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Characterization of cellulose regenerated from solutions of pine and eucalyptus woods in 1-allyl-3-methilimidazolium chloride

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ABSTRACT

Cellulose is currently separated from lignocellulosic materials using non-environmentally friendly processes. The development of new methods for treating biomass and separating cellulose remains a challenge and would be very useful in the context of the biorefinery philosophy. In this work, cellulose has been regenerated from solutions of *Pinus radiata* and *Eucalyptus globulus* woods in 1-allyl-3-methylimidazolium chloride. Wood dissolution was performed in a microwave oven at 120 °C for 20 min. Cellulose was characterized and compared to the reference material, microcrystalline cellulose (MCC). Regenerated celluloses showed lower crystallinity and thermal stability than MCC, although the ash contents at 400 °C were higher than in MCC. The regenerated celluloses were obtained without lignin and almost free from hemicellulose. Furthermore, cellulose was not significantly degraded in the dissolution process of both woods. The insoluble solids showed higher content of lignin and hemicellulose than the raw materials.

1. Introduction

In the last few years, a new philosophy has been developed due to the growing restrictions in the environmental laws, the biorefinery. This new concept is based on the sustainable processing of biomass into value-added products and energy. The application of this concept is assessed, among other aspects, in the availability of feedstock and the development of cost-effective methods to separate and transform these materials into chemicals and fuels. In this regard, the employment of wood and lignocellulosic materials in a biorefinery appears to be an attractive option (Moshkelani, Marinova, Perrier, & Paris, 2013).

Wood is one of the most abundant biorenewable resources in the world (Fort et al., 2007). The main components of wood are cellulose, hemicellulose, lignin and extractives. Cellulose is a polymer that consists of glucose units linked by glucosidic linkages (Ha, Mai, An, & Koo, 2011). Cellulose can be employed in applications such as in paper, polymer, textile, pharmaceutical, and food industries (Liu, Sun, Zhang, & Li, 2010; Mansouri et al., 2012). In addition, cellulose can be hydrolyzed to obtain glucose, which will be transformed in a variety of chemicals including ethanol, citric acid, glycerol, penicillin and sorbitol (Tan & MacFarlane, 2009). The structure of cellulose is highly crystalline, which is due to the presence of strong inter- and intra-molecular hydrogen bonds between the cellulose chains (Ha et al., 2011). The cellulose structure is very resistant and, consequently, it is very difficult to dissolve in common solvents. In fact, cellulose is only soluble in a few solvent systems such as DMAc/LiCl, or NMNO. However, these solvents are highly toxic, unstable and in many cases alter cellulose (Liu et al., 2010).

Lignin is the glue of the wood structure, and hampers the dissolution of the lignocellulosic material (Han et al., 2009). It is an irregular polymer with three main building blocks, which are coniferyl, sinapyl, and p-coumaryl alcohols. These blocks are present in the lignin structure in different amounts depending on the wood species (Tan & MacFarlane, 2009). Lignin can be used in dispersants, foams, surfactants or phenolic and thermosetting resins (Alonso, Oliet, Rodriguez, Astarloa, & Echevarria, 2004; Botello, Gilarranz, Rodriguez, & Oliet, 1999; El Mansouri & Salvadó, 2006). Nevertheless, lignin is a barrier in the enzymatic hydrolysis of biomass. The presence of lignin in the lignocellulosic materials decreases their value as source of chemicals (Tan & MacFarlane, 2009). Therefore, the efficient separation of cellulose from wood using environmentally friendly processes would be interesting in the context of the biorefinery philosophy. Some ionic liquids could be an attractive option for wood dissolution and cellulose regeneration.

According to literature, a variety of ionic liquids (ILs) has been shown as good cellulose and biomass non-derivatizing solvents (Casas, Palomar, et al., 2012; Casas, Alonso, Oliet, Rojo, & Rodriguez, 2012; Casas, Oliet, Alonso, & Rodriguez, 2012; Fort et al., 2007; Jiang et al., 2011; Kilpelainen et al., 2007; Li et al., 2011; Pu, Jiang, & Ragauskas, et al., 2007; Sun et al., 2009; Zavrel et al., 2009). They are

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salts composed by a large organic cation and an inorganic or organic anion. ILs can be used to directly extract the compounds present in biomass or transform these lignocellulosic materials into value-added chemicals (Xie et al., 2010). Furthermore, the pretreatment of wood with IL decreases the crystallinity of the cellulose structure and makes it more accessible for the acids or enzymes in the hydrolysis process (Torr et al., 2012; Zhang et al., 2009). Some of the most interesting properties of ILs in biomass processing are their high thermal stabilities and that they do not emit volatile organic compounds due to their very low vapour pressures (Fort et al., 2007). In addition, ILs exhibit low melting points, are non-flammable and can be designed to show certain properties by selecting the appropriate combination of anion and cation (Palomar, Torrecilla, Ferro, & Rodriguez, 2008, 2009; Tan & MacFarlane, 2009; Torrecilla et al., 2008). Specifically, in biomass dissolution, the anion plays a crucial role in the process; one of the most promising anions for wood dissolution is chloride. The role of the cation in the dissolution process is more secondary, and imidazolium-based ILs with short side chains are commonly used in literature (Casas, Palomar, et al., 2012; Casas, Alonso, et al., 2012; Casas, Oliet, et al., 2012; Fort et al., 2007; Jiang et al., 2011; Kilpelainen et al., 2007; Pu et al., 2007; Zavrel et al., 2009).

