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Selective extraction of hemicelluloses from spruce using switchable ionic liquids

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ABSTRACT

Switchable ionic liquids (SILs) made from alcohols, either hexanol or butanol, and CO_2 together with an amidine (1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU)) were investigated as dissolution/fractionation solvents for wood material. Both native spruce (*Picea abies*), and pre-extracted spruce were treated with either butanol SIL (SIL1) or hexanol SIL (SIL2) for 5 days at 55 °C under normal pressure. The SILs were formed by bubbling CO_2 through an equimolar mixture of either 1-hexanol or 1-butanol and DBU. The viscosity of the mixture increased from 7.1 mPa s to 2980 mPa s for SIL2 and 5.1 to 1600 mPa s for SIL1. Melting points of the SILs 1 and 2 were at 8 and 14 °C, respectively. After the treatment time (5 days), the undissolved fraction contained 38 wt.% less hemicelluloses compared to native spruce. There was an increase in the glucose content of the milled spruce treated with both SILs, since the milling step reduced the cellulose crystallinity of the wood and facilitated an easier SIL access into the wood. The solvents were very neutral in terms of lignin removal. Consequently, only about 2% of the lignin was removed from native wood. Moreover, a priori removal of the wood extractives did not influence the lignin removal.

1. Introduction

Wood is the most important and abundant bio-renewable resource available, with well established uses as fuel, construction and manufacturing material (pulp and paper) (Sjöström, 1993). Wood is composed of three main parts, cellulose (Fig. 1A), hemicelluloses (Fig. 1B) and lignin (Fig. 2). Cellulose is an abundant renewable polysaccharide consisting of a linear chain of 1–4-linked β-D-glucopyranosyl units aggregated to form a highly ordered structure. Hemicelluloses are mainly composed of carbohydrates based on pentose sugars, mainly xylose, as well as hexose sugars, such as glucose and mannose. Hemicelluloses are relatively amorphous and are readily degraded by glycosidases, primary xylanases (mainly hardwood) to yield fermentable sugars. Lignin is an amorphous, polyphenolic polymeric material arising from an enzymatic dehydrogenative polymerization of three phenylpropanoid monomers, which includes coniferyl, sinapyl and p-coumaryl alcohols (Fengel & Wegener, 1984).

All the major components in the wood can be utilized for the production of biofuels and chemicals, thus making fractionation of wood into the different components attractive.

However, fractionating the wood into its different major components can be quite challenging. Most methods used over the years for fractionation of wood have had their own shortcomings. For instance, the Kraft pulping process, which is the oldest and most dominant chemical pulping process in an industrial scale, produces black liquor as waste product and it contains caustic soda and sodium sulphide. These chemicals are harmful to the environment, in addition, the liquor also contains some dissolved hemicelluloses and if utilization of them is preferred, they should be recovered from the process, thus making the process more complicated and expensive (Sun et al., 2009).

Ionic liquids are salts composed of organic cations and inorganic or organic anions, and their melting points are below the boiling point of water. Ionic liquids are interesting due to their tuneable properties, making them suitable as reaction media and extraction solvents, among other applications. It should be noted that ionic liquids often have very low vapour pressures and, thus, the regeneration of spent ionic liquids with minor solvent losses is possible. Ionic liquids have high chemical and thermal stabilities, and a wide liquidus range (Wasserscheid & Welton, 2006). Conventional ionic liquids have been used in dissolution of pine wood, e.g. 1-butyl-3-methylimidazolium chloride [C4MIM][Cl] (Fort et al., 2007) and 1-ethyl-3-methylimidazolium acetate [C2MIM][OAc] (Kilpelainen

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Abbreviations: DBU, 1,8-diazabicyclo-[5.4.0]-undec-7-ene; SIL, switchable ionic liquid; SIL1, butanol/DBU/CO_2; SIL2, hexanol/DBU/CO_2; Butanol-SIL, SIL1; Hexanol-SIL, SIL2.

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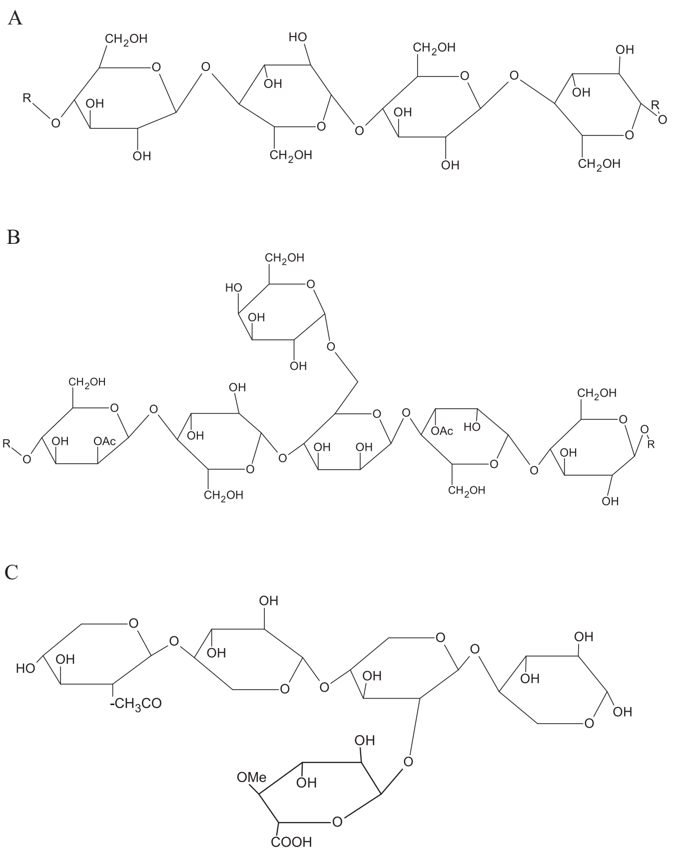


