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Deconstructing Fast Growing Biomass: Grass, Agricultural Residues and Eucalyptus Bark

Ikenna Anugwom[1*],Mattias Hedenström[1], Jyri-Pekka Mikkola[1,2]

[1]LUT RE-SOURCE Research Platform, School of Engineering Science, Lappeenranta University of Technology, Lappeenranta, Finland

[2]Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Finland

[*]**Corresponding author:** Ikenna Anugwom, LUT RE-SOURCE Research Platform, School of Engineering Science, Lappeenranta University of Technology, Lappeenranta, Finland. Email: ianugwom@abo.fi, ikenna.anugwom@lut.fi

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Abstract

Lignocellulosic non-wood biomass was treated in highly diluted, aqueous Switchable Ionic Liquid (SIL) system derived from an alkanol amine (Monoethanol Amine, MEA), an organic superbase (1,8-diazabicyclo- [5.4.0]-undec-7-ene, DBU) and 'switched' by SO2. Herein the aim was to demonstrate the power of SIL treatment on non-wood biomass as a sustainable, environmentally friendly and cost-efficient approach. The primary fraction obtained upon hydrated SIL fractionation process contains hemicelluloses as well as cellulose-rich pulp with very low lignin content. Also, a simple model was used to describe the weight loss obtained for the treated wood. The chemical analysis results revealed that substantial removal of lignin occurred which is consistent with results of SIL treatment of wood. The endeavor was to assess the potential of this type of poorly explored biomass types as a source of potentially valuable raw materials.

Introduction

Switchable Ionic Liquids (SIL) have more recently been intensively studied as promising solvents for the deconstruction of Nordic woody biomass and the results have demonstrated the feasibility of the concept under relatively mild conditions and at short treatment times [2-6]. SILs are solvents that undergo ionic to non-ionic transformations in the presence and absence of a reacting compound, a so-called 'Trigger' [2,7,8]. Additionally, SILs have been synthesized from low-cost chemicals such as Mono-Ethanol Amine (MEA) together with an organic superbase like amidine 1,8-diazabicyclo- [5.4.0]-undec-7-ene (DBU). Moreover, a typical trigger can be obtained from industrial flue gases, such as CO_2 or SO_2. SILs as solvents for lignocellulosic material can facilitate selective extraction or selective enrichment of the material, depending on the choice of the trigger (CO_2 or SO_2) alkanol amine or superbase. 'Traditional' ionic liquids, on the other hand, have also been widely studied as potential fractionation solvents for lignocellulosic materials due to their dissolution power as well as the desire to discover alternative, environmentally friendly processing practices upon appropriate choice of cations and/or anions. Typical ILs are salts composed of organic cations and organic or inorganic anions and frequently demonstrate melting points below 100°C. ILs also exhibit high thermal and chemical stability as well as a wide liquidus range [9]. In fact, many ILs are able to dissolve lignocellulosic material or one of its major components, cellulose, hemicelluloses, and lignin [10-15].

There is great, yet to be discovered potential in lignocellulosic biomass as a raw material for a variety of value-added products, albeit broad research efforts are required to ensure the feasibility of lignocellulosic biorefineries. One of the major limitations of many biorefinery concepts is the lack of an efficient biomass processing and separation tool, thus compromising the attractiveness of this sector for investors. Consequently, studies on biomass pretreatment and fractionation aim at creating tools to efficiently overcome the recalcitrance of lignocellulose and reduce the overall costs of biorefinery processes [16-21].

