



Integral valorization of *Acacia dealbata* wood in organic medium catalyzed by an acidic ionic liquid

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HIGHLIGHTS

- *Acacia dealbata* was delignified by ionic liquid catalyzed organosolv pretreatment.
- Temperature and IL-catalyst had the most significant effect on wood fractionation.
- High cellulose recovery was achieved at 190 °C, 60% of ethanol, 1 h and 0.6 g IL/g wood.
- 67 % of lignin was recovered and characterized from the black liquor.

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ABSTRACT

In this work, a novel delignification process was proposed for the fractionation of invasive species such as *Acacia dealbata* wood. Organosolv process catalyzed with an acidic ionic liquid, 1-butyl-3-methylimidazolium hydro-sulfate was evaluated to obtain cellulose-enriched solids and liquid fractions rich in hemicelluloses derived compounds and lignin. Under selected operating conditions (190 °C, 60% ethanol, 60 min of reaction time and 0.6 g 1-butyl-3-methylimidazolium hydro-sulfate/g wood), high solubilization of lignin and hemicelluloses and cellulose recovery (87.5%, 88.7% and 88.3%, respectively), with a pulp yield of 43.1% were achieved. Moreover, 62.6 % of lignin was recovered by precipitation from the black liquor (composed mainly by 4.43 g xylose/L, 7.66 g furfural/L and 3.59 g acetic acid/L). In addition, enzymatic digestibility of delignified wood was also assayed. Overall, this work presents an alternative biorefinery scheme based in the use of environmentally friendly solvent and catalyst for selective fractionation of *A. dealbata* wood.

1. Introduction

Society is increasingly demanding in caring for the environment, which together with the energy supply crisis related to the abuse of non-renewable and finite resources have prompted the search for abundant, cheap and renewable feedstocks. In this context, biomass arises as a potential alternative to petroleum-based materials to obtain sustainable products through more efficient and environmentally friendly processes developed in line with the biorefinery philosophy (Morales et al., 2020). The future of this type of facilities lies in the evolution towards integrated biorefineries, where a wide range of products are manufactured from biomass such as biofuels, biomaterials and different intermediate platform or building block chemicals; thus increasing flexibility towards market demands and the economic profitability of biorefineries (Alfaro

et al., 2009; Dragone et al., 2020; Ferreira and Taherzadeh, 2020).

However, the selective separation of the main lignocellulosic materials (LCM) components (cellulose (C), hemicelluloses and lignin) is significantly hindered by their structural complexity. Therefore, pre-treatment stages are usually required for the disruption of recalcitrant cell wall components (Kumar et al., 2020; Meng et al., 2020). These should focus on reaching high selectivity and recovery yields of the key components using the minimum number of stages. In this field, the application of organosolv process (employing alcohols, ketones, glycols, organic acids, phenols, esters and ethers as reaction media), promotes the solubilization of lignin and a large part of the hemicelluloses. Thus providing a solid fraction with high C contents, suitable for further conversion into biofuels and/or other chemicals (Cebreiros et al., 2020). Despite being one of the three main fractions of LCM, lignin has a few

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high value-added applications (Dragone et al., 2020; Meng et al., 2020; Rashid et al., 2021). It is mainly used for power generation (Kraft lignin) or for the recovery of lignosulfonates with commercial value from the sulfite spent liquors, hence the considerable interest in developing new lignin-based products (Dragone et al., 2020; Lu et al., 2017).

Since Klason, in 1893, first extracted lignin from wood using ethanol and HCl, several alcohol-based pretreatment methods have been tested with different raw materials, including the Alcell process, an ethanol-based autocatalyzed process; the NAEM process, catalyzed by neutral salts of alkaline earth metals; or the Organocell process, involving methanol/water, sodium hydroxide and anthraquinone (Zhang et al., 2016). The use of low molecular weight alcohols, such as ethanol and methanol, in organosolv processes, offers benefits such as low price, lack of toxicity, total miscibility with water, ease of recovery (Cebreiros et al., 2020; Cheng et al., 2018). Furthermore, the organosolv lignin, easily recovered by precipitation in aqueous medium (Silveira et al., 2015), presents lower sulfur content and a higher purity than the ones obtained by acid or alkali methods (Lu et al., 2017; Meng et al., 2020; Rashid et al., 2021). The design of biorefinery alternatives focused on enhancing the recovery of lignin is necessary to overcoming the existing technical limitations for the coproduction of renewable fuels, basic aromatic and phenolic compounds or fine chemicals; which is essential to promote the development of sustainable and economically viable advanced biorefineries (Dragone et al., 2020; Lu et al., 2017).

In this line of research, in the last years, several catalysts have been tested with the aim of improving the delignification and lowering the operating temperature, for example, mineral acids (sulfuric or phosphoric acids), organic acids (such as oxalic or acetylsalicylic acids) or more recently ionic liquids (IL) (Rashid et al., 2021). They are organic salts that are mostly in a liquid state below 100 °C. IL are considered as “green solvents” because of their negligible vapor pressures. Moreover, IL present excellent chemical and thermal stability and tuneable properties (Rodríguez, 2021). Unlike traditional solvents, IL are composed of large organic cations and small inorganic anions that play different roles during effective treatments (Xie and Wan, 2019). In particular, cations interact with the lignin establishing hydrogen bonds, while anions, as hydrogen bond receptors, do so with the hydroxyl group of C, thus altering the crystalline structure of the LCM (Kumar et al., 2020; Rajendran and Taherzadeh, 2014; Rashid et al., 2021). In this field, one of the most used are the imidazolium-based IL combined with anions such as chloride, acetate, hydrogen sulphate, bromide, hexafluorophosphate or tetrafluoroborate, since in addition to solubilize a large part of the hemicelluloses and lignin they also disrupt the crystalline cellulose, making it more accessible to further treatments (Usmani et al., 2020). In this context, effective delignification processes of lignocellulosic biomass using different ILs as alternative solvents were previously studied by several authors (da Costa Lopes et al., 2018; daCostaLopes and Łukasik, 2018; Sun et al., 2009).

Although acid-catalyzed organosolv pretreatments have been widely studied, their large-scale application is limited by the high cost associated with the need of non-corrosive materials. Another drawback is the severe operating conditions required (high temperatures and pressures), as well as the need to remove or neutralize the acid after the treatment (Chotirotukon et al., 2021; Ibrahim et al., 2020). In contrast, the use of acidic ionic liquids (AIL) as catalysts improves the fractionation efficiency, requires milder operating conditions and avoids equipment corrosion. AILs also causes less environmental pollution since their low vapour pressures limit evaporation losses and facilitate their recovery and reuse (Cheng et al., 2018). In this context, to our knowledge the application of AIL catalyst in organosolv pretreatments is rather limited, being few studies available on literature (Cheng et al., 2018, 2019; Zhao et al., 2021).