Fig. 1. Schematic diagram of (A) cellulose and hemicelluloses, (B) glucomannans and (C) xylan which are the most common units in soft and hard wood, respectively. *Source*: Sun et al. (2009), Fengel and Wegener (1984), and Sjöström (1993).

et al., 2007), have been reported to be the two most promising ionic liquids for wood dissolution, reaching the efficiency of 50 wt.% at 90 °C and 45 wt.% at 100 °C, respectively. However, the reuse and recycling of the above mentioned ionic liquids have been barely discussed. Several authors have reported to have recovered spent ionic liquids that have been used for wood dissolution mainly by the addition of an anti-solvent. The dissolved material can be precipitated out and the anti-solvent can be separated from the spent ionic liquid by evaporation (D'Andola, Szarvas, Massonne, & Stegmann, 2008). An ionic liquid can be recovered after treatment of cellulose with water or water/acetone mixture. Furthermore, a total recovery and reuse of an ionic liquid based on [C2MIM] [OAc] was demonstrated in the dissolution of poplar (*Populus tremula*) (Varanasi et al., 2008). At the end of the dissolution of poplar, the spent ionic liquid was recovered by addition of water or ethanol as an anti-solvent, and no additional cleaning steps were required for the reuse of this ionic liquid in the consecutive dissolution of wood-evaporation of anti-solvent.

It is has been evident that one of the limitations of the dissolution of wood using conventional ionic liquids is the high viscosity of the solution after dissolution, making recycling, recovery and reuse of the ionic liquid less viable. The dissolution of lignocellulosic material using novel switchable ionic liquids (SILs) is demonstrated in this work; their ability to be switched can facilitate an easy solvent recycling.

SILs can be formed by exposing an equimolar mixture of two molecular liquids, for instance an amidine such as 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) with an alcohol such as 1-hexanol to gaseous CO_2, under ambient pressure and at room temperature, causing an exothermic transformation of the molecular liquid mixture into an ionic liquid (Fig. 3). The formed viscous ionic liquid can be converted back to neutral liquid mixture upon the removal of CO_2 by bubbling nitrogen or applying vacuum at room temperature. The rate for the back transformation of the ionic liquid to molecular ones can be increased by elevating the temperature (Anugwom et al., 2011; Jessop, Heldebrant, Xiaowang, Eckert, & Liotta, 2005; Phan et al., 2008).

2. Experimental

2.1. Preparation and characterisation of SILs

DBU (99% grade), 1-hexanol (>99%, anhydrous) and 1-butanol (>99%, anhydrous) were used as received from Sigma–Aldrich. Supercritical grade CO_2 (99.999%, $H_2O < 0.5$ ppm) and nitrogen (99.998%, $H_2O < 3$ ppm)) were used as received from AGA. The switchable ionic liquids were prepared according to Jessop et al. (Jessop et al., 2005; Phan et al., 2008).

Thermogravimetric analysis (TGA) was carried out to determine the decomposition onset of the salt. Differential scanning calorimetry (DSC) (TA instrument Q1000 series) was applied for the determination of melting and freezing points of the salts. The solvatochromic dye Nile Red was used as a measure of polarity to estimate the liquid changes in polarity before and after exposure to CO_2. The Nile Red wavelength of maximum absorbance, λ_{max} directly correlates with solvent polarity and can be used as a polarity probe with ionic liquids (Phan et al., 2008). The water content of the SILs was determined using Karl–Fisher titration with hydranal composite 2 (Fluka) as a titrant. Miscibility tests were conducted under an inert atmosphere, in which various solvents were mixed with the SIL or precursor mixtures, both in ionic form and non-ionic form.

The viscosities of the solvents were measured using a VOR Bohlin Rheometer at 25 °C. The low viscosity samples were measured with a bob/cup geometry and the high viscosity samples with a cone/plate geometry. The viscosity was calculated by taking the average of ten experimental points (1 point every 30 s) at a constant shear rate of 11.6 per second.

