process.

The first decision is to select the ILs that are going to be used based on physical and chemical properties, reusability, and previous experience. Wood is pretreated with the selected ILs and washed with different volumes of water, which leads to having various amounts of IL in the enzymatic hydrolysis step. This is the second decision point: whether the enzymatic digestibility is not acceptable (maybe attributed to the IL present in the enzymatic hydrolysis step or to the IL pretreatment capacity), another IL has to be selected. If, on the contrary, the enzymatic digestibility is high enough, the vapor–liquid equilibria data acquisition and modeling of the IL–water system is carried out. With the model parameters, the separation of the IL–water mixtures (from washing with different volumes of water) can be performed, calculating the separation operating costs and the IL makeup cost. The IL makeup cost is directly linked with the washing step. Taking both costs into account, a total recovery cost can be calculated. Once it is calculated, the final decision point is presented: provided that the process is not cost-competitive, the simulation must be redone, changing conditions in order to lower the processing costs; however, if the simulation is already optimized, the IL is not suitable for the process, and hence another IL must be selected. When the process is cost-competitive, the calculation methodology is finished, and therefore the selected IL is suitable for the biorefinery pretreatment and IL recovery process.

Ionic Liquid Pretreatment and Washing Step. For ionic liquid pretreatment, 0.4 g of wood, free of extractives and sieved, were dissolved into 10 g of ionic liquid. Samples were heated in a Barnstead Steam RS9000 thermostatic block for 6 h at 120 °C. Then, 25 mL of

water were added as antisolvent to precipitate the pretreated biomass. The solutions were then stirred for 10 min at 40 °C. Solid and liquid fractions were separated by vacuum filtration. The pretreated biomass was washed 10 times with 10 mL each time and four times with 20 mL per wash, up to a total of 180 mL of washing water. For each washing volume, an aliquot was taken to determine the ionic liquid content in each washing volume by conductivity with a Mettler Toledo SevenCompact conductimeter. The pretreated biomass was stored at 4 °C for further analysis and enzymatic hydrolysis.

Biomass Characterization. Untreated eucalyptus wood and pretreated samples were characterized in terms of solid composition following the NREL/TP-510-42618 procedure adapted to small sample amounts.^{36,37} Two acid hydrolysis steps were performed, obtaining a solid phase, mainly formed by acid-insoluble lignin (gravimetrically quantified), and a liquid phase, formed by sugars and acid-soluble lignin. The acid-soluble lignin content was determined by UV spectroscopy at 205 nm with an absorptivity coefficient of 110 L g⁻¹ cm⁻¹.

Sugar content in samples from acid characterization was determined by HPLC in an Agilent 1260 Infinity equipment with a refractive index detector and a CarboSep CHO-682 lead column. Before analysis, samples were neutralized with CaCO₃ and filtered, so a Micro-Guard cartridge (BioRad, Life Science Group Hercules, Ca) was used to retain possible calcium carbonate residues. The column compartment temperature was set at 80 °C, and water was used as the mobile phase with a constant flow of 0.4 mL/min. Organic acids and degradation products in the acid characterization, as well as the glucan content in the pretreated samples for glucan digestibility calculation, were determined with a Phenomenex ROA Organic Acid H⁺ column, using acidulated (0.005 M H₂SO₄) water as the mobile phase with a constant flow of 0.6 mL/min. Column compartment temperature was set at 60 °C. Sugar recovery standards (SRS) corrections were applied according to the NREL/TP-510-42618 procedure.³⁶

Enzymatic Hydrolysis. The enzymatic hydrolysis step was carried out following the NREL/TP-5100-63351 procedure.³⁸ Pretreated biomass (80 mg) was suspended in citrate buffer (pH = 5) containing 0.002% of sodium azide in a total volume of 8 mL. The recovered IL was added to the medium to represent biomass containing IL in a range of 0–10 g IL/g pretreated biomass as a function of the water employed to wash it (2.5–20 g water/g IL). The enzymatic cocktail Accellerase 1500 was added with a dosage of 0.25 mL/g glucan after pH adjustment with acetic acid. The reaction was performed in an IKA 4000i orbital incubator at 50 °C and 150 rpm. Aliquots were taken at 3, 6, 12, 24, 48, and 72 h and centrifuged for 10 min at 9000 rpm to stop the reaction. The enzymatic hydrolysis yield was expressed as the glucan conversion, according to eq 1:

$$\text{glucan conversion} = \frac{\text{released glucan in EH step(g)}}{\text{added glucan to the EH step(g)}} \times 100 \quad (1)$$

Sugar concentration for glucan conversion calculation was determined using a Phenomenex ROA Organic Acid H⁺ column, at the same conditions as explained before.