A. dealbata is an invasive species native to southeastern Australia, which is currently widely naturalized in southwest Europe (Pereira and Ferreira, 2021). Its use as a raw material, in addition to helping to control its distribution, would be motivated by environmental reasons,

since the invasion of this species causes structural modifications in native ecosystems and threatens the biodiversity of the area (Dominguez et al., 2014; Nunes et al., 2020; Yáñez et al., 2014). From a chemical point of view, it should be noted that it is an underexploited hard wood with a chemical composition very similar to that of *Eucalyptus globulus* or *Eucalyptus nitens* (Penín et al., 2019; Romaní et al., 2011). They present high contents of polysaccharides and considerable amounts of lignin, suitable for the production of compounds with high added-value and different industrial applications (Dominguez et al., 2014; Ferreira et al., 2011; Lorenzo et al., 2010; Yáñez et al., 2014). To date, there are few works in literature that have evaluated the integral valorization of *A. dealbata*, such as the acacia fractionation by sequential biological treatment and organosolv (Muñoz et al., 2007) and glycerol organosolv process (Dominguez et al., 2014).

For the first time to the best of our knowledge, organosolv process catalyzed by AIL was used for processing of an invasive species, such as *Acacia dealbata* wood. Therefore, this work provides an experimental assessment on the ethanol organosolv delignification catalyzed with 1-butyl-3-methylimidazolium hydrosulfate ([Bmim][HSO₄]). With this purpose, the effects of the main variables (temperature, time, ethanol content of the reaction medium and catalyst load) on wood delignification and cellulose recovery were studied. Furthermore, the organosolv lignin was recovered from selected black liquor and the enzymatic digestibility of several delignified solids was also assessed.

2. Materials and methods

2.1. Raw material and chemicals

A. dealbata wood samples, collected locally, were manually debarked and chipped. After air dried, they were milled (using a Retsch SM1 74,075 instrument, Germany) and sieved (Retsch AS200 Basic, Germany), in order to select the particle size fraction of 1–0.25 mm. The samples were homogenized by hand and stored in a dry place for further uses.

The chemicals and solvents employed in this work were as follows: [Bmim][HSO₄] (≥94.5% purity), xylose (≥99% purity), acetic acid (99.7% purity), formic acid (≥95% purity), levulinic acid (≥97% purity), hydroxymethylfurfural (99% purity), and furfural (99% purity) from Sigma–Aldrich; sulfuric acid (95–98% purity), from Fisher Scientific; ethanol (96% purity) from Merck.

2.2. Processing of *A. dealbata* wood: Organosolv pretreatment

Isothermal delignification pretreatments were performed in a 0.6 L stainless steel Parr reactor (model 4563, Parr Instruments Company, Illinois, USA). The reactor is equipped with the following components: four blade turbine impellers, an external heating jacket and an internal cooling loop and PID temperature controller (model 4842, Parr Instruments Company, Moline, Illinois, USA). To evaluate the effects of the temperature, reaction time, ethanol and [Bmim][HSO₄] contents on the *A. dealbata* wood fractionation, a set of 17 experiments were carried out. In all tests, the stirring speed was adjusted at 150 rpm and the liquid to solid ratio (LSR) to 6 g/g of LCM on a dry basis. Table 1 summarises the experimental conditions of each assay. The effect of the ethanol content has been evaluated in the range 40–80%, the catalyst content between 0.2 and 0.8 g [Bmim][HSO₄]/g LCM, the temperature in the range 170–210 °C and the reaction time from 30 to 105 min. In order to clarify the experimental procedure performed, Fig. 1 illustrates a flowchart summarizing the main steps followed in this study. Briefly, after treatment, the delignified solids and the liquid phases (black liquors) were separated by vacuum filtration. The solid fractions were firstly washed with 100 mL of ethanol at 60 °C, then with 200 mL of ethanol at room temperature (to avoid lignin reprecipitation) and finally with abundant distilled water and dried at room temperature. On the other hand, three volumes of distilled water were poured into the black liquor and

Table 1
Operational conditions considered in *A. dealbata* organosolv pretreatments.

| Experiment | T (°C) | t (min) | Ethanol (% weight) | [Bmim][HSO ₄] (g/g LCM) |
|------------|--------|---------|--------------------|-------------------------------------|
| 1 | 170 | 60 | 60 | None |
| 2 | 170 | 60 | 60 | 0.2 |
| 3 | 170 | 60 | 60 | 0.4 |
| 4 | 170 | 60 | 60 | 0.6 |
| 5 | 190 | 60 | 60 | None |
| 6 | 190 | 60 | 60 | 0.2 |
| 7 | 190 | 60 | 60 | 0.4 |
| 8 | 190 | 60 | 60 | 0.6 |
| 9 | 190 | 60 | 60 | 0.8 |
| 10 | 210 | 60 | 60 | 0.6 |
| 11 | 190 | 30 | 60 | 0.6 |
| 12 | 190 | 45 | 60 | 0.6 |
| 13 | 190 | 75 | 60 | 0.6 |
| 14 | 190 | 90 | 60 | 0.6 |
| 15 | 190 | 60 | 40 | 0.6 |
| 16 | 190 | 60 | 50 | 0.6 |
| 17 | 190 | 60 | 80 | 0.6 |

refrigerated for 24 h to precipitate the dissolved lignin. It was collected by filtration, washed, dried at 50 °C and weighted. The lignin of the washing liquors was also recovered by the same procedure. The resulting liquors enriched in hemicellulose derived compounds were also collected and further characterized by high performance liquid chromatography (HPLC), as explained below.

2.3. Enzymatic hydrolysis

Enzymatic assays were performed with commercial concentrates ('Celluclast 1.5L' cellulases from *Trichoderma reesei* and 'Novozym 188' β -glucosidase from *Aspergillus niger*), provided by Novozymes (Madrid, Spain). The methodology has been previously described in detail by

Domínguez et al., (2014). The experimental conditions selected for the enzymatic hydrolysis of spent organosolv solids were the following: temperature 48.5 °C, pH 4.85 (0.05 N citric acid–citrate buffer), LSR = 12 g liquid/g of pretreated solid, cellulase to substrate ratio of 15 FPU/g of pretreated solid and 5 IU/FPU of cellobiase to C ratio. Samples were withdrawn for the media at several hydrolysis times, centrifuged, filtered and analysed by HPLC as collected below.