2.2. Preparation of wood sample

Spruce (*Picea abies*) wood chips were milled to obtain particle size range between 350 μm and 1 mm and they were freeze dried to ensure that all moisture is being removed and to avoid influence of moisture. Wood-extractives were removed from the milled wood using a Soxhlet method applying acetone: water (95:5, v/v) as an extractive solvent, for 8 h at 98 °C.

2.3. Determination of cellulose content

The carbohydrates (cellulose) contents were determined by acid hydrolysis, in which 0.075 mL of 72% H_2SO_4 was added to 10 mg (exact amount) of wood sample in a test tube and kept at room temperature for about 120 min. The secondary hydrolysis was conducted under vacuum on the sample in an autoclave at 125 °C during 90 min. 1–2 droplets of bromocresol green indicator were added and the hydrolysate was neutralized by the addition of $BaCO_3$. The sugar quantification was performed by adding 1 mL of the internal standard (250 mg of sorbitol in 50 mL water) into the sample. Then 1 mL of hydrolysate and 1 mL of acetone were, mixed and evaporated to dryness. Thereafter the sample was silylated. The following chemicals were used for silylation: 150 μL HMDS (hexamethyldisilazane 99% Fluka), 80 μL TMCS (trimethylchlorosilane 98% Fluka) and 100 μL of pyridine (99% Sigma) and the solution was allowed to stand overnight and analyzed by gas chromatography

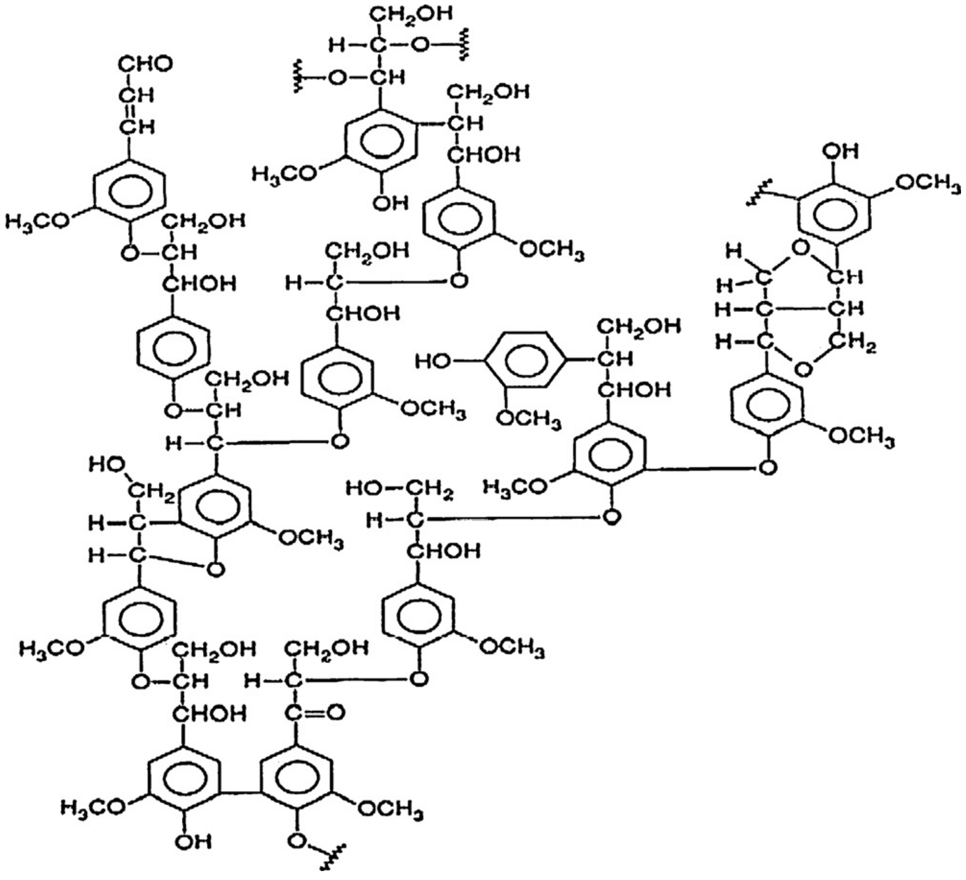


Fig. 2. Schematic representation of wood lignin.

Source: Sjöström (1993).

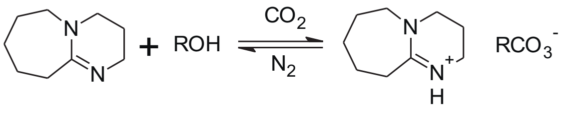
(GC) (Sundberg, Sundberg, Lillandt, & Holmbom, 1996; Willför et al., 2009).

2.4. Determination of hemicelluloses

Acid methanolysis of the wood sample was performed to analyze the hemicelluloses and pectin as follows: 2 mL of 2 M HCl in dry MeOH was added to 100 mg of wood sample, and heated at 105 °C for 5 h (Sundberg et al., 1996). The excess of acid was then neutralized with pyridine. 1 mL of an internal standard (0.1 mg/mL sorbitol) was added to the solution. Thereafter, it was dried under nitrogen and silylated as described above, and the sample was analyzed by gas chromatography (GC) as described in next section.