As we know, lignocellulose is made up of three main components, namely, cellulose, hemicelluloses, and lignin. The

separation of each fraction from lignocellulose is a vital first step when aiming at maximal valorization of low-cost feedstocks and producing valuable commodities like Hydroxymethylfurfural (HMF) and levulinic acid [22,23] or, furfural and xylitol [24,25] as well as phenolic compounds or other lignin depolymerization products [26]. The SIL solvents offer a new and attractive alternative that enables mild deconstruction of biomass into cellulose, hemicellulose, and lignin as separated fractions [1-6]. Consequently, their physical and chemical properties allow their use for biomass processing in pretreatment and/or extraction processes. SILs have the ability to dissolve biomass by efficiently disrupting the complex network of non-covalent interactions between carbohydrates and lignin [27,28]. Generally speaking, complete biomass dissolution is attainable during the treatment but this might not improve the feasibility of the process. After pretreatment under predefined conditions (temperature, residence time, and biomass-to-solvent ratio), a typical approach is to add an anti-solvent to the solution mixture, promoting biomaterial precipitation as the recovered material. Besides carbohydrates, lignin and other soluble compounds are partially extracted to the liquid phase [29]. Lignin can be further recovered by acidification of the anti-solvent/IL medium [13,30]. From the regenerated material, hemicellulose and cellulose can be obtained as separated fractions using specific solvents to complete the fractionation process [30-33].

Wood bark makes up a substantial fraction of wood. Upon wood pulping, the bark is removed from the logs and this mill residual is often burnt for energy. In addition, being considered a valuable solid biofuel, bark could also be transformed to valuable products and should be considered for its potential in terms of its specific chemical composition and properties [34]. Therefore, valorization of bark, in line with the biorefinery vision, should be studied. Bark is often very rich in extractives (both organic solvent and water soluble) and polyphenolics, but it can also contain a high amount of inorganic material [35]. Structurally bark have complex tissues and their sampling, characterization and processing, poses a lot of unknown difficulties usually during processing [36]. In recent years, growing efforts has been based on the use of new waste sources, with aim to obtain biological active compounds which can be applied in different fields and applications. These lignocellulosic residual (by-products) are compatible with the environment and could provide the sources for specialty chemicals [37]. Examples of such material are the so called Cereal waste products (Wheat straw) are annually produced renewable fibers and they are abundantly available in large volume worldwide. There is an estimated worldwide production of 682 million metric tons, of which 9 million metric tons is from the EU alone [37].

The aim of the present investigation relies on taking advantage on the versatility of the Short Time High Temperature (STHT) procedure [5] and verifying its suitability for other types of lignocellulosic biomass than soft or hardwood. Since these other types of biomass are fast growing and they are abundantly available. In addition, lignin extraction capacity was quantified as well as the possible changes in the crystallinity of cellulose.

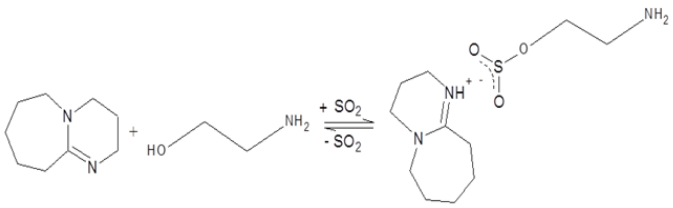
Experimental Section

Materials

1,8-diazabicyclo- [5.4.0]-undec-7-ene (DBU) (99%) and monoethanol amine (99 %) were used as received from Sigma Aldrich. SO_2 (99.998%, H_2O < 3 ppm) were provided by AGA Oy (Linde group, Finland). The isopropyl alcohol (2-propanol) (Merck, 99%, USA) applied as the anti-solvent and for washing of the fractions was used as received. The following chemicals were used for silylation: HMDS (hexamethyldisilazane 99% Fluka), TMCS (trimethylchlorosilane 98% Fluka) and pyridine (99% Sigma). The raw materials of this study were wheat straw obtained from the Swedish University for Agricultural Sciences Umeå, Eucalyptus bark (*Eucalyptus globulus*) provided by Dr. Hardy Agustin Medina Sanhueza (R.U:t 76.098.157-5 Fundo quilamapu, Nueva Imperial, Chile) and Bamboo (*Bambusa bambos* L.) supplied by Dr. Dhanapati Dek Tezpur University (Napaam, India).