2.4. Analytical methods

The chemical compositions of the raw material and pretreated solid and liquid fractions were determined as follow. Milled samples (particle sizes < 0.5 mm, using an IKA M–20 grinder, Germany) were examined for moisture (TAPPI T-264-om-88 method), extractives (ISO 638:1978 method) and ash (T-244- om-93 method). Moreover, the chemical composition of *A. dealbata* wood samples and pretreated solid fractions were determined following the TAPPI T13 m-54 assay (Domínguez et al., 2014). The Klason lignin (KL) content was determined by gravimetric determination of the solid from the TAPPI assay. C, xylan (Xn), arabinan and acetyl groups (Ac) were calculated from glucose, xylose, arabinose and acetic acid contained in quantitative acid hydrolysis liquors.

The concentration of sugars (glucose, xylose, arabinose), organic acids (formic, acetic, levulinic acids) and other compounds such as furfural and hydroxymethylfurfural were assayed by HPLC. Analyses were carried out with an Agilent 1200 Series device (Agilent Technologies, Santa Clara, CA, USA), equipped with a refractive index detector operating at 35 °C and an Aminex HPX-87H (BioRad, USA) column eluted with 0.003 M H₂SO₄. Other analysis conditions were: flow rate of 0.6 mL/min, column oven temperature 50 °C and 5 μ L injection volume. Analyses were performed in triplicate.

The thermal behaviours of lignin samples were evaluated by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetric (DSC) analysis, using a simultaneous thermogravimetric analyzer

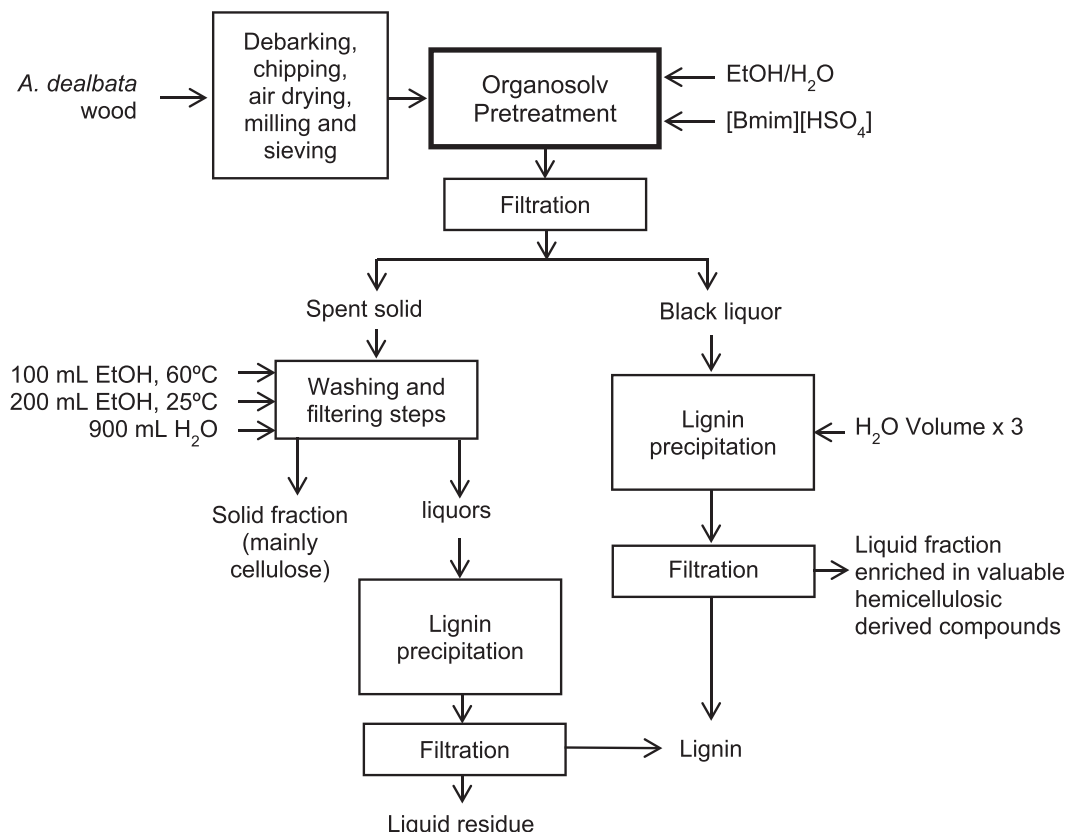


Fig. 1. Process diagram proposed for the *A. dealbata* wood biorefinery.

(SETARAM SETSYS Evolution 1750). The measurements were performed at a heater rate of 10 °C/min under N₂ atmosphere in the range of 20–600 °C, followed by a heater rate of 20 °C/min under air atmosphere in the range 600–900 °C (Romaní et al., 2016).

3. Results and discussion

3.1. Composition of the raw material

The chemical composition of the *A. dealbata* wood (expressed in g/100 g oven-dry wood ± standard deviation) was the following: C, 42.5 ± 0.72; Xn, 20.1 ± 1.03; Ac, 3.07 ± 0.45; KL, 23.9 ± 0.42; extracts, 4.50 ± 0.63; and ash, 0.53 ± 0.11. It is worth highlighting the high content of