Cellulose has been successfully regenerated from wood liquors in ionic liquids using different antisolvents (Fort et al., 2007). However, long dissolution times were required (above 12 h) due to the complex structure of wood, which hampers the solubility in the IL. The use of microwave heating can decrease the wood dissolution times and would be an attractive alternative to the thermal heating.

Note that, when applied to biomass, the recyclability of the ionic liquid is a vital issue. The classical way to recycle the ionic liquid consists of evaporating the antisolvent under vacuum. Then, the IL could be reused in the process, with a decrease in the efficiency due to the progressive accumulation of wood soluble compounds (Auxenfans et al., 2012; Haykir, Bahcegul, Bicak, & Bakir, 2013).

The aim of this paper is to thoroughly characterize the celluloses regenerated from solutions of *Pinus radiata* and *Eucalyptus globulus* woods in the 1-allyl-3-methylimidazolium chloride (AmimCl) ionic liquid. Both wood species were dissolved in the IL in a microwave oven and cellulose was regenerated by precipitation with methanol. The regenerated celluloses were analyzed by solid-state ^{13}C nuclear magnetic resonance (NMR), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results were compared to those of microcrystalline cellulose, which is used in this study as reference material. The wood bulk solutions in the IL before cellulose regeneration were also characterized using high performance liquid chromatography and liquid ^{13}C NMR. In addition, the insoluble solids were studied by solid-state ^{13}C NMR, FTIR and thermal analysis (DSC and TGA).

2. Experimental

2.1. Materials

In this work, the ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl, >98%, Iolitec) was employed for wood dissolution. Pine (*P. radiata*) and eucalyptus (*E. globulus*) woods were procured by CIFOR-INIA ("Instituto Nacional de Investigación y Tecnología Agraria y Alimentación") and "Torras Papel", respectively. The contents of lignin and holocellulose in both wood species were determined according to literature procedures (T222 Om-88, 1988; Wise, Murphy, & D'Adieco, 1946); the lignin content is 25.8% and 19.3% in pine and eucalyptus, respectively, and the holocellulose content is 72.5% in pine and 74.2% in eucalyptus woods. Wood chips were subjected to a pretreatment in order to promote their solubilities in the ionic liquid. Thus, both woods were firstly extracted with acetone and water to remove the wood extractives. Then, the resulting extractive-free wood was milled, sieved and dried in a vacuum oven at 60 °C for 24 h.

Dimethyl sulfoxide (DMSO, ≥99.9%, Sigma Aldrich) and dry methanol (max. 0.005% water, Panreac) were employed as cosolvent and antisolvent, respectively. In addition, microcrystalline cellulose (Avicel PH-101) was used as reference material in the characterization of the regenerated cellulose.

2.2. Dissolution of pine and eucalyptus woods in AmimCl

Pine and eucalyptus woods (4%, w/w) were mixed with the AmimCl ionic liquid (20 g) under an inert atmosphere of dry nitrogen. The resulting samples were sealed and introduced in a Berghof SpeedWave Four microwave oven. An infrared thermometer that permits the temperature to be quickly determined and regulated is integrated in the microwave oven. Both temperature and time can be controlled by the oven. The woods dissolution programme consisted on two stages. In the first step, the ionic liquid was melted by heating the wood/ionic liquid samples for 10 min at 110 °C. In the second step, in which wood is dissolved in the IL, temperature was increased to 120 °C and maintained for 20 min. These solubilized biomass samples in the IL were analyzed by high performance liquid chromatography and ^{13}C nuclear magnetic resonance.

2.3. Cellulose regeneration from the solubilized biomass samples in AmimCl

Solutions of pine and eucalyptus woods in AmimCl were dissolved in DMSO in a 1/1.3 (w/v) ratio. The DMSO acted as a cosolvent, decreasing the viscosity of the wood/IL solutions and allowing their filtration. The resulting mixtures wood/IL/DMSO were filtered in a Buchner and Kitasato system using a nylon filter (pore size: 1.2 μm) in order to separate the insoluble solids. The 66% of both woods was dissolved in the ionic liquid; the remaining 34% was recovered as insoluble solids. Then, the filtered solutions were added to 200 mL of dry methanol, the antisolvent, and stirred at 300 rpm and 40 °C for 10 min in order to regenerate the cellulose. After that, cellulose was collected by vacuum filtration and dried overnight at 105 °C. The 16% and 11% of cellulose was regenerated from the solubilized biomass samples from pine and eucalyptus woods, respectively. The insoluble solids and the regenerated celluloses were characterized using different techniques.