2.5. GC analysis for the carbohydrates

About 2 μL of the silylated sample was injected through a split injector (260 °C, split ratio 1:5) into the capillary column coated with dimethyl polysiloxane (HP-1, Hewlett Packard). The column length, internal diameter and film thickness were 30 m, 320 μm, and 0.17 μm, respectively. The following temperature programme was applied: 100 °C – 4 °C/min – 175 °C followed by 175 °C – 12 °C/min – 290 °C. The detector (FID) temperature was 290 °C. Hydrogen was used as a carrier gas. The different peaks were identified using GC–MS. The following analytical grade sugars or their acids were used as standard for calibration of the GC method: arabinose, rhamnose, xylose, galactose, glucose, mannose, glucuronic acid, and galacturonic acid. The calibration factors were determined for each series of analyses by performing the methanolysis or hydrolysis, silylation and GC analysis on two parallel samples containing equal amounts (0.1 mg) of the above mentioned sugars and their derivatives. The calibration factors were determined by calculating the ratio of the total area of the different sugar unit peaks to the area of the sorbitol peak. The calibration factor for 4-O-methylglucoronic acid was assumed to be equal to the calibration factor of glucuronic acid (Sundberg et al., 1996; Willför et al., 2009).



(1)

Fig. 3. The reaction scheme for the formation of switchable solvents.
Source: Adopted from Phan et al. (2008).

2.6. Lignin analysis

The lignin content was determined by using acetyl bromide method (Iiyama & Wallis, 1988). 5 mL of 25% (v/v) acetyl bromide in glacial acetic acid was added to 1–4 mg of pre-extracted wood sample and 0.2 mL of 70% $HClO_4$ was added. The mixture was heated at 70 °C for 30 min. The solution was transferred into a 50-mL volumetric flask containing 10 mL of 2 M NaOH and diluted to 50 mL with acetic acid. The absorption of the solution was then measured with UV–Vis spectrophotometer (UV 1240, Shimadzu) with wavelength of 280 nm (Iiyama & Wallis, 1988).

2.7. Dissolution of wood in SIL and analysis

Dried pre-extracted wood flour with a size range of 350–500 μm and chips with a size of 30 mm × 30 mm, were immersed in the

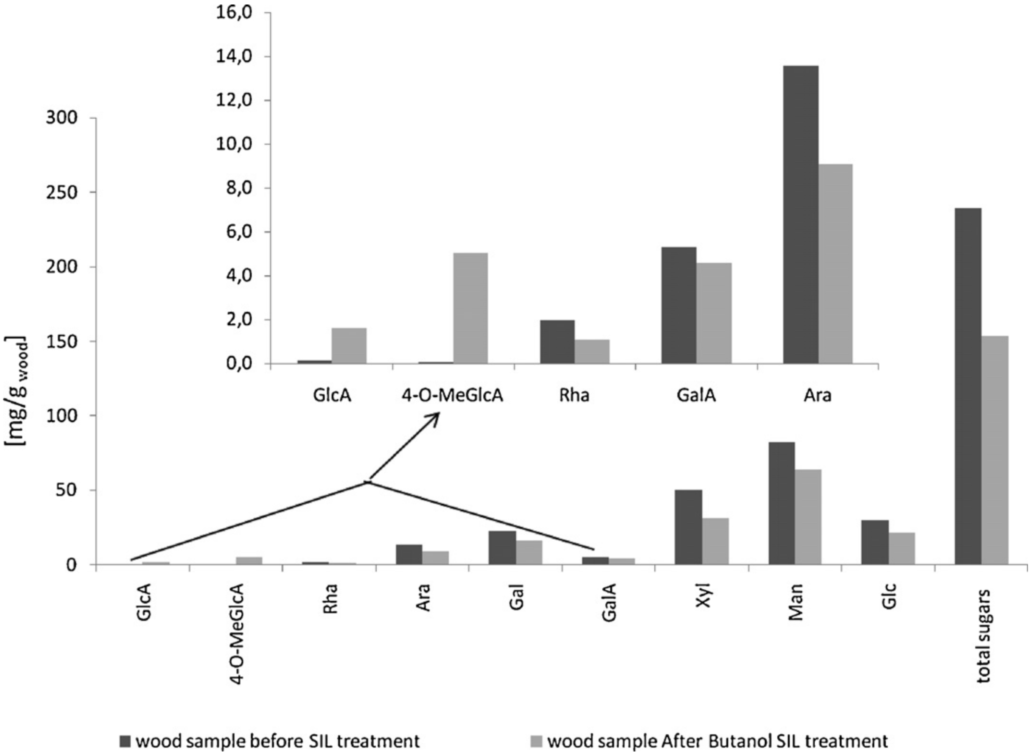


Fig. 4. The total sugar content of wood sample before and after pretreatment with SIL1 at 55 °C for 5 days, no stirring.