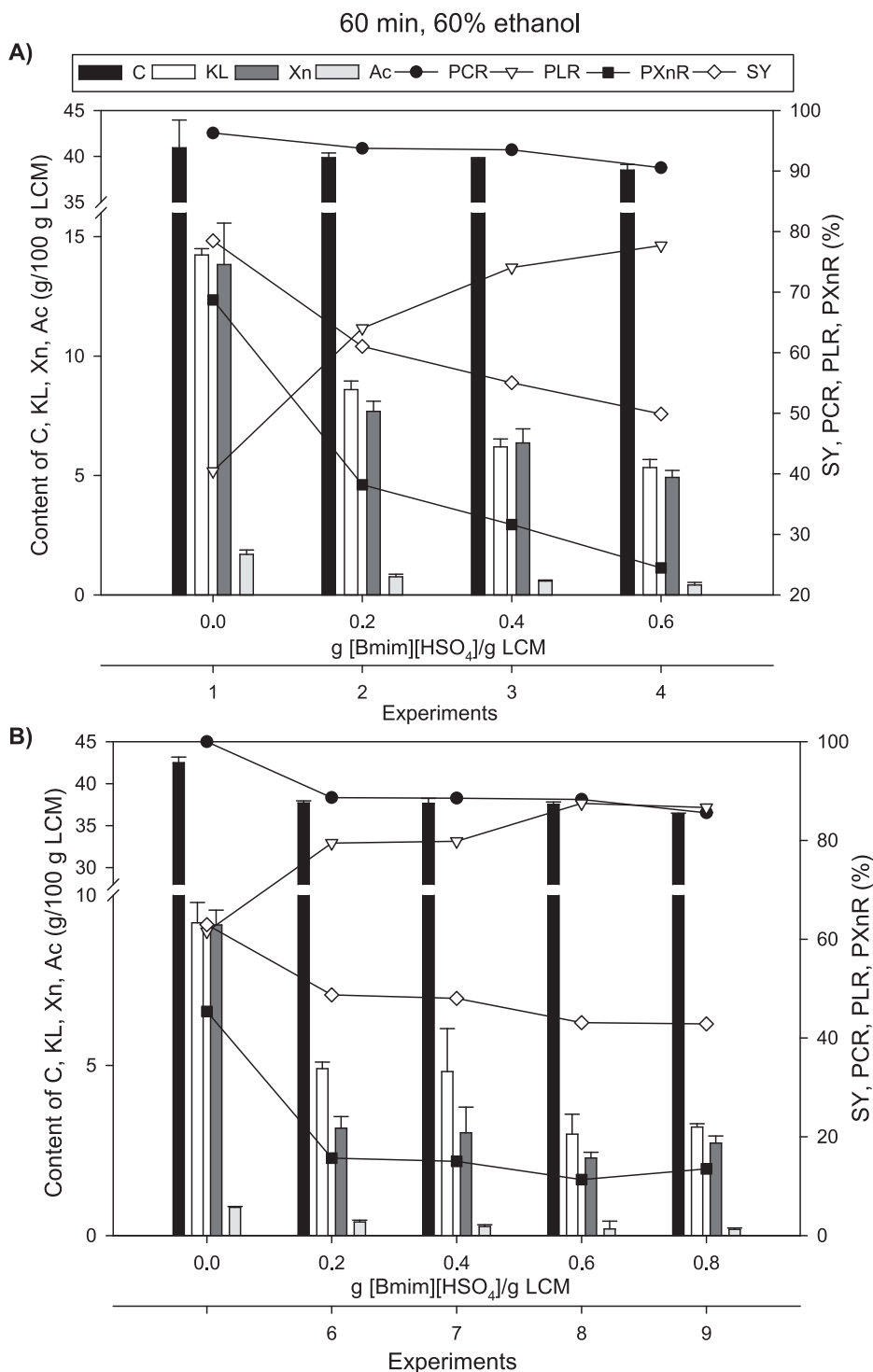


Fig. 2. Effect of the catalyst load on the solid yield (SY) and on the chemical composition of the *A. dealbata* wood samples treated at (A) 170 °C and at (B) 190 °C. Error bars represent the standard deviation. Nomenclature: C, cellulose; KL, Klason lignin; Xn, xylan; Ac, acetyl groups; PCR, percentage of cellulose recovery; PXnR, percentage of xylan recovery; PLR, percentage of lignin removal.

polysaccharides (close to 60%), followed by an interesting lignin percentage and other minority components such as Ac or extracts. The values obtained are comparable with those available in *A. dealbata* wood literature (Domínguez et al., 2014; Muñoz et al., 2007; Yáñez et al., 2014).

3.2. Organosolv pretreatments catalyzed by [Bmim][HSO₄]

In order to evaluate the effects of the most important variables (temperature, catalyst load, reaction time and ethanol concentration in the reaction medium) on the solid yield (SY) and on the chemical composition of the spent solid fractions and black liquors, a series of experiments was performed (see operating conditions in Table 1). The main results will be discussed in the next sections.

3.2.1. Effect of temperature and catalyst load

Previous literature concerning biomass organosolv delignification (Domínguez et al., 2014; Pan et al., 2006) reported temperature and catalyst load as the most influential variables on this kind of pretreatments. With the purpose of addressing the influence of these parameters on *A. dealbata* wood fractionation, a total number of 10 experiments have been conducted (denoted in the text as experiments 1–10) at temperatures between 170 and 210 °C; both without the addition of catalyst and with catalyst loads in the range 0.2–0.8 g [Bmim][HSO₄]/g LCM. Other operational variables were selected according to studies performed with the same raw material (Muñoz et al., 2007) or even other LCM (Cybulska et al., 2017; Pan et al., 2006), and fixed as follow: LSR at 6 g/g of LCM, the ethanol load at 60% in weight and the reaction time in 60 min.

In a first set of 8 experiments, temperatures of 170 °C (experiments 1–4) and 190 °C (experiments 5–8) were only considered. Fig. 2A shows the SY, C, KL, Xn and Ac contents as well as the percentage of cellulose recovery (PCR), the percentage of lignin removed (PLR), and the percentage of xylan recovery (PXnR) in the pretreatments carried out at 170 °C. On the other hand, the results obtained at 190 °C are presented in Fig. 2B.

As can be observed in Fig. 2, the SY decreases with increasing severity of the treatment, observing a similar influence for temperature and for catalyst. Therefore, the lowest values for this parameter were observed in the experiments carried out at the highest temperatures and with the highest loads of catalyst. For example, in the tests carried out at 170 °C, a SY of 78.5% was obtained in the uncatalyzed pretreatment and further increases in catalyst loading resulted in a decrease up to 49.9% in the experiment performed with 0.6 g [Bmim][HSO₄]/g LCM (experiments 1 and 4, respectively, in Fig. 2A). The same trend was observed operating at 190 °C, where the SY varied in the range 63–43%. Comparable yields were obtained when the same raw material was processed in ethanol and glycerol media and in sulfuric acid-catalyzed organosolv (Domínguez et al., 2014; Ferreira et al., 2011; Muñoz et al., 2007, respectively).

Regarding the influence of temperature on solid composition, from the information provided in Fig. 2A and B, it is concluded that, as might be expected a priori, higher PCR and PXnR were obtained in the experiments carried out at 170 °C; whereas delignification was greatly enhanced by increasing temperature, especially at low catalyst loads. Similar behaviours were found by Sun and Chen (2007) and Novo et al. (2011) during organosolv treatments of wheat straw and sugarcane bagasse, respectively.