2.4. Characterization of insoluble solids, solubilized biomass samples in AmimCl and regenerated celluloses

The presence of sugars in the pine and eucalyptus solutions in AmimCl was analyzed by high performance liquid chromatography (HPLC). These sugars may appear due to the degradation of the wood carbohydrates (cellulose and hemicellulose) as a consequence of the dissolution process in the microwave oven. A 1200 Infinity HPLC system (Agilent Technologies) was employed with a Hi-Plex Pb column (300 mm × 7.7 mm) at 70 °C and a guardcolumn. The effluent was milli-Q water at a flow rate of 0.5 mL/min using an injection volume of 20 μL. The sugar peaks were detected by a refractive index detector (1260 Infinity, Agilent Technologies) at 55 °C and compared to standards (Sigma Aldrich), i.e., D-(+)-glucose (≥99.5%), D-(+)-xylose (≥99%), D-(+)-mannose (≥99.5%), D-(−)-arabinose (≥98%), and D-(+)-galactose (≥99.5).

The solubilized biomass samples in AmimCl were also studied by liquid ^{13}C nuclear magnetic resonance (NMR) in DMSO-d$_6$, which was performed in a Bruker Avance 500 MHz instrument at 70 °C using 20,000 scans.

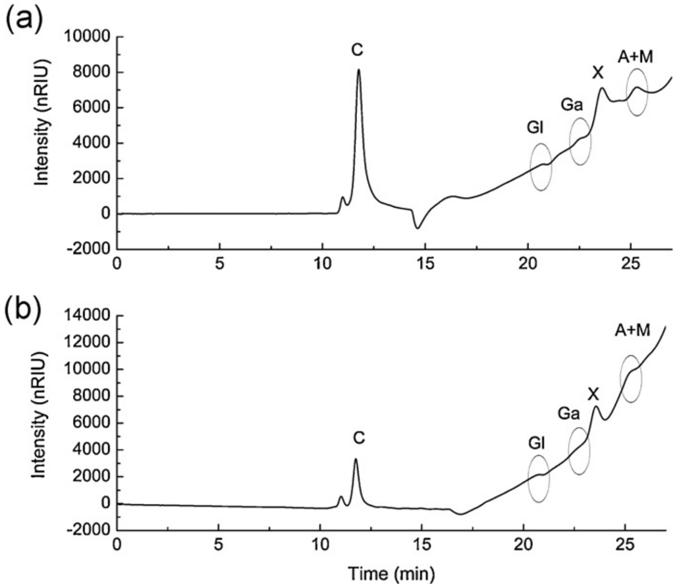

Fig. 1. HPLC analysis of (a) pine and (b) eucalyptus solubilized samples in AmimCl at 120 °C for 20 min (C: cellulose, Gl: glucose, Ga: galactose, X: xylose, A: arabinose, M: mannose).

Solid-state ^{13}C NMR spectroscopy of regenerated celluloses and the insoluble solids was performed in a Bruker Avance 400 MHz instrument using 20,000 scans.

X-ray diffraction (XRD) patterns of the regenerated celluloses were measured on an X'Pert PRO MPD system. The diffracted intensity of Cu Kα radiation (45 kV and 40 mA) was analyzed in a 2θ range between 4° and 80°.

FTIR spectra of the regenerated celluloses and the insoluble solids were recorded in a Satellite 5000 spectrometer (Mattson) between 2000 and 600 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 32 scans at 2 cm^{-1} of resolution.

Thermal behavior of regenerated celluloses and insoluble solids was studied on a TGA/DSC1 Mettler Toledo instrument, which provides both the DSC (differential scanning calorimetry) and TGA (thermogravimetric analysis) curves. Temperature was increased from 40 to 750 °C with a heating rate of 10 °C/min. Dry nitrogen was employed in a flow rate of 50 mL/min and the experiments were performed in an alumina crucible. For each experiment 8–9 mg of sample were used. The characteristic parameters of the TGA and DTGA curves were determined, i.e., the onset (T_{onset}), the temperature at which the 10% of the initial weight is loss ($T_{10\%}$), the temperature of the maximum loss of weight ($T_{\max}$), and the ash content at 400 °C.

3. Results and discussion

3.1. High performance liquid chromatography

Pine and eucalyptus woods were dissolved in the AmimCl ionic liquid under microwave radiation at 120 °C for 20 min. The HPLC analysis of solubilized biomass samples is shown in Fig. 1. In the chromatograms, a peak assigned to cellulose is observed, and also a peak corresponding to xylose, which is due to the degradation of hemicelluloses as a consequence of the dissolution process; cellulose is more difficult to degrade than hemicellulose because of its high crystallinity. In addition, some variations in the slope of both chromatograms are observed in Fig. 1, which can be assigned to glucose, galactose, and arabinose plus mannose, though the amount of these sugars in the solution is small. Thus, the dissolution in the IL and the employment of microwave radiation lead to the degradation of hemicelluloses to xylose whereas non-substantial degradation of the cellulose is attained.