Switchable Ionic Liquid Preparation

The SIL (SO_2 switched DBU MEASIL) was prepared from DBU, MEA, and SO_2 by methods described in detail previously [2,7,38]. An equimolar mixture of DBU and MEA was added into a three-necked flask, the flask is in a cooling bath since upon addition of the acid gas, an exothermic reaction occurs. In practice, SO_2 was bubbled through the mixture under rigorous stirring. The readily exothermic reaction was allowed to proceed freely upon sparging through the mixture until the reaction to form the SIL was completed (Scheme 1). After the reaction was completed, the as formed SIL was kept in a freezer to exclude the possibility of any decomposition until the moment it was needed.



Scheme 1: The structure of the SIL, SO_2 switched DBU MEASIL. Adapted from [1].

SIL Treatment of Biomass in a Batch Reactor in the Absence of Stirring

For the treatment for the biomass, a batch autoclave (Parr Inc., USA) with an inner volume of 300 mL provided with an electric heater and an internal thermocouple was used. The procedure (the STHT method) has been previously described in detail [5]. The procedure is carried out as follows: 30 g of the native biomass sample (no pretreatment) was cut to chips (ca 2.3 cm × 8 cm) and submerged in a mixture of 150 g SO_2 switched DBU MEASIL ***and 90 g water (a wt-ratio of 1:5:3 biomass-***SIL***-water). The mixture was placed in a reactor and heated to 160°C for 2 hours. No stirrer was applied in order to avoid mechanical fibrillation of the sample during the treatment.*** Upon completion of the treatment, the undissolved residue was washed with a mixture of propanol and water until there was no visual evidence of any traces of the SIL remaining. Also, periodical test for traces of sulphate ion was carried out in the filtrate using 10% barium chloride. The spent water-propanol mixture used for washing was collected and the dissolved compounds were recovered upon concentration of the solvent and precipitation with methanol.

Determination of Cellulose Content

The carbohydrate (cellulose) content was determined by acid hydrolysis. Upon this procedure 0.075 mL of 72% H_2SO_4 was added to 10 mg (exact amount) of solid sample in a test tube that was kept at room temperature for about 120 min. The secondary hydrolysis of the sample was conducted under vacuum in an autoclave at 125°C during 90 min. 1-2 droplets of bromocresol green indicator was 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. Consequently, 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: 150µL HMDS (hexamethyldisilazane 99% Fluka), 80µL TMCS (trimethylchlorosilane 98% Fluka) and 100µL of pyridine (99% Sigma) and the solution was allowed to stand overnight and analyzed by gas chromatography [39,40].

Determination of Hemicelluloses

Acid methanolysis of the non-woody biomass sample was performed to analyze the hemicelluloses and pectin as follows: 2 mL of 2 M HCl in dry MeOH was added to 10 mg of sample and heated to 105°C for 5 h [39]. The excess of acid was then neutralized with pyridine. An internal standard 4 mL of (0.1 mg/mL Resorcinol) was added to the solution. Thereafter, drying under nitrogen was carried out and the samples were silylated as described above. Finally, the samples were analyzed by Gas Chromatography (GC) as described below.

Gas Chromatographic Analysis for Carbohydrates

About 2µL 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, 320µm, and 0.17µm, respectively. The following temperature programme was applied: 100°C-4°C/min-175°C followed by 175°C-2°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 of two parallel samples containing equal amounts (0.1 mg) of the above-mentioned sugars and their derivatives was performed. 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 [39,40].

Lignin Analysis

The lignin content was determined using Klason lignin method with slight modification so that the boiling for 4 hours to complete hydrolysis of the polysaccharides was replaced with an autoclave treatment at 125°C at 1.4 bar for 90 mins [41,42]. Further, the ash content was determined in line with the procedure developed by the National Renewable Energy Laboratory's (NREL) Analytical Procedures[43].

Scanning Electron Microscopy (SEM)

Images of the morphology of the non-woody sample before and after SIL treatment as well as the recovered solid materials from the spent SIL and wash solvent 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.