Vapor–Liquid Equilibria Equipment and Procedure. Isobaric vapor–liquid equilibria data were determined in a dynamic still, Fischer Labodest VLE-602-D, where both liquid and vapor phases are recirculated. For each measurement, 80 mL of ionic liquid/water feed mixtures was added to the equipment in a range of 0.2–1% water (w/w), according to the composition of the feed mixtures obtained from the biomass washing curves. Different feed mixtures were prepared using the recovered IL from the biomass pretreatment. The equilibrium experimental points were determined at 101.3, 75.0, 50.0, and 25.0 kPa, controlling pressure at every moment with a WIKA EN837-1 vacuum measuring probe connected to a vacuum solenoid valve. The uncertainty for the measured pressure was 0.01 kPa. The equilibrium was considered reached when the temperature remains constant for 30 min, as previously indicated for these types of systems.^{39–41} The equilibrium temperature was measured by a PT100 TMG digital precision thermometer with an uncertainty of 0.01 K.

Aliquots of the liquid and condensed vapor phases were taken directly from the collectors to analyze the equilibrium compositions, as explained below. Although the vapor phase is supposed to be only composed of water due to the nonvolatile character of the ionic liquid, the composition of the vapor phase was verified.⁴² Finally, the water saturation pressure for each equilibrium point was calculated by means of Antoine's equation.⁴³ The ionic liquid concentration in the equilibrium liquid phase was measured by refractive index analysis in a Rudolph J357 Automatic Digital Refractometer at 293.2 K and atmospheric pressure. The refractive index uncertainty was 0.00004.

Vapor–Liquid Equilibria Correlation. The vapor–liquid equilibria correlation was carried out using the *Non-Random Two Liquids* (NRTL) model (presented in eqs 2 and 3 for a binary system), due to the suitable performance shown in a previous work with ionic liquids and water.^{44–46}

$$\ln \gamma_1 = x_2^2 \left[\frac{\tau_{21} G_{21}^2}{(x_1 + x_2 G_{21})^2} + \frac{\tau_{12} G_{12}^2}{(x_2 + x_1 G_{12})^2} \right] \quad (2)$$

$$\ln \gamma_2 = x_1^2 \left[\frac{\tau_{12} G_{12}^2}{(x_2 + x_1 G_{12})^2} + \frac{\tau_{21} G_{21}^2}{(x_1 + x_2 G_{21})^2} \right] \quad (3)$$

where γ_1 and γ_2 are the activity coefficients for water and IL, respectively, x_1 and x_2 are molar fractions in the liquid phase for water and IL, $G_{12} = \exp(-\alpha_{12}\tau_{12})$ and $G_{21} = \exp(-\alpha_{21}\tau_{21})$ are the temperature dependent binary interaction parameters, and $\tau_{12} = \Delta g_{12}/RT$ and $\tau_{21} = \Delta g_{21}/RT$ are dimensionless interaction parameters, related to the temperature independent energy interaction parameters, Δg_{12} and Δg_{21} , which are going to be adjusted to model the systems.

The systems were adjusted by minimizing the next objective function (eq 4):

$$\text{OF} = \frac{a\Delta x + \Delta T}{N} \quad (4)$$

where a is the weighting coefficient for the liquid mole fraction deviation to balance their difference of magnitude with the temperature deviation and was fixed to 1000 and N refers to the number of points. The solver tool from Microsoft Excel software was used to run the algorithm. For all of the systems, the nonrandomness parameter (α_{ij}) was set at 0.3.

The temperature-independent binary interaction parameters (Δg_{ij}) were obtained from the regression of the vapor–liquid equilibria data for the water/ionic liquid binary systems. The liquid mole fraction and temperature deviations, Δx and ΔT , were calculated as follows (eqs 5 and 6):

$$\Delta x = \sum_{i=1}^N |x_{i,\text{calc}} - x_{i,\text{exptl}}| \quad (5)$$

$$\Delta T = \sum_{i=1}^N |T_{i,\text{calc}} - T_{i,\text{exptl}}| \quad (6)$$

where $x_{i,\text{calc}}$ and $T_{i,\text{calc}}$ are the predicted molar fractions in the liquid phase and temperatures and $x_{i,\text{exptl}}$ and $T_{i,\text{exptl}}$ are the experimental molar fractions in the liquid phase and temperatures. So, the modeling objective was to minimize the deviations in both variables between the experimentally measured and predicted values.