Moreover, compared to uncatalyzed tests, the lowest catalyst content studied (0.2 g [Bmim][HSO₄]/g LCM), had a great influence on the delignification of the raw material, the PLR increasing by 24% in the treatment at 170 °C and by 18% at 190 °C (experiments 2 and 6, respectively). Higher AIL loads led to increasing PLR, this increase being more significant at 170 °C. Regarding the PCR, the addition of 0.2 g [Bmim][HSO₄]/g LCM resulted in a decrease of 11% in this parameter at 190 °C (see experiments 5 and 6); whereas additional catalyst did not

suppose important C degradation, keeping the PCR at values higher than 85% even under the severest conditions. Finally, in general terms, the solubilization of hemicelluloses was favored both by increasing in the catalyst load and by the temperature, with this variable having a greater influence.

The delignification effectiveness of [Bmim][HSO₄] in alcohol-aqueous solutions has been also reported with poplar wood and coconut fiber (Cheng et al., 2018). Other previous studies have shown the crucial role of AIL in the breakdown of biopolymer bonds and in accelerating the cleavage of lignin-carbohydrate complexes by degrading part of the carbohydrates (Guo et al., 2012; Zhang et al., 2010).

However, given that the maximum delignification (PLR of 87.5% in experiment 8) was obtained at the upper extreme temperature and catalyst load tested (190 °C and 0.6 g [Bmim][HSO₄]/g LCM), it was decided to extend the study area. For this, a set of two additional experiments was carried out: one raising the catalyst load to 0.8 g [Bmim][HSO₄]/g LCM, keeping the temperature at 190 °C (experiment 9, Fig. 2 B), and the other increasing the temperature to 210 °C, with the same load of AIL, 0.6 g [Bmim][HSO₄]/g LCM (experiment 10, data not shown).

As can be seen in Fig. 2B, when the concentration of [Bmim][HSO₄] increased to 0.8 g/g LCM, the slight decrease in the SY and PLR (with values of 42.9 and 86.6%, respectively), was accompanied by an increase in C degradation, reflected in a slight lower PCR, if compared with experiment 8 (PCR of 88.3% and 85.6% in experiments 8 and 9, respectively).

Regarding the temperature, although increasing temperature from 170 to 190 °C enhanced the PLR a 10%, further increase up to 210 °C did not bring any improvement in the delignification. Moreover, it had a negative impact on the SY and on degradation of polysaccharides, which led to decreasing in PCR and PXnR close to 10%. This pattern was earlier described in organosolv treatments, where increasing temperature favored the solubilization of C and hemicelluloses (Cheng et al., 2019; Cybulska et al., 2017; Nitsos et al., 2018). Slight increases in KL contents at high severities have been also previously described by Pan et al. (2006), during acid-catalyzed organosolv delignification of poplar wood, attributing it to lignin condensation reactions in pulping process. This explanation is consistent with the increase in the lignin content of the solid fraction due to the increasing of hemicellulose solubilization and the sugar degradation processes to form a compound called pseudo-lignin (Melati et al., 2019). However, from the results obtained, it can be concluded that an increase in the severity did not result in the expected improvements and to continue the study the experimental conditions leading to greater delignification were selected (catalyst load of 0.6 g [Bmim][HSO₄]/g LCM and 190 °C).

Concerning the liquid fractions, they are mainly made of xylose, acetic acid and furfural as well as minor quantities of glucose and hydroxymethylfurfural. No xylooligosaccharides were detected in the reaction media in all the tested conditions. This fact would be associated with the acid catalysis of hemicellulosic fraction to monomers and further conversion into dehydration products. Maximum xylose, acetic acid and furfural contents (4.92, 3.59, 7.81 g/L respectively), were obtained in experiments 4, 8 and 9. In general lines, the highest catalyst load evaluated led to the highest hemicelluloses solubilisation and furfural obtaining.

3.2.2. Effect of the reaction time

Other parameter that could be relevant in the AIL-catalyzed organosolv is the reaction time. In order to assess its effect on the *A. dealbata* wood fractionation the following times were tested: 30, 45, 75, 90 min (denoted as experiments 11–14), while maintaining other parameters in the experimental conditions selected previously (experiment 8): 190 °C, 0.6 g [Bmim][HSO₄]/g LCM, 60% de ethanol. This would allow evaluating the possibility of shorter reaction times or improving the results achieved at 60 min, with its prolongation. Fig. 3A shows the SY, C, KL, Xn and Ac contents as well as the PCR, the PLR and the PXnR in