SILs (about 20 g) making a 5 wt.% wood mixture. The dissolution of wood chips was performed at 55 °C and under ambient pressure for 5 days, with continuous flow of CO_2 into the SIL. Since the SIL would slowly be converted back to its molecular form at around 55 °C. However, by constantly feeding CO_2 into the liquid the chemical equilibrium is on the ionic liquid side, thus most of the solvent is in ionic liquid form during the experiment. Five days was chosen as the treatment time during the experiments, since in that time almost all the dissolution has occurred and, further dissolution would not give any more information. The effectiveness of the

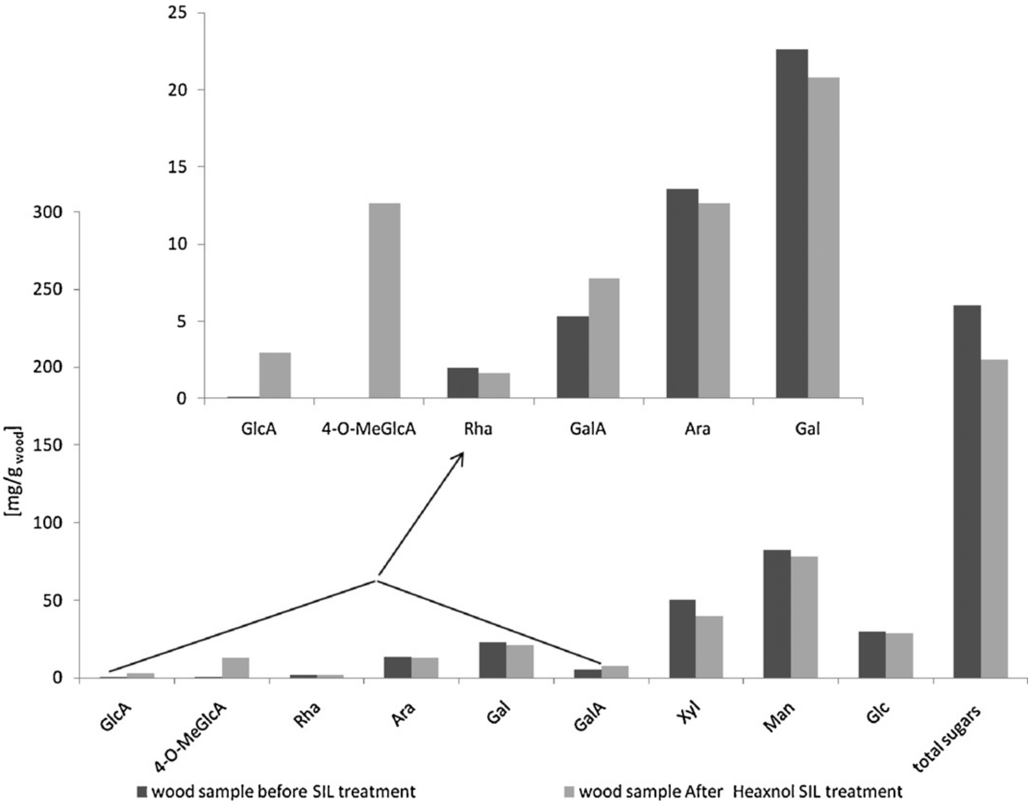


Fig. 5. The total sugar content of wood sample before and after pretreatment with SIL2 at 55 °C for 5 days, no stirring.

Table 1
The characterisation results of the switchable ionic liquid (SIL).

SIL	Water content [%]	Melting point [°C]	Decomposition temp [°C]	Viscosity [mPa s] at 25 °C
DBU/Hexanol/CO_2	0.08	14	55	2980[a]
DBU/Butanol/CO_2	0.04	8	55	1600[a]

[a] The viscosity of DBU–hexanol and DBU–butanol were 7.1 mPa s and 5.1 mPa s, respectively.

SILs on the wood dissolution was the main objective of this study. Therefore, effect of any external influence, such as mechanical agitation or microwave heating, has not been studied. Subsequently, SILs/wood mixture was filtered, and the remaining solid residue was separated and washed several times with a methanol–water mixture (50:50, v/v), until there were no noticeable traces of the SILs on the solids. The weight reduction of the dried wood sample was recorded after the treatment. The carbohydrate content from the undissolved wood sample was analyzed by acid hydrolysis and acid methanolysis, followed by gas chromatography (GC) (see Sections 2.3 and 2.4). The lignin content of the undissolved wood was also quantified using the acetyl bromide method (see Section 2.6). These values were compared to the corresponding values of the native wood sample. The differences obtained indicate the amount of cellulose, hemicelluloses (and possibly lignin) that have dissolved into the SILs.