3.2. ^{13}C nuclear magnetic resonance

The insoluble solids, the solubilized biomass samples in the IL and the regenerated celluloses were analyzed by solid-state or liquid ^{13}C NMR, as displayed in Fig. 2.

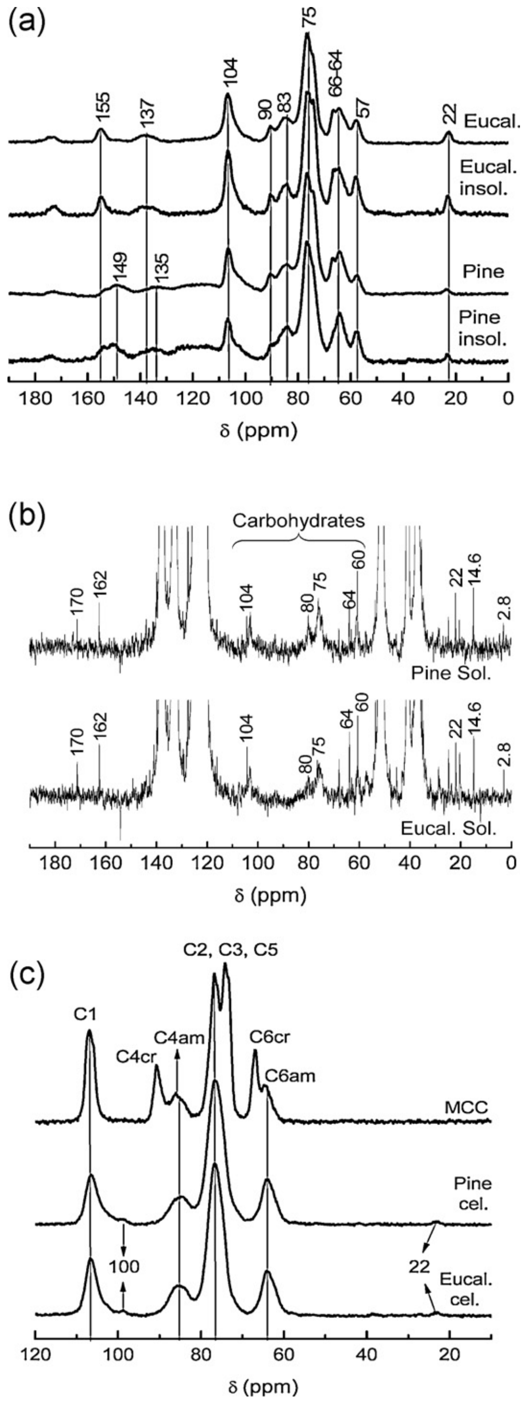

Fig. 2. ^{13}C NMR spectra of (a) pine, eucalyptus and insoluble solids, (b) solubilized biomass samples and (c) MCC and regenerated celluloses (cr: crystalline, am: amorphous).

In the insoluble solids (Fig. 2a), the characteristic peaks of cellulose, hemicellulose and lignin are observed. At 22 ppm appears the CH_3 in acetyl groups of hemicellulose (Mathers, Xu, Blumfield, Berners-Price, & Saffigna, 2003). The signals of cellulose are observed at 64 (C6 amorphous), 66 (C_6 crystalline), 75 (C_2, C_3, C_5), 83 (C_4 amorphous), 90 (C_4 crystalline), and 104 ppm (C_1) (Husson et al., 2011; Lan, Liu, Yue, Sun, & Kennedy, 2011; Liu et al., 2007). In addition, the signals of lignin are found at 57 ($O\text{-}CH_3$), 135 (C_1 guaiacyl), 137 (C_1, C_4 syringyl), 149 (C_3, C_4 guaiacyl), and 155 ppm (C_3, C_5 syringyl) (Casas, Oliet, et al., 2012; Fort et al., 2007). Comparing the spectra of the insoluble solids to those of pine and eucalyptus woods, an increase of the intensity of peaks corresponding to hemicellulose and lignin is observed. Furthermore, in the spectrum of the pine insoluble solid, the peaks of cellulose corresponding to the crystalline regions at 66 and 90 ppm almost disappear; the reduction of these peaks may be due to the disruption of the hydrogen bonds in the treatment with the IL and the consequent decrease of cellulose crystallinity (Liu et al., 2007; Lan et al., 2011). Therefore, under the studied conditions, the insoluble solids show higher contents of lignin and hemicellulose than the raw materials, and the dissolution of cellulose in AmimCl is promoted.