Ionic Liquid/Water Separation Simulation. The separation of the water/ionic liquid mixture via flash distillation was simulated using the Aspen Plus V.11 software. A schematic flowsheet of the process can be found in Figure S1. Both ionic liquids were implemented in Aspen Plus as pseudocomponents, specifying their molecular weights, densities, molecular volume, and normal boiling points, taken from the literature.^{47,48} The heat capacity of the ionic liquids was also introduced in Aspen Plus together with their dependency on temperature, both taken from the literature.^{49,50} The NRTL was selected as the thermodynamic model, including the binary interaction parameters obtained from the regression of the vapor–liquid equilibria.

The block FLASH2 was used to simulate the ionic liquid regeneration step. Four feed stream compositions resulting from washing with different amounts of water in the pretreatment step were evaluated. A 99.9% (w/w) IL recovery with an IL purity of 95% (w/w) has been fixed in all cases as the main objective of the simulation. A sensitivity analysis was carried out varying temperature and pressure to compare both ILs at the operating conditions that ensure the lowest operating costs for each IL. The temperature was always kept under the decomposition temperature (T_{decomp}) of the ionic liquids to avoid IL degradation.⁵¹ Moreover, the operating costs needed for each simulation were determined with Aspen Plus Economics Analyzer. The vacuum costs have been estimated by a COMPRESSOR block carrying out the opposed pressure drop taking place in the process, as can be found in the literature.^{10,27,52} Among all of the operating conditions that ensure that the simulation objectives are accomplished, those that minimized operating costs in each case have been selected.

RESULTS AND DISCUSSION

Ionic Liquid Pretreatment and Washing Curve. Solid yield recovery and composition of untreated and pretreated wood are shown in Figure 2. A decrease in solid recovery is

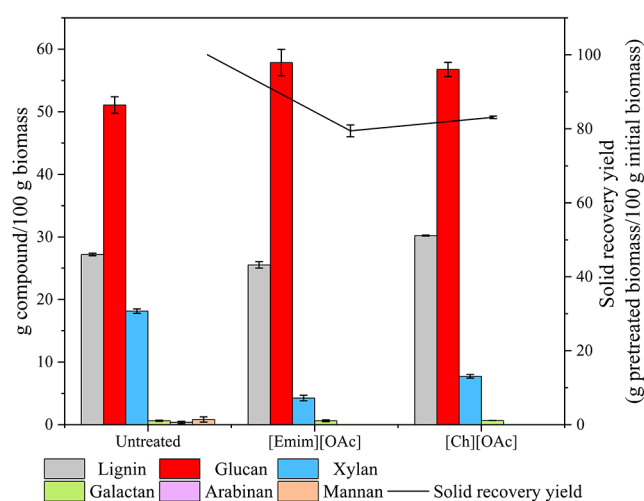


Figure 2. Solid recovery and compositional analysis of untreated and pretreated eucalyptus wood.

observed for both ILs, especially in the case of wood pretreated with [Emim][OAc]. The relative composition for wood pretreated with both ILs, compare with the untreated eucalyptus, indicates that biomass fractions are selectively removed.⁵³ Glucan composition increases compare to untreated wood due to hemicelluloses degradation. Galactan content remains constant, but xylan, arabinan, and mannan relative abundance drastically decrease by the IL action. Lignin content is higher in wood pretreated with [Ch][OAc] than [Emim][OAc], and glucose is not degraded, which makes the wood pretreatment with ILs interesting.⁵⁴ Solid recovery is higher in wood pretreated with [Ch][OAc] than that pretreated with [Emim][OAc], probably due to a larger unrecovered amount of lignin and xylan with the [Emim]-[OAc].

IL content in different washing fractions was calculated, as shown in Figure 3, where the washing curves of both ILs are represented.