The percentage of wood components dissolved was calculated according to Eq. (1):

$$\text{Wood dissolved } [\%] = \frac{m_{\text{wood}} - m_{\text{residual}}}{m_{\text{wood}}} \times 100 \tag{1}$$

where m_{wood} is the mass of the wood before the dissolution in SILs, m_{residual} is the mass of the undissolved residual after the dissolution in SILs. The water–methanol mixture was used for washing of the undissolved residual to avoid futher dissoluion.

Scanning electron microscopy (SEM) images of the morphology of the wood chips sample before and after SIL treatment were taken using a Leo Gemini 1530 scanning electron microscope equipped with a ThermoNORAN Vantage X-ray detector for EDXA analysis. The images were taken using the Secondary Electron and Backscattered Electron detector at 15 kV, and the In-Lens Secondary Electron detector at 2.70 kV.

FTIR analysis was applied to study the recovered material from the spent SIL. A Bruker IFS 66/S FTIR spectrometer was used for the FTIR measurements. The FTIR spectra were recorded using a KBr disc (300 mg) containing 1% finely ground samples. In the spectra gathering 64 scans were taken of each sample in the spectral range from 3800 to 400 cm^{-1} using a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Characterisation of SILs

Two switchable ionic liquids were synthesised from DBU–hexanol–CO_2 (SIL1) and DBU–butanol–CO_2 (SIL2), respectively, and characterised by measuring their melting point, water content, conductivity, viscosity and polarity (Table 1). The viscosities of these solutions were much higher in their ionic form compared to their non-ionic form, the viscosities of DBU–hexanol and DBU–butanol were 7.1 mPa s and 5.1 mPa s, respectively and in ionic form they were 2980 and 1600 mPa s, respectively (Table 1). This is a clear indication that the carbonate formation really occurred. The decomposition points of the SILs were 55 °C for both tested alcohols (hexanol and butanol), whereas the SIL1 exhibited, slightly higher melting point 14 °C compared to the SIL2 whose melting point was 8 °C. This could be related to the chain length of the alcohol (Ejae, 2007). Analogously, the lower viscosity of the SIL1 could be related to the chain length of the alcohol. Some values of physical properties obtained in the characterisation of the SILs used in this work (Table 1) were close to the ones reported in references (Ejae, 2007; Jessop et al., 2005; Phan et al., 2008).

3.2. The composition of wood chips before dissolution

The composition of the native spruce wood and its water content are presented in Table 2. The amounts of the three major components in wood, namely cellulose, hemicelluloses and lignin are consistent with the ones presented in references (Fengel & Wegener, 1984; Sjöström, 1993; Willför et al., 2009).

3.3. Dissolution effect of different SILs

The effect of the wood extractives on the dissolution of wood was studied using, the following wood samples: (1) wood samples which have been pre-extracted using the Soxhlet method, and (2) dried native wood. The dissolution results are presented in Figs. 4 and 5 and Table 3. The SIL1 showed higher dissolution efficiency with about 36 wt.% reduction of the total amount of hemicelluloses in the wood chip compared to the SIL2 which had 14 wt.%, for the native spruce wood. While for the pre-extracted wood sample 15 and 29 wt.% reductions in the hemicelluloses content were achieved for the SIL1 and SIL2 treatment, respectively. This result could be explained by the fact that the lower viscosity of SIL1 compared to SIL2, might improve the mass transfer of fluid in and out

Table 2
The results from wood sample analysis before pretreatment with SILs.

Wood sample	Spruce
Extractives	13 [mg/g] dry mass
Lignin	270 [mg/g] dry mass
Hemicelluloses	260 [mg/g] dry mass
Cellulose	450 [mg/g] dry mass
Inorganics (ash forming matter)	7 [mg/g] dry mass

Sundberg et al. (1996) and Willför et al. (2009).

Table 3
The effect of wood extractives on wood dissolution, at 55 °C, without stirring under normal atmosphere, 5 days.

Wood	SIL	Weight reduction [wt.%]	Reduction in the sugar content [wt.%]
Dried native spruce wood	SIL2	10	14
Dried native spruce wood	SIL1	13	36
Pre-extracted spruce wood	SIL2	10	15
Pre-extracted spruce wood	SIL1	11	29

Table 4
The effect of wood chip size on wood dissolution in SIL1 and in SIL2 at 55 °C, under normal pressure for 5 days, without stirring.