The liquid ^{13}C NMR analysis of the solubilized samples of both woods in the AmimCl is displayed in Fig. 2b, though the resolution of the spectra is low due to the high concentration of ionic liquid in both solutions. In the spectra, the characteristic peaks of the carbohydrates are found in the region 104–60 ppm (Mathers et al., 2003). Signals of hemicellulose and lignin are also observed at 2.8 (anhydroxylose units in hemicellulose), 14.6 (CH_3 of $Ar–COCH_3$ in lignin), 22 (CH_3 of acetyl groups in hemicellulose), 162 (phenolic C in lignin), and 170 ppm (carboxylic C) (Mathers et al., 2003; Sun, Sun, Sun, & Su, 2004). Although the studied conditions promote the cellulose dissolution in the AmimCl, also hemicellulose and lignin are dissolved in some extent.

The solid-state ^{13}C NMR spectra of regenerated celluloses and microcrystalline cellulose (MCC) are shown in Fig. 2c. The characteristic peaks of cellulose mentioned before are observed in the spectra of regenerated celluloses. In addition, the peaks corresponding to the crystalline regions at 66 and 90 ppm are not found, due to the decrease of cellulose crystallinity as a consequence of the dissolution and regeneration processes, as indicated above. Furthermore, the peak of the methoxyl groups of lignin at 57 ppm is not observed in the spectra of regenerated celluloses. On the contrary, two little peaks characteristic of hemicellulose appear at 22 and 100 ppm (Mathers et al., 2003; Sun, Fang, Tomkinson, Geng, & Liu, 2001). Therefore, cellulose has been successfully regenerated from solutions of pine and eucalyptus woods in AmimCl. These regenerated celluloses are not obtained together with lignin, and are practically free from hemicelluloses.

According to these results, the insoluble solids exhibit higher amounts of lignin and hemicellulose than the initial woods; in the solubilized biomass samples the three main wood compounds are observed, whereas lignin is not found in the regenerated cellulose.

3.3. X-ray diffraction

The X-ray diffraction (XRD) patterns of microcrystalline cellulose and regenerated celluloses from solutions of pine and eucalyptus woods in AmimCl are displayed in Fig. 3. The microcrystalline cellulose shows the characteristic diffraction peaks of the cellulose I structure at 22.5° and 15°, and the reflection peak at 34.5° (Blokhin et al., 2011; Sundar, Sain, & Oksman, 2010). On the contrary, the regenerated celluloses show a wide amorphous peak centred at 20°, typical of cellulose II (Blokhin et al., 2011; Lan et al., 2011). The width of these amorphous peaks at half-height is higher in pine cellulose (7.7°) than in eucalyptus cellulose (6.96°); this means that cellulose regenerated from pine wood is less crystalline than eucalyptus cellulose (Adel, Abd El-Wahab, Ibrahim, & Al-Shemy, 2011), which is in agreement with the results of the ^{13}C NMR analysis of the insoluble solids. In that analysis, the crystalline peaks of cellulose disappeared in the spectrum of the pine insoluble solid. Hence, it seems like pine cellulose is more affected by the treatment with the ionic liquid than eucalyptus cellulose. This fact is probably due to the lower cellulose content in pine than in eucalyptus woods (Sjostrom, 1981). The XRD results show a decrease on the crystallinity of regenerated celluloses as a consequence of the dissolution and regeneration processes, which agrees with both the results of the ^{13}C NMR analysis and the literature (Kadokawa, Murakami, & Kaneko, 2008; Kilpelainen et al., 2007).

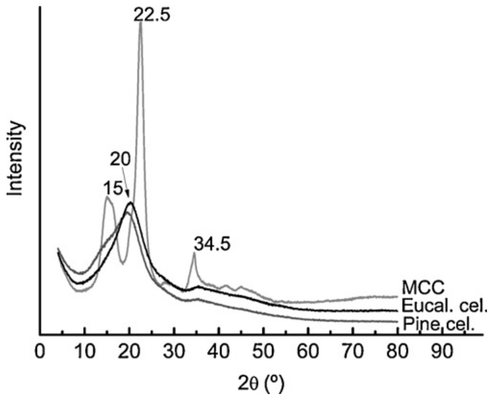

Fig. 3. XRD patterns of MCC and regenerated celluloses.

Table 1
TGA and DTGA thermal parameters of pine, eucalyptus, insoluble solids, MCC and regenerated celluloses.