[Emim][OAc] and [Ch][OAc] washing curves have almost the same slope, with a very similar washing rate up to 2.5 g water/g IL, where approximately 9 g IL/g initial biomass are

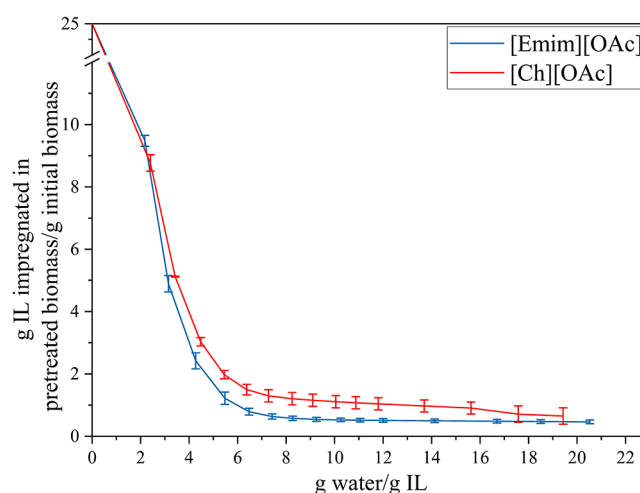


Figure 3. Washing curve of both acetate-based ILs.

still bounded to the pretreated biomass, which represents a 65% (w/w) recovery of both ILs. The main difference in the washing curves of both ionic liquids occurs between 2.5 and 3.5 g water/g IL: the [Emim][OAc] presents a washing rate of -0.19 g IL/mL water against -0.14 g IL/mL water for the [Ch][OAc]. For that reason, [Emim][OAc] is more efficiently washed since less water/g IL is needed to remove the [Emim][OAc] in comparison with the [Ch][OAc]. From 4 g water/g IL ahead, slopes and washing rates of both curves are practically identical. The employment of more than 9 g water/g IL is unnecessary since the washing curve is constant for both ILs from that point ahead.

Kamlet–Taft parameters are often used as indicative of IL–cellulose interaction and subsequent regeneration and can be correlated to the IL ability of dissolving wood.⁵⁵ Ionic liquids with higher β parameter values present a stronger interaction with the cellulosic fraction, and consequently, the washing is slower and less efficient.⁵⁶ However, the bibliographic values of β parameter, 1.23 for [Emim][OAc] and 1.22 for [Ch][OAc],⁵⁵ indicate that the washing curve should be the same for both ionic liquids, although the [Emim][OAc] is washed slightly more efficiently. These ILs have the same anion, which has been widely described as the main factor in the cellulose–IL interaction, which supports the similarity in β parameter.⁵⁷ The main reason for the difference in the washing curves is probably the higher viscosity of the [Ch][OAc] (89.5 mPa s at 80 °C) vs the [Emim][OAc] (17 mPa s at 80 °C).^{22,23,58} This higher viscosity would cause a stronger interaction between wood and IL, needing higher water volumes to wash it.

Enzymatic Hydrolysis. The pH of the suspensions that were subjected to enzymatic saccharification in this work were slightly more basic than the optimal enzymes pH due to the presence of IL, so it was adjusted before saccharification. pH was also measured at the end of the reaction to control that the enzymatic hydrolysis conditions have been unaltered. Samples with [Ch][OAc] have slightly higher pHs due to a higher basicity of the [Ch]⁺ cation compared with the [Emim]⁺ one. In every case, more mol of acid were needed per mol of IL to adjust pH in the case of [Ch][OAc]. Samples more concentrated in IL present a pH increase during the reaction time, but in every case final pH is within the enzyme limits (4.5–5.5).

From the obtained washing curves for both ILs (Figure 3), four different washing volumes were selected to test the enzyme tolerance to these ILs. The selected points were 2.5, 3.5, and 5.5 g water/g IL and 20 g water/g IL (IL content of 7.95, 4.12, 1.21, and 0.00 g IL/g biomass for [Emim][OAc], respectively, and 8.41, 4.97, 1.95, and 0.00 g IL/g biomass for [Ch][OAc], respectively).

The enzymatic hydrolysis yield at 72 h for the different volumes of washing water selected is depicted in Figure 4. Enzymatic digestibility is calculated as g produced glucan/100 g added glucan.