Fourier Transformed Infrared Spectroscopy

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}.

Crystallinity Changes for Cellulose

Fourier Transformed Infrared Spectroscopy (FTIR) techniques have earlier been successfully applied in the characterization and the structural analysis of cellulose-based polymers. Typically, cellulose characterized as crystalline I, crystalline II and amorphous cellulose (unevenly ordered cellulose chains) can be found [3,44,45]. A comparative spectral study was performed in the region of 850-1500 cm^{-1} and results were obtained by comparing the bands at 1420, 893-897 and the band at 1111 cm^{-1}. The Total Crystallinity Indices (TCI) were obtained from the ratio of the absorption bands at 1420/893 cm^{-1} while the Lateral Order Indices (LOI) were obtained from the absorbance band ratios at 1375/2900 cm^{-1}. These spectral ranges were proposed by Nelson and O'Connor [44] and were used to study the crystallinity changes.

Nuclear Magnetic Resonance Spectroscopy

The ^{13}C CP/MAS NMR spectra were acquired on a Bruker Avance III spectrometer (Bruker Biospin, Germany) operating at 125.75 MHz and equipped with a 4-mm magic angle spinning (MAS) probe. Samples were moisturized by adding 50 wt% deionized water before packing them into 4mm ZrO_2 rotors. 1 ms contact time was used and 4096 scans were collected for each sample at a spin rate of 10 kHz. A Gaussian window function was used in the spectral processing performed in Topspin 3.2 (Bruker Biospin, Germany). Samples were analyzed at ambient temperature [5].

Results and Discussion

The weight of the biomass samples as well as the SIL were monitored at each and every process step (SIL treatment, washing and drying of the undissolved fraction; recovery and washing of the dissolved fraction) in order to obtain a reliable mass balance. It was also verified that no substantial losses of material occurred during handling and SIL treatment. The chemical composition of dissolved (and later precipitated) as well as non-dissolved fractions were compared with that of their native counterparts. A 49 % weight reduction (on dry weight basis) was recorded in case of Bamboo after 2 hours of SIL fractionation (the STHT procedure, on dry weight basis). In case of bark and wheat straw, weight reduction of 50 and 48 %, respectively, was recorded (the STHT procedure, on dry weight basis).

- **Characterization of the Non-dissolved Residuals**

Chemical Analysis

Compositional analysis of cellulose, hemicellulose, and lignin was performed directly on the non-treated (native) biomass. It was found that the cellulose and lignin contents were in good agreement with previously published data in literature [36,46,47]. The native wheat straw contains 40.8% cellulose, 21.8% hemicelluloses, and 21.3% lignin by mass. In case of Bamboo, 44.5% cellulose, 15.8% hemicelluloses, and 24.3% lignin by mass was recorded. Eucalyptus bark contained 47.7% cellulose, 21.8% hemicelluloses, and 22.4% lignin (Table 1). Meanwhile the rest of biomass cell wall components are comprised of non-lignin phenolics and proteins that are not detected by analytical methods used in this work. After the treatment of the biomass with SIL at 160°C for 2 hours, compositional analysis was performed on both the non-dissolved, as well as the regenerated fractions. Methanol was used as the anti-solvent.

Component	Bark (wt-%)		Bamboo (wt-%)		Wheat straw (wt-%)	
	Native	SIL treated	Native	SIL treated	Native	SIL treated
Cellulose	47.7	89.2	44.7	73.7	40.7	66.7
Hemicellulose	24	7.3	24	9.1	30.1	10.8
Lignin	22.3	0.9	24.3	9	21	13
Extractives	1.5	0	1.4	0	1.8	0
Ash	1.1	0.85	1	0.8	1	0.9
Total	84.2	98.4	86.7	92.8	91.6	91.5

Table 1: Chemical compositions of the biomass before and after SIL treatment.