Dried native wood	Weight reduction [wt.%]		Sugar reduction [wt.%]	
	Wood flour	Larger wood chip 30 mm × 30 mm	Wood flour	Larger wood chip 30 mm × 30 mm
SIL2	12	4	29	12
SIL1	10	2	36	10

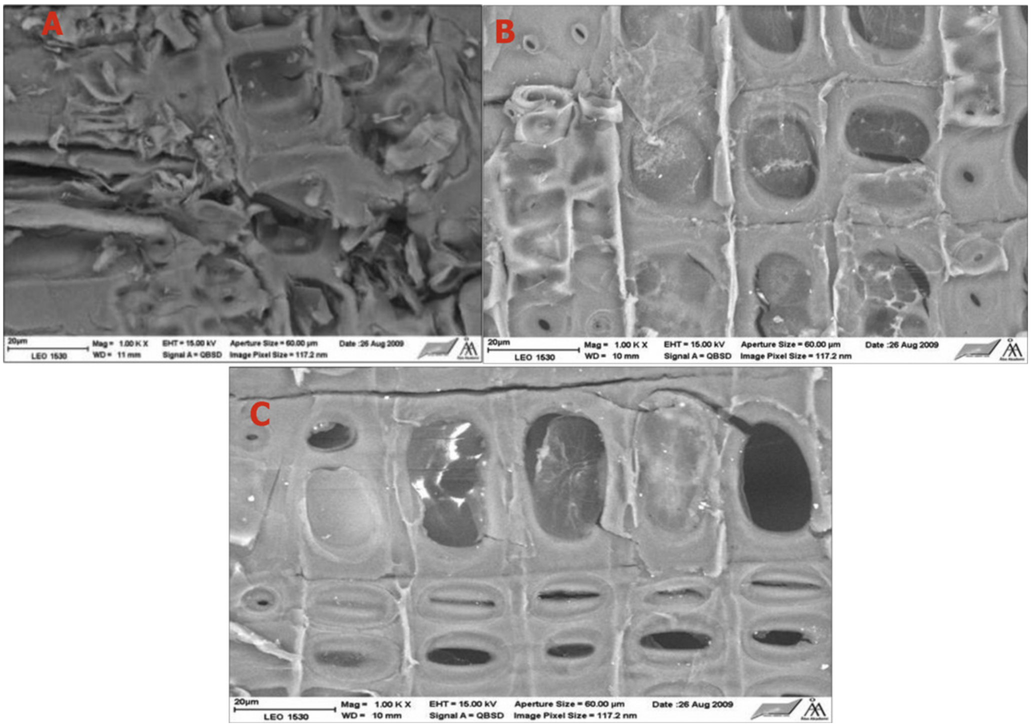


Fig. 6. SEM images of the morphology (A) native spruce wood, (B) wood pretreated with SIL1, (C) wood pretreated with SIL2 for 5 days, the pretreatment was performed at 55 °C under normal atmosphere and pressure.

of the wood chip during SIL treatment. On the other hand, it was only a minor effect of the absence of wood extractives on the dissolution efficiency of the SILs. This indicates that pre-extraction does not improve the dissolution efficiency and it is not necessary. Moreover, a priori removal of the wood extractives did not influence the lignin removal.

SEM morphology of the samples is presented in Fig. 6. It can be seen that after the treatment of wood (*P. abies* spruce chip) with both SIL1 and SIL2 (Fig. 6B and C), the middle lamella becomes clear. This result indicates the dissolution of pectin (also seen as galacturonic acid), with a significant reduction of the sugar content in the wood sample.

3.4. Effect of milling of the wood flour with SIL

Dissolution of the wood chips was studied to see if there is any noticeable effect of the milling of the wood. Wood flour with size about 350 µm was as expected to be more efficient than that performed with the larger wood chips (30 mm × 30 mm). This is likely because of the increased external surface area of the flour and the