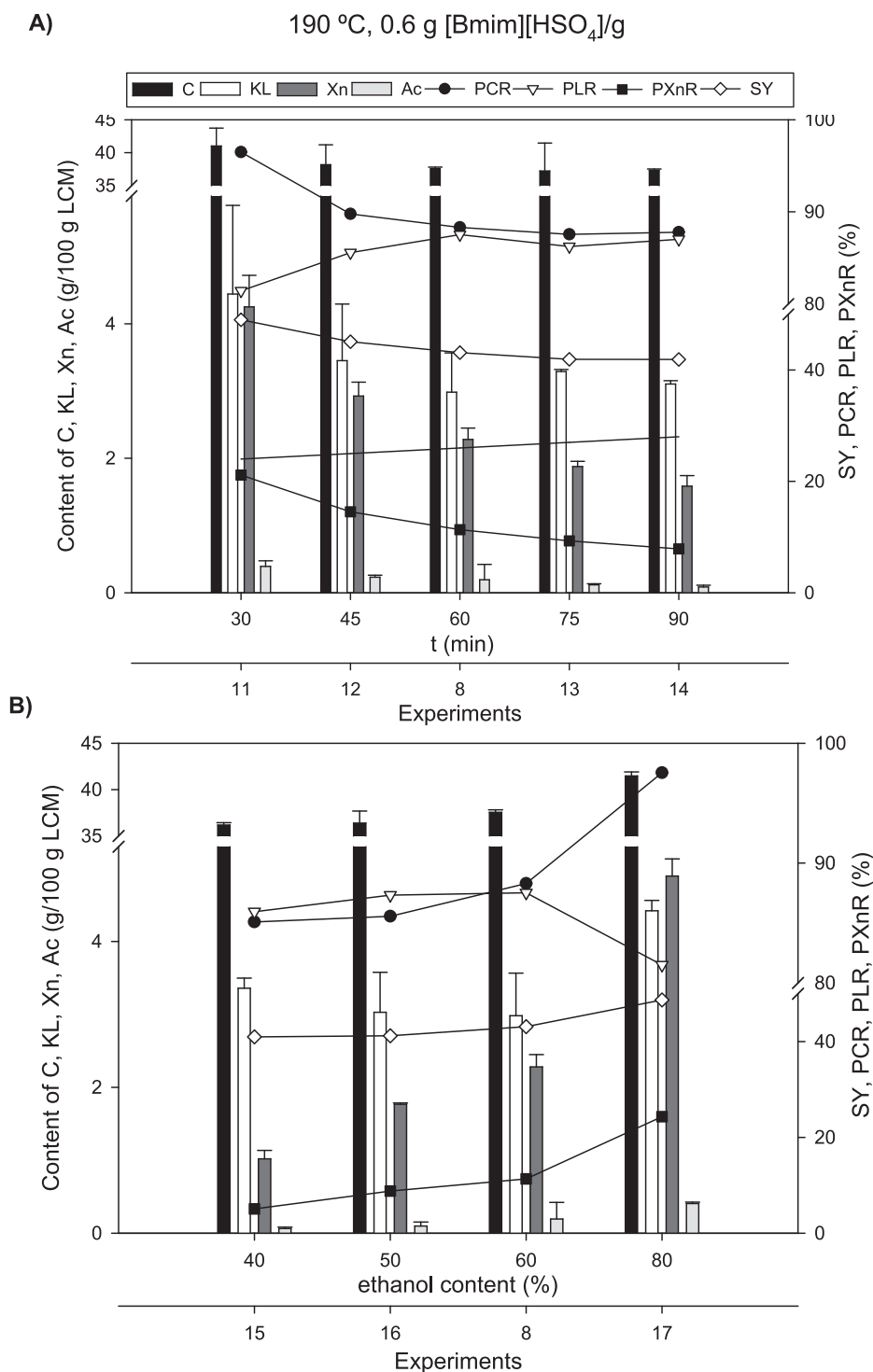


Fig. 3. Effect of (A) temperature and (B) reaction time on the solid yield (SY) and on the chemical composition of de *A. dealbata* wood samples treated. Error bars represent the standard deviation. Nomenclature: C, cellulose; KL, Klason lignin; Xn, xylan; Ac, acetyl groups; PCR, percentage of cellulose recovery; PXnR percentage of xylan recovery; PLR, percentage of lignin removal.

experiments 11, 12, 8, 13 and 14.

Comparing the results of experiments 11–14 with those of 8 (of 60 min duration), it can be concluded that noticeably lower PLS were obtained at shorter reaction times and further prolongation of the pretreatment to 75 and 90 min did not result in the expected improvements in lignin solubilization, keeping PLS at values close to 87%. Moreover, no significant differences were observed in the PCR. However, the time had a great influence on the solubilization of hemicelluloses, reaching a

decrease in PXnR of 13.2% and low Ac contents of so only 0.09 g/100 g MLC after 90 min of reaction (see experiments 11 and 14 in Fig. 3A). Accordingly, an increase in the furfural concentration in the liquid phase was observed, reaching values of 9.06 g/L in experiment 14, associated to the presence of sugars degradation reactions at higher severities (data not shown).

Sun and Chen (2007) also observed that prolonged pretreatment times in an organic medium resulted in a stabilization of the lignin

content, attributed to its recondensation. The authors suggest that this phenomenon is due to the fact that the dissolved organosolv lignin tends to react with itself or with other polymers, such as hemicelluloses, to form macromolecules, which precipitate on the insoluble fiber. This repolymerization reaction is affected by high pretreatment temperatures and long run times. In this study, during the organosolv pretreatment of wheat straw reaction times longer than 4 h resulted in the degradation of C, as well as in a stabilization of the PLR around 70%. Similar results were previously reported by Pan et al. (2006) in a work dealing with the acid-catalyzed organosolv of poplar wood, where despite extending the reaction time up to 94 min, the delignification reached a maximum at 60 min (74%) and by Cheng et al. (2019) where an extension of the AIL catalyzed organosolv duration after 1 h did not result in improved lignin recoveries.

Regarding the study of the influence of time, it can be concluded that this parameter had a lower effect than the temperature and the catalyst load on the delignification of *A. dealbata* wood. Therefore, the results obtained would not justify the use of longer times and to continue the study a treatment duration of 60 min was selected.

3.2.3. Effect of ethanol content

Finally, in order to assess the influence of the ethanol content, the effect of lowering it from 60 to 50 and 40% and increasing it to 80% has been evaluated (experiments 15, 16 and 17, respectively), keeping other variables in conditions of maximum delignification: 190 °C, 0.6 g [Bmim][HSO₄]/g LCM and 60 min. The more relevant results are shown in Fig. 3B.

Under the tested conditions, a higher concentration of ethanol leads to an increase in SY and in the recovery of C and hemicelluloses, however, the PLR decreases by 6% (see results of experiment 8 and 17 in Fig. 3B). Pan et al. (2006) in the study cited above observed the same behavior, stating that the lower chemical activity of water at high ethanol concentrations probably affects the hydrolysis of carbohydrates.

When decreasing the ethanol concentration from 60 to 40%, the SY dropped slightly (from 43.1 to 41.0%), as well as the PCR (from 88.3 to 85.1%), whereas the PXnR was the parameter most affected, with a decrease of 6% (experiments 8 and 15 in Fig. 3B). Regarding the PLR, this parameter also decreased slightly, but to a lesser extent than when the ethanol content in the reaction medium was increased.

The observed drop in delignification with increasing ethanol concentration from 60 to 80% could seem contradictory, since lignin is soluble in polar organic solvents such as ethanol (Wildschut et al., 2013; Zhao et al., 2009). However, hemicelluloses and lignin are structurally linked and, to dissolve lignin these bonds must first be broken. In addition, the cleavage of the ether bonds within the lignin polymer would improve its solubility since it would lead to a decrease in its molecular weight. Therefore, in general terms, the selected ethanol concentration in the delignification processes would be a compromise between the optimum for the hydrolysis of Xn and the solubility of lignin and the pH of the organosolv liquor necessary for the breakage of the ether bonds (Wildschut et al., 2013). Moreover, as McDonough (1992) and Cybulska et al. (2017) describe during acid catalysis, the low pH of the reaction medium facilitates delignification, and this could be modulated either with a variation of the water content or by adding a greater quantity of acid catalyst.