As expected, the treatment resulted in increased relative amount of cellulose due to dissolution of lignin and hemicellulose. In case of Eucalyptus bark, the treated sample (mass loss 48 wt-%) contained 89.2 wt-% cellulose, 7.3 wt-% hemicellulose and 1 wt-% lignin. Further, in case of Bamboo, the treated sample (mass loss 49 wt-%) contained 74 wt-% cellulose, 9 wt-% hemicellulose and 9 wt-% lignin. Finally, in case of wheat straw, the treated sample (mass loss 50 wt-%) contained 67 wt-% cellulose, 11 wt-% hemicellulose and 13 wt-% lignin. Thus, 88 wt-% of hemicelluloses

and 99 wt-% lignin was removed in case of Eucalyptus bark, whereas in case of Bamboo and Wheat straw, 91 wt-% of hemicelluloses and 94 wt-% of lignin was removed (Tables 1 & 2).

Materials	Weight loss biomass, %	Cellulose, g	Sugars, g*	Lignin, g	Sugar removal, %	Lignin removal, %
SIL treated bark Native bark	48 ± 3 N/A	13.9 ± 0.8 14.3 ±1.3	1.1 ± 0.4 3.0 ±1.2	0.1 ±0.7 7.2 ± 1.1	88 N/A	99 N/A
SIL treated bamboo Native bamboo	49 ± 1.9 N/A	11.3 ±0.6 13.4 ± 2	1.4 ±0.3 4.7 ±1.1	1.4 ±0.1 7.2 ±1	91 N/A	94 N/A
SIL treated wheat straw Native wheat straw	50 ± 1.5 N/A	10.0 ±0.9 12.2 ±1.6	1.6 ±0.7 5.4 ±1.5	2.0 ±0.3 9.0 ±1.2	91 N/A	94 N/A
*hemicelluloses are reported as sugars. N/A: not analyzed						

Table 2: Compositional analysis of the SIL treated biomass.

The solid residues recovered from the spent SIL amounted to about 77.9 wt-%. In general, the results obtained upon chemical analysis performed in this work (acid hydrolysis, methanolysis and Klason lignin methods) were consistent with those presented in our earlier work with soft and hardwood (Refs. [48,49]).

All in all, the non-dissolved wood residue contained 67 wt-%,73 wt-%, and 89 wt-% cellulose after being subject to the SIL treatment, for Wheat straw, Bamboo, and Eucalyptus bark, respectively (Table 1). The relative amount of cellulose was clearly increasing while hemicelluloses, lignin and extractives (and ash elements) were removed. Thus, more glucose per mass was obtained during acid hydrolysis of the non-dissolved wood residue. Subsequently, only minor amount of cellulose (yielding glucose) was dissolved during the SIL treatment.

Structure of the SIL treated wood

The morphology of the non-treated (native) and SIL treated bamboo, bark and wheat straw are presented in Figure 1. We can clearly observe that the treated biomass was fibrillated, indicating dissolution of hemicelluloses. Upon fibrillation, the strands of each fiber can be seen at the presented magnification [3]. Thus, this supports the observations obtained from chemical analysis that hemicelluloses and lignin were partially dissolved while cellulose remained essentially untouched (Figure 1).