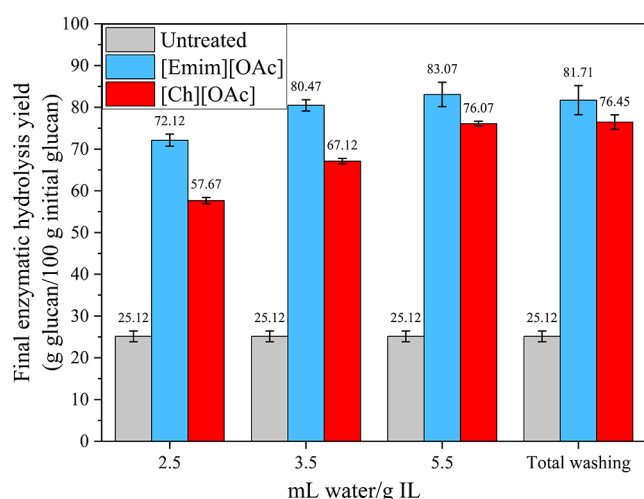


Figure 4. Enzymatic hydrolysis yield at 72 h for different volumes of washing water.

The presence of IL usually causes enzyme deactivation due to denaturalization by the interaction of the IL anion with hydrogen bonds in the enzyme proteins.^{24,26,59} Enzymatic hydrolysis yield is less affected by the volume of water employed in wood pretreated with [Emim][OAc] than it is in wood pretreated with [Ch][OAc]. Samples treated with [Emim][OAc] present the same digestibility when washing with 3.5, 5.5, and 20 g water/g IL (from Figure 3, IL content in biomass of 4.12, 1.21, and 0.00 g IL/g biomass, respectively), and their difference with the sample washed with 2.5 g water/g IL (7.95 g IL/g biomass) is approximately 10%. On the other hand, wood pretreated with [Ch][OAc] is significantly affected by the IL presence, with a sharp decrease in digestibility at samples washed with 2.5 and 3.5 g water/g IL (from Figure 3, IL content of 8.41 and 4.97 g IL/g biomass). Since the ILs tested in this work have the same anion, the difference in viscosities of both ILs can explain the observed results, with the [Emim][OAc] having a lower viscosity than [Ch][OAc], which enhances enzyme activity and stability.^{22,23,26} Pretreated wood washed with 5.5 g water/g IL (1.95 g IL/g biomass) presents the same enzymatic digestibility than that washed with 20 g water/g IL (0.00 g IL/g biomass), which makes the additional washing unnecessary. In every case, wood pretreated with [Emim][OAc] has higher digestibilities than wood pretreated with [Ch][OAc]. Biobased ILs are described as less cytotoxic than conventional ones, as they are formed by natural compounds and their derivatives.^{15,16} Nevertheless, it has been proved that a microbial cellulase only lost 10% and 15% of its total activity when incubated with [Ch][OAc] and [Emim][OAc], respectively, at the IL concentrations used in

this work.²⁶ Under these conditions, pretreated eucalyptus with [Emim][OAc] has been proven to have higher enzymatic digestibilities than eucalyptus pretreated with [Ch][OAc].⁵¹ The highest glucan digestibility reached was around 80–83%, when washing biomass pretreated with [Emim][OAc] with 2.5–20 g water/g IL.

In addition to the enzymatic hydrolysis yield, the reaction rate is another important factor to consider. The enzymatic digestibility evolution with time can be found in Figure S2, where the reaction rate can be deduced from the slopes of the different curves. In both cases, the two higher contents of IL in the pretreated wood cause a decrease in reaction rate, taking more than 48 h to get the final digestibility in the case of [Emim][OAc]. This is, once again, attributed to the enzyme deactivation in the presence of high contents of IL.²⁴ With the [Ch][OAc] IL, reaction rates are always slower than those for [Emim][OAc], with which the final digestibility is reached in 24 h in the pretreated woods washed with 2.5 and 3.5 g water/g IL. This is an important factor to take into account in order to optimize the washing step since the enzymatic digestibilities with [Emim][OAc] at 72 h are the same when washing the pretreated wood with 3.5, 5.5, and 20 g water/g IL; however, it takes 24 h to get to that value in the cases of 5.5 and 20 g water/g IL and 48 h in the case of 3.5 g water/g IL. Reaction rates and digestibility values are the same with both ILs when washing with 5.5 and 20 g water/g IL, which indicates that a diminution on the volume of washing water is feasible.