Concerning the composition of the liquors, it should be noted that experiment 15 (carried out with 40% ethanol), allowed to reach the maximum concentrations of furfural and acetic acid (10.5 and 4.85 g/L, respectively). Moreover, 2.33 g/L of HMF were also detected, a value very close to the highest one obtained at the maximum temperature evaluated (2.85 g/L, in experiment 10 at 210 °C).

As can be seen in Fig. 3B, no great differences were observed regarding experiments 8 and 16, the SY increases by 2% and the PCR and PXnR by 3% when the treatment was carried out at 60% of ethanol vs. 50%. Moreover, in terms of delignification the two pretreatments showed a similar potential. So, it can be assumed that the optimal

ethanol concentration would be between 50 and 60%, with the results obtained at 60% being slightly better.

This allow concluding that after the evaluation of the ethanol concentration and the isothermal reaction time, the most influential variables of the process are the temperature and the catalyst load, and that, meeting the commitment to solubilize the greatest amount of lignin and preserve the C, at an acceptable process yield, the experiment 8 (at 190 °C, 60 min, 60% ethanol and 0.6 g [Bmim][HSO₄]/g of LCM) was selected.

3.2.4. Discussion of the results obtained in the selected operational conditions

As can be expected the main compound found in the organosolv solid from experiment 8 was C, followed by minor amounts of lignin and Xn (37.5, 2.98 and 2.28 g/100 g LCM, dry basis, respectively). Therefore, the selected pretreatment, in addition to result in the highest PLR (87.5%), it also allowed achieving important C recoveries (PCR = 88.3%); thus demonstrating, the selectivity of AIL-catalyzed organosolv treatments in the *A. dealbata* wood fractionation. On the other hand, in the liquid fraction it should be noted the presence of furfural, xylose and acetic acid (7.66, 4.43, 3.59 g/L, respectively) as well as some glucose and hydroxymethylfurfural.

Uncatalyzed organosolv pretreatment of eucalyptus wood (a reference hardwood with a chemical composition very similar to that of acacia), at higher severities resulted in higher PCR but in much lower PLR than the obtained in this work, 63% vs. 88% (Romaní et al., 2011). Previously, Pan et al. (2006) treated poplar wood in sulfuric acid-catalyzed ethanosolv. In this study, similar operating conditions to those of maximum delignification (experiment 8), resulting in PCR values of the same order, although without reaching such high PLR. However, in the same reaction medium and with willow wood, Huijgen et al. (2011) reported higher PCR but a lower percentage of delignification, despite the long duration of the treatment (3 h). Cheng and co-workers in the few delignification studies employing [Bmim][HSO₄] as catalyst in several organosolv media with coir, reached the highest PLR and PCR (88 and 87%) with 80% 1,4-butanediol at 200 °C, 60 min, 1 g [Bmim][HSO₄] (Cheng et al., 2019, 2018; Ouyang et al., 2018). Favourable results were also reported with this catalyst during the treatment of *Populus ussuriensis* samples (Zhao et al., 2021).

Finally, with *A. dealbata* wood, Domínguez et al. (2014) in a pretreatment at high glycerol load and higher temperature (80% glycerol, 230 °C, 1 h), obtained a lower PLR and a slightly higher PCR (80 and 93%, respectively). However, in a previous study, the sequence of a biological treatment followed by an organosolv processing allowed to achieve high PLR values using both *A. dealbata* wood and *Pinus radiata* wood, 98 and 94%, respectively (Muñoz et al., 2007). The main disadvantage of this process is the need for two sequential stages and the long duration of the biological treatment (30 days), so the economic profitability should be assessed. Therefore, the favorable degrees of delignification reached in this study, strengthens the value of the results obtained with the proposed process and opens a door to the use of AIL as catalysts in organosolv processes.

3.3. Lignin recovery and characterization

Under selected conditions (experiment 8), lignin was recovered from black liquor as described in section 2.2 and illustrated in Fig. 1. This method of precipitation allowed the recovery of 62.6 g of lignin per 100 g of lignin in raw material in a separated stream, showing the high selectivity of organosolv treatment for delignification of *A. dealbata* wood. In order to evaluate the chemical composition of extracted lignin from pretreatment, thermochemical and FTIR analyses were carried out and compared to standard lignin, as described and discussed below.

FTIR spectra of standard lignin and organosolv lignin were evaluated in the range of 4000 to 400 cm⁻¹ (data not shown), showing a typical pattern of lignin from organosolv process. In the range of 3600 and

3200 cm^{-1} hydroxyl groups and phenol compounds were reported. Aromatic ring was detected at 1500 cm^{-1} . Moreover, carboxyl and carbonyl groups were found in the band of 1700 cm^{-1} . Typical peaks for syringyl (1329 cm^{-1}) and guaicyl (1265–1130 cm^{-1} bands) units were also observed, showing some differences between standard and organosolv lignins. Syringyl units are typically more present in hardwood species than guaicyl units. Based on FTIR analysis, recovered lignin in this work presented similar chemical composition to commercial lignin. The peaks detected around 1125 and 920 cm^{-1} bands were attributed to C–H in-plane deformation of syringyl and guaicyl units (Morales et al., 2021). Hemicellulosic and cellulosic impurities can be found at 1030 cm^{-1} and 829 cm^{-1} bands, respectively.

On the other hand, thermochemical properties of both lignins were also analyzed, including the TGA and DTG (derivative thermogravimetric) curves (see Fig. 4A). The first weight loss observed is typically due to evaporation of moisture taking place from 30 to 125 °C. These

weight losses were about 1.09% for organosolv lignin and 1.6% for standard lignin. Until temperature of 225 °C, both lignins were thermally stable, with slight weight losses (2.1 and 5.6% for organosolv lignin and standard lignin, respectively). The highest degradation happened in the second stage (from 300 to 450 °C) with a weight loss of volatile matter about 50.8% for organosolv lignin at 365 °C and 51.3% for standard lignin at 386 °C. As seen in the thermochemical behaviors of both lignins, the third weight loss (41.5 and 46.1% of weight were lost for organosolv and standard lignin, respectively) was observed from 600 to 750 °C, which is related to the oxidation and breakdown of carbonized residue in low molecular components (Morales et al., 2020). In addition, two main thermal events were reported in the DSC curves (Fig. 4B). For organosolv lignin the endothermic event was defined at 74.8 °C with an enthalpy change of 47.6 J/g, whereas for standard lignin, this event occurred at 81 °C with an enthalpy of 52.7 J/g. The exothermic events took place at 411 °C (enthalpy change of 194.6 J/g)