	T_{onset} (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	Ash content$_{400\,°C}$ (%)
Pine insoluble solid	261	228	335	37
Eucalyptus insoluble solid	254	264	350	30
Pine	265	284	354	32
Eucalyptus	267	282	355	29
Pine cellulose	298	299	337	28
Eucalyptus cellulose	272	270	294	39
MCC	311	309	333	16

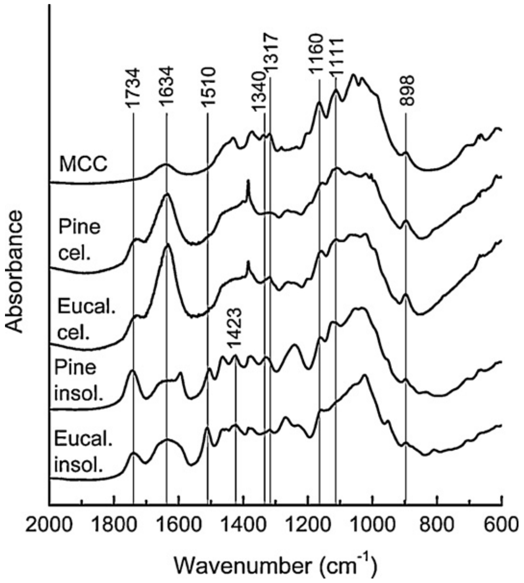

Fig. 4. FTIR spectra of MCC, regenerated celluloses and insoluble solids.

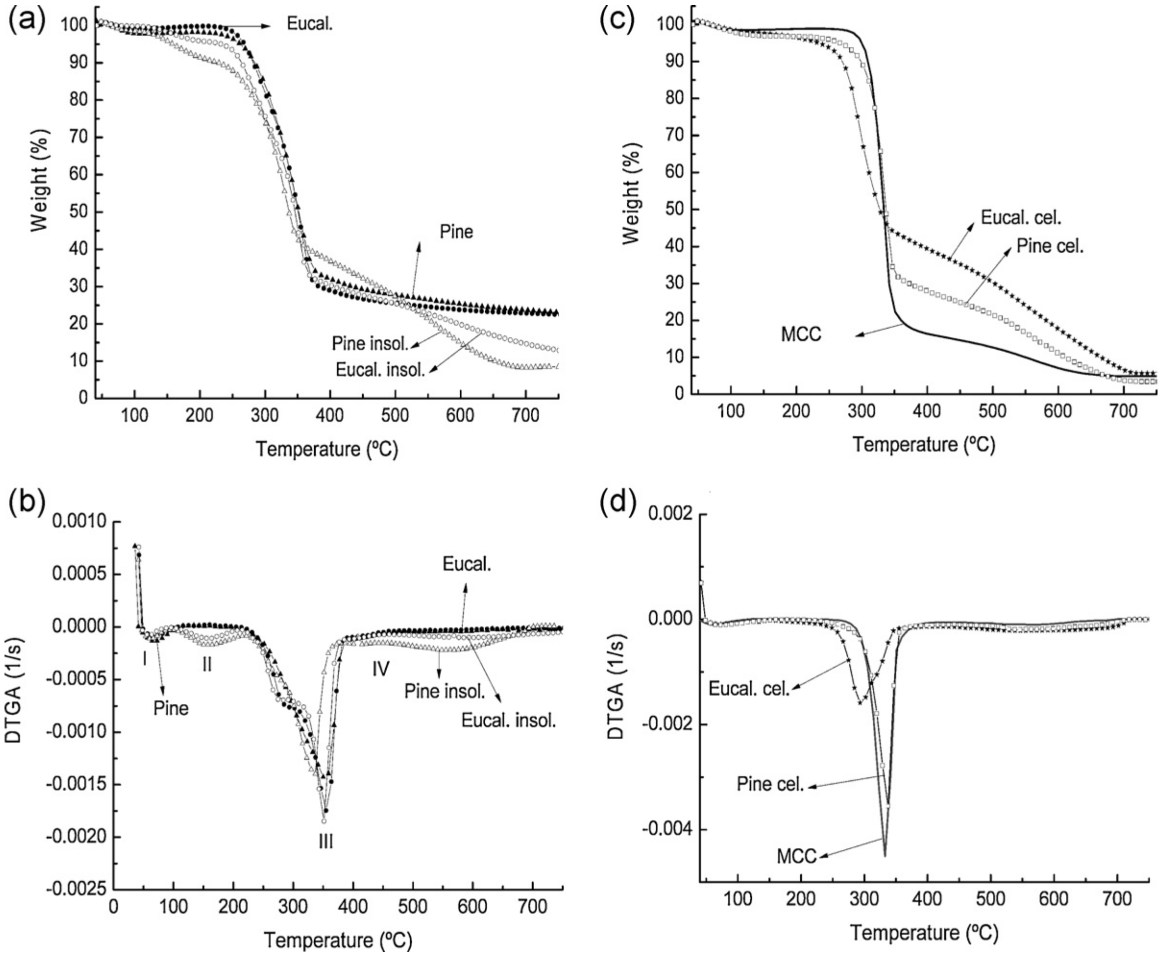

Fig. 5. TGA and DTGA analysis of (a and b) pine, eucalyptus and insoluble solids and (c and d) MCC and regenerated celluloses.