Vapor–Liquid Equilibria and Modeling. The vapor and liquid phase compositions were obtained for each experimental point. Diagrams for water/ionic liquid binary systems at the four pressures evaluated can be found in Figure S3. Liquid phase composition is represented as the mass fraction of water since the washing process is always explained in a mass basis composition. The bubble temperature increases as the ionic liquid composition increases (or water composition decreases) in the liquid phase. The temperature for ionic liquid-rich compositions in the liquid phase was not experimentally determined because the IL decomposition temperature is exceeded.⁵¹ The equilibrium temperatures are almost the same for both ionic liquids for a given composition at the same pressure since the [OAc][−] anion and water interact strongly, presenting a dominant role in the whole interaction.^{28,60} Ionic liquid was not detected in the vapor phase.

The vapor–liquid equilibria data described by the NRTL model can be found in Figure S3, where the accuracy of the model can be noted. The binary interaction parameters are collected in Table 1 together with the mean deviations for liquid mole fraction and temperature, also showing the suitable description of the experimental data provided by the model.

Table 1. Randomness Binary Interaction Parameters (Δg_{ij}) of the NRTL Model Obtained from the Fittings for the VLE Data of Binary Systems^a

<i>i</i> – <i>j</i>	$\Delta g_{ij}/\text{K}$	$\Delta g_{ji}/\text{K}$	Δx	$\Delta T/\text{K}$
water (1) + [Emim][OAc] (2)				
1–2	−5891.28	61.18	0.02	0.73
water (1) + [Ch][OAc] (2)				
1–2	−4812.96	34.79	0.0009	0.33

^a α_{12} values were set to 0.3 for all systems.

The NRTL binary interaction parameters obtained from the modeling were implemented in the Aspen Plus software to simulate the IL recovery process.

Ionic Liquid Recovery Simulation. Among all conditions tested for every feed composition, 150 °C and 70 kPa and 160 °C and 50 kPa were established as the optimal conditions for [Emim][OAc] + water and [Ch][OAc] + water systems, respectively, as they minimized as much as possible the vacuum costs. Under these conditions, an IL purity of 95% is achieved. This purity is high enough for another pretreatment cycle since there are studies in which ILs with higher contents of water are used to pretreat biomass with similar results in enzymatic digestibility than those experiments performed with pure IL.⁶¹ In any case, it should be taken into account that several simulations have been carried out at temperatures and pressures outside the range of the experimental conditions since higher IL contents cause experimental problems in the vaporization step. The simulation results must be carefully taken because of the extrapolations made. However, the slope of this work involves only an initial approximation of the utilities needed in the ionic liquid recovery step.

Once the optimal conditions in the flash drum were determined, the operating costs of the recovery step have been calculated using the Aspen Plus Economics Tool, which has a database of different utilities price. The heating requirements were provided by medium pressure steam, which is considered to have a cost of 2.20×10^{-6} \$/kJ. In addition, the electricity cost is estimated to be 1.58×10^{-5} \$/kJ. These prices have been previously used in the literature.²⁷ The software calculates the operating costs associated with each utility by considering the energy requirements of each process unit. Figure 5 represents the

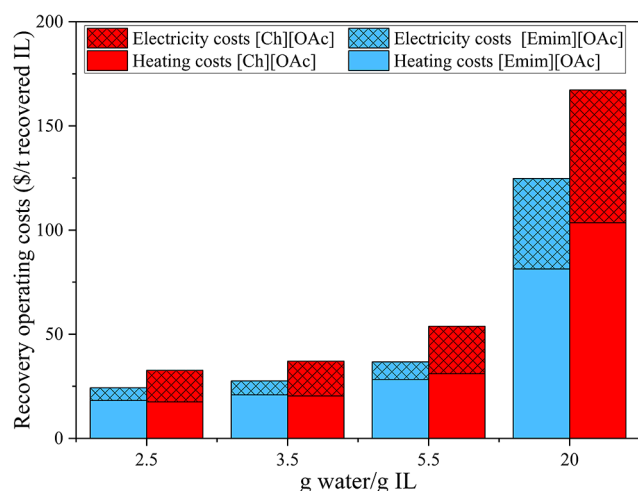


Figure 5. Operating costs for recovering both ILs at different feed stream compositions.

recovery operating costs, divided into electricity costs and heating utility requirements, at the most favorable conditions for both ILs and with the 4 feed streams composition, those resulting from washing the pretreated wood with different volumes of water. Cooling costs are not shown in Figure 5 since they represented less than 1% of recovery costs.