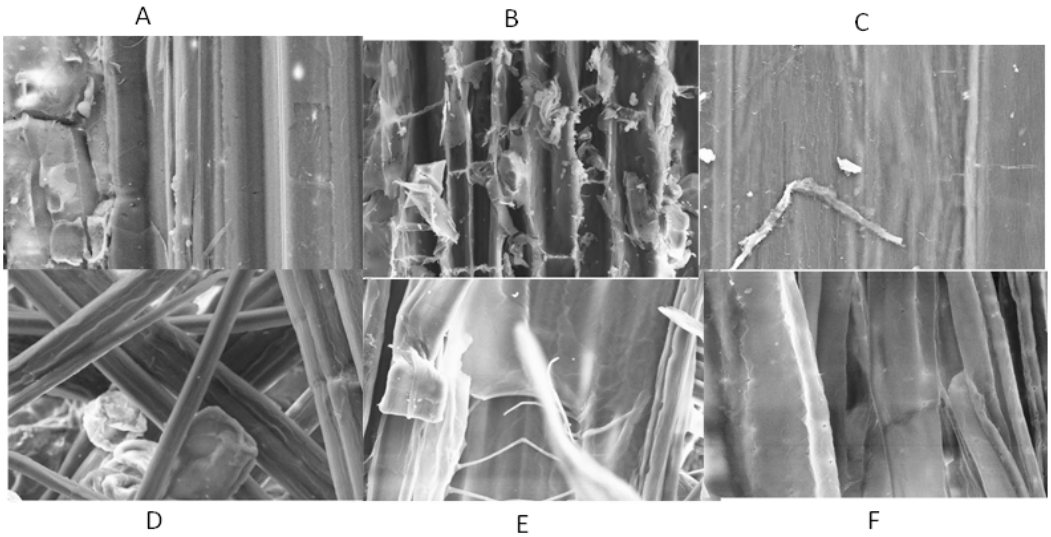


Figure 1: SEM images of the A) native Bamboo, B) Eucalyptus bark, C) Wheat straw. D, E, F depicts the corresponding SIL treated samples. (For all sample magnification:1KX, size 20µm).

FTIR analysis of native and treated biomass

The main chemical bond vibrations of native Wheat straw and SIL treated Wheat straw are detected in the region of 1800-800 cm^{-1}. Therefore, analysis of the region would be used to describe changes that occur due to the SIL treatment. Absorption bands at 1376, 1161, 1107, 1049 and 898 cm^{-1} are attributed to carbohydrates in native Wheat straw. The band at 1376 cm^{1} relates to a bending of C-H group in cellulose. The C-O asymmetric band could be observed at 1161 cm^{-1} [50,51].

The band at 898 cm^{-1} corresponds to the vibration of β-glycosidic C-H deformation with a ring vibration contribution (hexoses/pentoses) characteristic of glycosidic bonds in carbohydrates [50-52]. Lignin characteristic bands visible in native Wheat straw spectrum are at 1508, 1458 and 1420 cm^{-1}, respectively, associated with aromatic skeletal vibrations and bands at 1508 and 1458 cm^{-1} are assigned to C=C stretching vibration and C-H deformations (CH and CH_2) in phenol rings, respectively [50-52]. Further, the symmetric bending vibrations of C-H bonds in methoxyl groups of syringyl and guaiacyl units correspond to the 1420 cm^{-1} band [30,50,52]. Also, the strong absorption at 1251 cm^{-1} is originated by the C-O stretching of acetyl groups present in hemicellulose molecular chains [50-53] whereas the vibration band at 1734 cm^{-1} was assigned to ester-linked acetyl, feruloyl and p-coumaroyl groups between hemicellulose and lignin. Furthermore, bands at 2852 and 2920 cm^{-1} are attributed to asymmetric and symmetric C-H stretching of CH, CH_2 and CH_3 groups [51]. The SIL treated Wheat straw contains essentially only carbohydrates due to extensive lignin removal. This is obvious since absorbance of the lignin bands at 1508, 1458 and 1420 cm^{-1} decreased demonstrating lower lignin content compared to native wheat straw. The vibration band at 1734 cm^{-1}, assigned to ester-linked acetyl, feruloyl and p-coumaroyl groups between hemicellulose and lignin, was not observed in this sample. Bands characteristic of carbohydrates at 1376 and 1161 cm^{-1}, respectively, can be observed in the spectrum of SIL treated Wheat straw. The absorption peak at 1066 cm^{-1} observed is coming from the C–O–C ether linkage, i.e. the skeletal vibration of both pentose and hexose unit contribution from hemicellulose and cellulose. The peak at 1046 cm^{-1} is attributed to hemicellulose absorptions explicitly to C–O stretching in C–O–C linkages. Arabinosyl side chains are represented by the absorption peak at 996 cm^{-1}. Vibrations related to pyranosyl rings at 1112 cm^{-1} corresponds to the C–OH skeletal vibration, while 1061 cm^{-1} is associated with the C-O-C ether linkage of skeletal vibration and 1035 cm^{-1} is attributed to C–O stretching vibration characteristic of cellulose are found in the spectra of the SIL treated Wheat straw. The band at 1376 cm^{-1} was very pronounced and the glycosidic bond vibration was detected at 897 cm^{-1}. The band at 1320 cm^{-1} has a contribution of C–C and C–O skeletal vibrations. Additionally, a band at 998 cm^{-1} indicates the existence of arabinose (arabinosyl side chains). It is worth mentioning the absence of the band at 1734 cm^{-1} in the SIL treated wheat straw, which responsible for the hemicellulose-lignin interaction in pulp, (Figure 2) [31,50-53].