3.4. Fourier transform infrared spectroscopy

The Fourier transform infrared (FTIR) spectra of MCC, the insoluble solids and the regenerated celluloses are displayed in Fig. 4. The characteristic vibration bands of cellulose and lignin were assigned according to literature (Faix, 1991; Faix & Bottcher, 1992). With respect to the insoluble solids, intense bands characteristic of lignin at 1510 and 1423 cm^{-1} (aromatic skeletal vibrations) are observed in their spectra. On the contrary, the intensity of the characteristic cellulose bands at 898 (glucose ring stretching), 1160 (C—O—C stretching asym.) and 1111 cm^{-1} (glucose ring stretching asym.) is low. In addition, an intense band characteristic of acetyl groups in hemicellulose appears at 1734 cm^{-1} (Colom, Carrillo, Nogués, & Garriga, 2003). Therefore, the characteristic bands of cellulose, hemicellulose and lignin are found in the spectra of the insoluble solids. These results are in agreement with the data obtained in the ^{13}C NMR spectra.

The FTIR spectra of the regenerated celluloses are similar to that of MCC. The characteristic vibration bands of lignin are not found in the spectra, in agreement to the results of the ^{13}C NMR analysis of regenerated celluloses. Some differences can be noticed between the spectra of MCC and those of regenerated celluloses. These differences may be due to the decrease of cellulose crystallinity, observed in the XRD and ^{13}C NMR analysis, as a consequence of the dissolution in the AmimCl and the regeneration processes. Bands at 1340 (OH in plane deformation) and 1317 cm^{-1} (CH_2 rocking vibration) are affected by this decrease in the cellulose crystallinity and the breakage of the hydrogen bonds in the dissolution process (Casas, Palomar, et al., 2012; Colom & Carrillo, 2002). Furthermore, the weakening of the hydrogen bonds as a consequence of the wood dissolution process changes the cellulose vibrational energy, which is reflected in band at 1160 cm^{-1} (C—O—C stretching asym.). In addition, the decrease in cellulose I in the XRD cellulose patterns is also observed in the band at 1111 cm^{-1}, characteristic of this cellulose structure (Casas, Palomar, et al., 2012). On the contrary, the intensity of the characteristic band of the amorphous fraction of cellulose at 897 cm^{-1} increases in regenerated celluloses (Korte & Staiger, 2008). An intense band at 1634 cm^{-1} characteristic of the C—O—O′ bonds in cellulose is also observed in the spectra of the regenerated materials. Comparing the FTIR spectra of regenerated celluloses, the characteristic vibration bands of pine cellulose are more affected by the treatment than that of eucalyptus cellulose. This fact may be due to the lower crystallinity shown by pine cellulose, as mentioned before in the ^{13}C NMR and XRD analysis.

The results of the FTIR analysis are in agreement with those of the XRD and ^{13}C NMR techniques and show that amorphous cellulose has been successfully regenerated from solutions of pine and eucalyptus woods in AmimCl. This amorphous cellulose would be useful in applications such as in enzymatic or acid hydrolysis to obtain fermentable sugars (Kilpelainen et al., 2007).

3.5. Thermal analysis

The TGA (thermogravimetric analysis) and DTGA (first derivative of the TGA curve) curves of insoluble solids, regenerated celluloses, MCC and pine and eucalyptus woods are displayed in

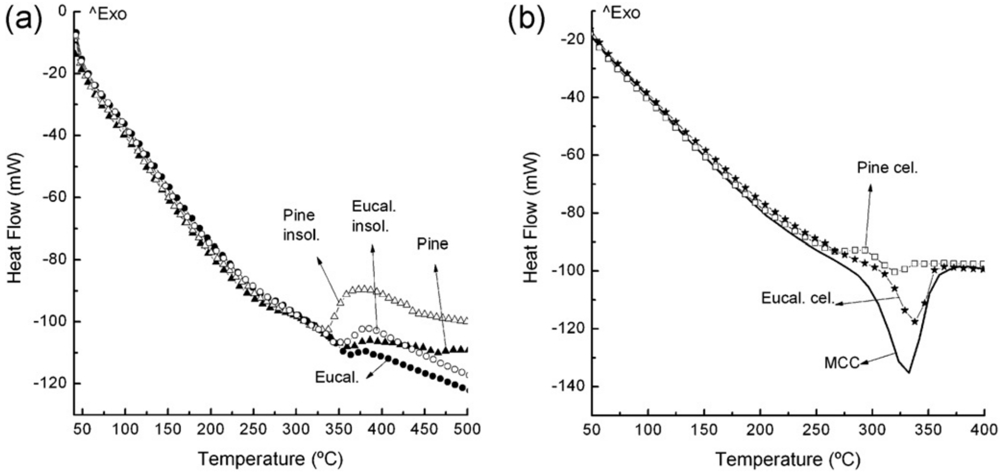

Fig. 6. DSC curves of (a) pine, eucalyptus and insoluble solids and (b) MCC and regenerated celluloses.