Operating costs associated with the recovery of [Ch][OAc] are higher than those for [Emim][OAc]. Higher volumes of water in the washing step entail higher operating costs in the

IL recovery step. Heating costs are similar at 2.5, 3.5, and 5.5 g water/g IL between the two ILs as their heat capacities are almost the same.^{49,50} Increasing the amount of water in the mixture leads to the biggest difference in heating costs since there is a higher amount of water on the [Ch][OAc] + water system (from Figure 3). Heating costs increase from approximately 20 \$/t recovered IL to 80 \$/t recovered IL and from 20 \$/t recovered IL to 100 \$/t recovered IL for [Emim][OAc] and [Ch][OAc], respectively. Electricity costs are directly associated with vacuum generation (simulated by a COMPRESSOR block with the same pressure jump, as explained before). Vacuum costs remain practically constant at 2.5, 3.5, and 5.5 g water/g IL for both ILs, being approximately 6 \$/t recovered IL and 16 \$/t recovered IL for [Emim][OAc] and [Ch][OAc], respectively. Incrementing the volume of water employed in the biomass washing step to 20 g water/g IL increases drastically the costs associated with vacuum generation, up to 43 \$/t recovered IL for the [Emim][OAc] and 63 \$/t recovered IL for the [Ch][OAc], due to the larger volume of water that is removed from the mixture. They are always higher in the [Ch][OAc] case, a fact that could be attributed to a higher solubility of the [Ch⁺] cation versus the [Emim⁺] one since the [Emim⁺] cation is larger than the [Ch⁺], causing a weaker interaction between the [OAc⁻] anion and water.⁶⁰

Comparing vacuum costs and heating costs, it can be seen that heating costs are always higher, independently of the volume of water employed in the washing step. At 2.5, 3.5, and 5.5 g water/g IL, these represent a 75% of the total costs in the case of the [Emim][OAc] and a 55% in the case of the [Ch][OAc]. However, heating costs contribution to recovery operating costs changes when washing with 20 g water/g IL, representing a 65% and 62% for [Emim][OAc] and [Ch][OAc], respectively. At this feed composition, the high amount of water in the system is key for the IL recovery, establishing the vacuum costs as the limiting factor in the case of the [Emim][OAc]. However, the heating costs contribution to total costs is increased at 20 g water/g IL for the [Ch][OAc], probably owing to the higher amount of water that needs to be heated in the [Ch][OAc] + water system compared to the [Emim][OAc] + water one.

Economic Balance of the Recovery Step. The sum of the operating costs in the flash distillation unit and the costs related to the fresh IL makeup (higher at the less washed samples) has been calculated. These calculations have been carried out for a calculation basis of 100 kg of initial IL/kg of treated wood. The results are shown in Figure 6. Enzymatic digestibility values are from Figure 4 but are also presented here to ease the understanding of the importance of water washing volume.

The costs of fresh ILs are estimated due to a lack of data in this area. [Emim][OAc] is usually estimated to be 2.5 \$/kg, but no data can be found on [Ch][OAc].³¹ Chen et al.⁶² proposed an equation for cost estimation of ILs formed by a simple acid–base reaction, as is the case. With this equation, ILs costs can be calculated from acid and base molecular weights and prices, which can be obtained from ICIS and others pricing data sets.⁶³ The estimated cost for [Ch][OAc] is 1.48 \$/kg, approximately one dollar per kg cheaper than the conventional IL. These costs are consistent with those reported by Pin et al.³³ for several protic ionic liquids (also formed by simple acid–base reaction) and conventional ones.

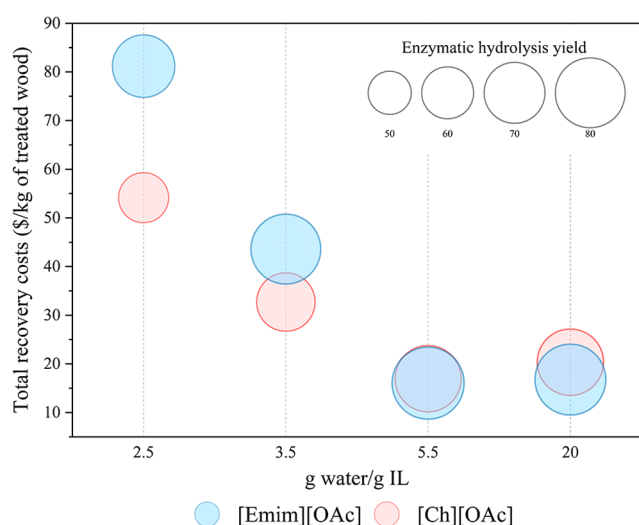


Figure 6. Total recovery costs estimation for [Emim][OAc] and [Ch][OAc] ILs for different water washing volumes.