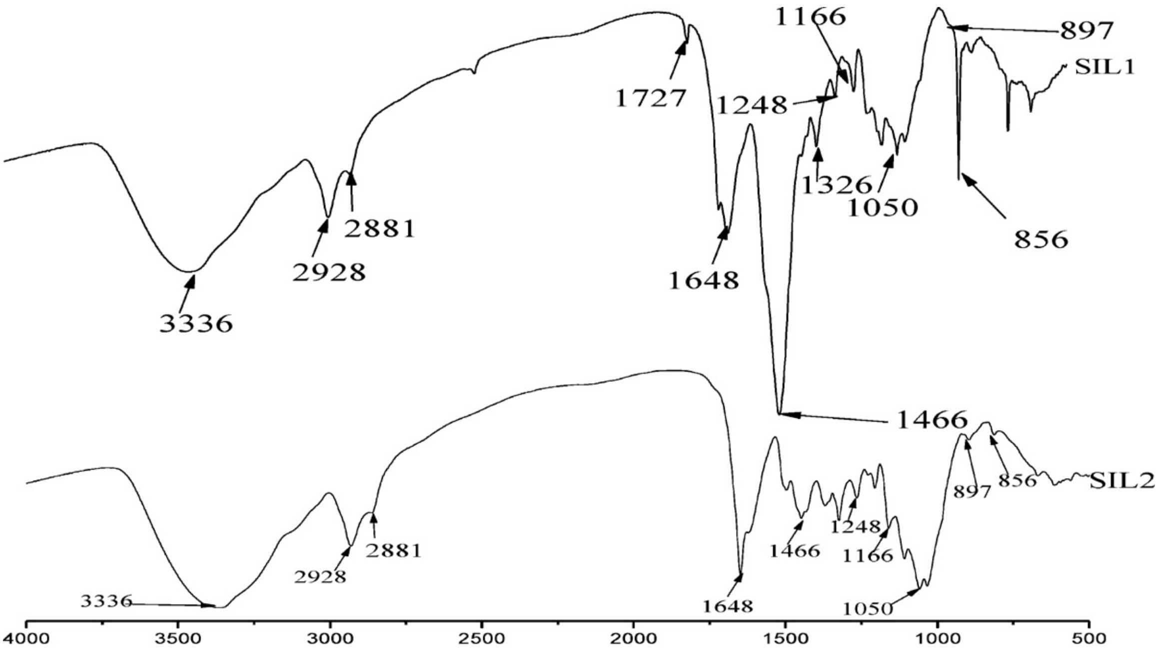


Fig. 7. FTIR spectra of the recovered hemicelluloses form spent SIL1 and SIL2.

increased mechanical breaking down of the internal structure of the wood chips during the milling process. The milling process has been shown to decrease the crystallinity of wood material (Zhao, Kwak, Franz, White, & Holladay, 2006). Furthermore, the amount of glucose after acid hydrolysis was reduced by 6 wt.% with the milled wood compared to the wood chips of the native spruce Table 4. It is assumed that the acid methanolysis process would not break down glucose in the cellulose fiber and thus, the glucose after this treatment is mainly originated from the hemicelluloses (Sundberg et al., 1996; Willför et al., 2009). Therefore, some of the cellulose was also dissolving during SIL treatment, when pre-milled wood was used as raw material. Both the hexanol and butanol SILs were rather neutral in terms of lignin removal. After the treatment of spruce wood with both hexanol and butanol SILs, about 2 wt.% of the lignin in the undissolved wood was removed compared to the native wood.

3.5. FTIR analysis of the recovered hemicelluloses from the spent SILs

The FTIR spectra in Fig. 7 shows spectra of the recovered hemicelluloses from the spent SILs, recovered by the addition of an anti-solvent (methanol) to the spent SIL; their chemical compositions were demonstrated by FTIR in the region of 500–4000 cm^{-1}. Strong broadband due to the stretching of –OH groups occurs at 3336 cm^{-1}. The C–H stretching vibration gave signals at 2931 and 2859 cm^{-1}. It can be observed that both recovered hemicelluloses materials showed the typical signal pattern of hemicellulosic moiety and the bands in the 1200–1000 cm^{-1} region, which are dominated by ring vibrations overlapped with stretching vibrations of side groups C–OH and the glycosidic bond vibration C–O–C (Peng et al., 2009; Xu et al., 2010). The absorbance band observed at 1331 cm^{-1} arises from the C–C and C–O skeletal vibrations. Two peaks at 1727 and 1166 cm^{-1} are observed due to carbonyl stretching vibrations of C=O groups present in anhydride groups and the C–O vibration were also present. In the anomeric region 950–700 cm^{-1}, at 897 cm^{-1}, which is due to the C-1 group frequency or ring frequency, is indicative of β-glycosidic linkages in hemicelluloses, whereas strong peaks at 856 cm^{-1} in spectrum for SIL1 and at 897 cm^{-1} in spectrum for SIL2 are characteristic of R-anomers in side chains (Peng et al., 2009). The recovered hemicelluloses can be of great industrial importance, they can be used for pulping and papermaking. Furthermore, spruce hemicelluloses which are mainly galactoglucomannans (GGM) can be utilized as, for instance, bioactive polymers, hydrocolloids, papermaking chemicals, or coating polymers (Xu et al., 2010).

4. Conclusions

In this study, it was demonstrated that novel switchable ionic liquids, prepared by bubbling CO_2 through a mixture of DBU and alcohol, can be applied for the selective extraction of hemicelluloses from spruce wood.

Total weight reduction of the wood was depended on the wood size and the alcohol used for the preparation of the SIL. With the hexanol-SIL, the weight reduction of the milled spruce was 12 wt.%, while the chip resulted in 4% weight. For the butanol SIL, the corresponding values were 10 wt.%, and 2 wt.%, reductions, respectively. The hemicellulose content was reduced by 38%-wt for spruce treated with butanol SIL and by 29%-wt for spruce treated with hexanol-SIL. The SIL treatment was in reality not very efficient in lignin removal; the residual lignin fraction (extractives free wood) left in undissolved wood after SIL treatment were 16 and 20 wt.% of the total wood mass for the butanol and hexanol SIL, respectively. The non-extracted wood contained 22 wt.% lignin after treatment by both the butanol and hexanol SILs, respectively.

Moreover, the dissolution of wood with switchable ionic liquid was carried out only at 55 °C and at normal pressures. Therefore, less energy was needed compared to many existing wood treatments technologies. Furthermore, the possibility of switching the ionic liquid back to its molecular components gives more possibilities in recycling and reuse of the ionic liquid. These recycling possibilities should be further studied.

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