Fig. 5. The characteristic parameters obtained from these curves are shown in Table 1. The insoluble solids (Fig. 5a) are thermally less stable than the original woods, probably due to the treatment with the IL and to the exposure to microwave radiation. The T_{onset}, the $T_{10\%}$ and the T_{max} are lower in the insoluble solids than in the correspondent wood species. The ashes at 400 °C, on the contrary, are slightly higher in the insoluble solids (37% in pine and 30% in eucalyptus woods), than in the original woods (32% in pine and 29% in eucalyptus woods). When temperature increases above 500 °C the loss weight in the wood species is stabilized, whereas the insoluble solid continue loosing weight. The DTGA curves of the insoluble solids (Fig. 5b) exhibit that the thermal decomposition takes place in four major steps. At temperatures below 100 °C (I), the dehydration of the samples occurs (Casas, Oliet, et al., 2012). Between 100 and 220 °C (II) the decomposition of the residual hemicellulose is observed (Liu et al., 2006). The peak found at temperatures between 220 and 400 °C (III) can be attributed to the decomposition of cellulose, lignin and hemicellulose (Liu et al., 2006). The fourth step, above 400 °C and up to 700 °C (IV), corresponds to the final breakage of cellulose, inorganic compounds and lignin (Casas, Oliet, et al., 2012; Liu et al., 2006). In Fig. 5b, steps II and IV are more pronounced in the curves of insoluble solids; this difference in the curves may be due to the higher content of lignin and hemicellulose in the insoluble solids than in the raw woods, as observed in the FTIR and ^{13}C NMR analysis.

With respect to the results obtained in the TGA analysis for the regenerated celluloses (Fig. 5c), their thermal stabilities are lower than that of MCC. The onset temperature is 298, 272 and 311 °C in pine cellulose, eucalyptus cellulose and MCC, respectively, and the $T_{10\%}$ are 299 (pine cellulose), 270 (eucalyptus cellulose) and 309 °C (MCC). This decrease in the thermal stability may be related to the low crystallinity of regenerated celluloses, which consequently, are easier to degrade than MCC (Szczesniak, Rachocki, & Tritt-Goc, 2008). On the contrary, the residue at 400 °C is higher in regenerated celluloses (28% for pine cellulose and 39% for eucalyptus cellulose) than in MCC (16%), behavior in agreement with the results shown in literature (Fort et al., 2007). This fact may be due to the presence of inorganic salts in the regenerated celluloses from the dissolution process in the IL (Lan et al., 2011). Furthermore, in the DTGA analysis of the regenerated celluloses (Fig. 5d), a single peak is observed, and therefore, the regenerated celluloses show high purity.

The DSC curves of insoluble solids, pine, eucalyptus, MCC and regenerated celluloses are displayed in Fig. 6. In the DSC curves of insoluble solids (Fig. 6a), an endothermic peak is observed at 325–350 °C, which corresponds to the breakage of the glucosidic bonds in cellulose (Ciolacu, Ciolacu, & Popa, 2011). In addition, an exothermic peak attributed to the combustion of carbohydrates (above 350 °C) and lignin (475 °C) is also observed in the DSC of insoluble solids (Tsujiyama & Miyamori, 2000); this peak is more prominent in the insoluble solids than in the original woods, which may be due to the higher lignin content of these insoluble solids. In the case of the regenerated celluloses and MCC (Fig. 6b), an endothermic peak at ~330 °C is observed in their DSC curves, due to the depolymerization of cellulose, as mentioned before (Ciolacu et al., 2011; Jandura, Riedl, & Kokta, 2000). The area of these peaks is lower in regenerated celluloses than in MCC, probably due to the low crystallinity of regenerated celluloses, which makes easier their depolymerization.

Summarizing the results of the thermal analysis, the wood dissolution and regeneration processes lead to a decrease in the thermal stabilities of the regenerated celluloses and the insoluble solids. The ash content at 400 °C, on the contrary, increases.

4. Conclusions

Cellulose has been successfully regenerated from solutions of pine and eucalyptus woods in AmimCl after heating in a microwave oven for 20 min at 120 °C. The XRD patterns and the ^{13}C NMR spectra show that the crystallinity of the regenerated celluloses decreases as a consequence of the wood dissolution and regeneration processes. These more amorphous celluloses would be easier to hydrolyze than the crystalline celluloses, and consequently could be employed to obtain fermentable sugars. In addition, these celluloses are obtained without lignin, and basically hemicellulose-free. The structure of the regenerated celluloses is similar to that of MCC according to the FTIR analysis. However, the thermal stability is higher in MCC than in regenerated celluloses. Both the dissolution in the AmimCl and the employment of microwave radiation do not degrade significantly the cellulose contained in wood, as displays the HPLC analysis. Finally, the FTIR and ^{13}C NMR results show that the insoluble solids display higher amounts of lignin and hemicellulose than the raw materials, which confirms that the cellulose dissolution is improved in the studied experimental conditions.

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