Total recovery costs (Figure 6) exhibit an opposite trend than the results observed in Figure 5, which showed that the recovery operating costs of [Ch][OAc] were always higher than those of [Emim][OAc], indicating that the ammonium-based cation is more heavily attracted to water. Lower volumes of washing water increase the amount of fresh IL that must be fed since more IL is still bounded to the pretreated wood and not recovered. [Emim][OAc] is more expensive than [Ch][OAc], which causes higher total recovery costs at lower washing volumes; however, the economic balance performed at 5.5 and 20 g water/g IL shows that their recovery costs are the same or even the opposite than before. From Figure 3, it can be seen that the [Emim][OAc] is washed more efficiently than the [Ch][OAc]. Thus, the [Emim][OAc] is completely removed (and, consequently, recovered) at 5.5 and 20 g water/g IL, but the [Ch][OAc] is still bounded to the pretreated wood in some amount, which leads to the necessity of adding more fresh [Ch][OAc] comparing to [Emim][OAc]. The use of washing volumes that ensured the total IL recovery compensates this difference by considering the lower cost of the [Ch][OAc]. This would indicate that the economy of the process is mainly affected by the IL cost, a fact that has already been reported, and the capacity of recovering as much IL as possible after pretreatment.^{31–33} In this line, studying the IL washing step is necessary, not only to minimize water consumption but also to ensure that the IL is totally (or almost totally) recovered. In addition, ILs that are easily synthesized by acid–base reaction (the case of [Ch][OAc]) are usually considered cheaper than the conventional ones.^{1,11,33,64}

Looking at enzymatic digestibility values, washing with 3.5 g water/g IL seems to be appropriate, especially with [Emim][OAc]. However, when analyzing the economic balance, the recovery costs are heavily increased. Figure 6 brings out the importance of studying every aspect affecting the economy of the process, where the IL recovery and makeup play a crucial role in it. Reducing water washing volume is possible in terms of enzymatic digestibility values achieved after pretreatment and washing (but must be evaluated if a subsequent step involving microorganisms is to be carried out), but a reduction in water volume to the minimum possible may not be the most

efficient option in terms of a whole economic balance. A washing of 5.5 g water/g IL seems to be the most efficient option, as shown in Figures 3 and 6, since it ensures that all IL is recovered but no excess of water is used, even though lower volumes of water could be used to achieve suitable enzymatic digestibilities, reaching total recovery costs of 16 \$/kg of treated wood. The economy of the process urges to minimize the volume of water used to wash the pretreated wood, but the environmental costs associated with water usage make water consumption reduction even more important.

The obtained results in this study have made it possible to identify the most important factors to take into account for the economy of an IL-based biorefinery. However, there are still some issues that need to be more deeply studied. IL content toxicity toward microorganisms depending on the volume of water employed in the pretreated biomass washing step, as well as including the costs associated with water consumption and stirring power in the economic balance, are considered for further research in the future.

CONCLUSIONS

A methodology to carry out a technoeconomic assessment of the IL recovery step in a eucalyptus pretreatment process with ILs is proposed. The minimal total recovery costs (16 \$/kg of wood) were found washing pretreated biomass with 5.5 g water/g IL, obtaining the highest glucan digestibility (83.07%) employing [Emim][OAc]. The distillation operating costs, regarding the total costs, demonstrates the importance of IL complete recovery. The proposed approach has been found to be appropriate since pretreatment efficiency, recovery, and IL makeup costs are considered and points out the key aspects to evaluate the viability to recover the IL in a biomass pretreatment process.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.1c01361>.

Scheme of the ionic liquid recovery Aspen Plus simulation, curves of enzymatic digestibility vs time, and VLE experimental data and NRTL modeling (PDF)

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The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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