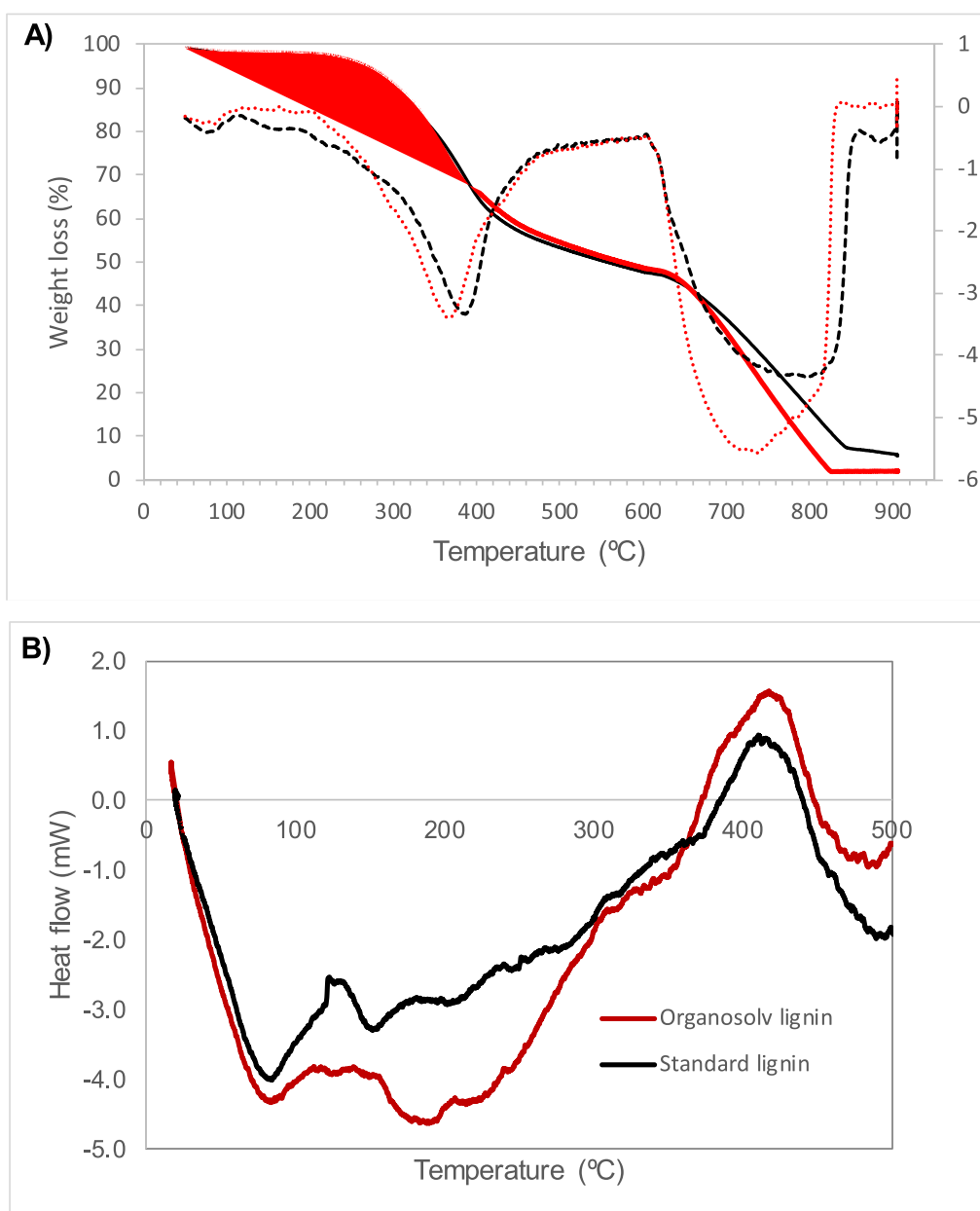


Fig. 4. (A) Curves of TGA (solid lines) and DTG (dotted lines) of standard lignin (black lines) and recovered lignin from catalysed-organosolv treatment (red lines). (B) Differential scanning calorimetry (DSC) curves obtained from organosolv lignin and standard lignin. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

for organosolv lignin and at 410 °C (enthalpy of 298.8 J/g). The first transition corresponds to evaporation of humidity and the second transition is related to generation of phenolic compounds produced by the breaking of the bonds between lignin samples and monomeric units.

3.4. Enzymatic hydrolysis assays and surface morphologic analysis

In order to evaluate further potential applications of organosolv cellulosic fractions, their enzymatic digestibility was analysed in the conditions previously summarised. With this purpose, solid samples of pretreatments 5 (without catalyst), 8, 9, 10 and 14 were selected (data not shown). The presence of the catalyst in the organosolv pretreatment led to a considerable improvement in enzymatic hydrolysis yield. For example, the enzymatic hydrolysis of the solid fraction obtained under the optimal delignification conditions (experiment 8) resulted in glucose concentrations and C conversion into glucose close to 48 g/L and 63% at 96 h, respectively. These values were 2.1 and 1.7-fold higher than the obtained in the experiment without catalyst. The improvement of enzymatic hydrolysis is related to structural changes produced by the chemical pretreatment. These changes were usually observed by SEM images, comparing treated and untreated biomass (Zhang and Wu, 2015). Typically, untreated wood shows an ordered, rigid and non-uniform structure, while morphology of spent solid after delignification process shows disrupted structure with defragmented fibres (Romaní et al., 2016). These structural changes have been related to lignin and hemicellulose removal and to increase of surface area after ethanol-organosolv treatment, improving the further enzymatic saccharification of cellulose.

4. Conclusions

In this work, the evaluated organosolv process, catalyzed by an avant-garde solvent as [Bmim][HSO₄], allowed the selective fractionation of *A. dealbata* wood. Overall, 88.2% of cellulose remained in the pretreated solid phase, suitable for the successful production of glucose by enzymatic saccharification. On the other hand, 14.9 kg of lignin/100 kg of r.m. was recovered and separated from black liquor. Moreover, solubilized xylan was recovered as value-added products such as xylose and furfural, corresponding to 14.5 and 25.03 kg per 100 kg of xylan in r.m., respectively. This study contributes to the development of biorefineries based on invasive species.

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CRediT authorship contribution statement

A. Portela-Grandío: Conceptualization, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft. **S. Peleteiro:** Formal analysis, Investigation, Methodology, Validation, Writing – original draft. **R. Yáñez:** Conceptualization, Funding acquisition, Supervision, Validation, Writing – review & editing. **A. Romaní:** Supervision, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biortech.2021.126013>.

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