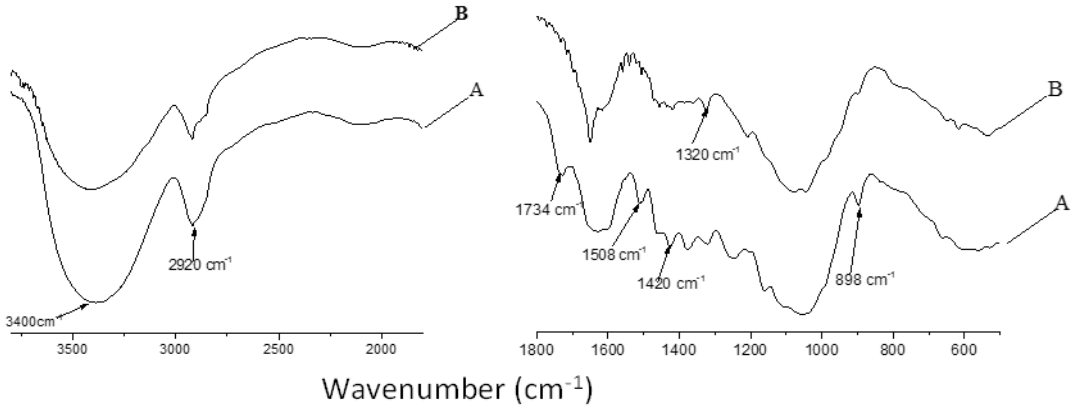


Figure 2: FTIR spectra for A, native wheat straw and B SIL treated wheat straw.

Let us now discuss the changes that occur during the SIL treatment of Eucalyptus bark. Characteristic assignment of hemicellulose at 1738/1734 cm^{-1} (C = O conjugates in xylans) was only observed in native bark, while in the spectra of the SIL treated bark this peak was absent, confirming substantial removal hemicelluloses (Figure 3). A gradual decrease in intensities in the regions comprising the aromatic ring vibration and the C = O stretch around 1600 cm^{-1} as well as the aromatic skeletal vibration in lignin at 1505/1511 cm^{-1} are common in bark (evidently lignin) but these peaks are not visible in the SIL treated sample. Small differences in the intensity of the peak at 1375 cm^{-1} can be related to the C-H deformation in cellulose and hemicellulose, while a significant decrease of the peak at 1325 cm^{-1} was detected (C-H vibration in cellulose and C1-O vibration in syringyl derivatives). Low intensities were detected at around 1268 and 1230 cm^{-1} that can be assigned to guaiacyl derivatives (C-O stretch in lignin and C-O linkage in guaiacyl aromatic methoxyl groups). When comparing the spectra of the native and SIL treated eucalyptus bark, it is rather evident that the SIL treatment resulted in reduced intensities for a number of bands that are associated with aromatic and ether-containing structures: aliphatic and phenolic OH groups (3500 to 3100 cm^{-1}), C-H stretching in methyl and methylene groups (2940, 2870 cm^{-1}), and aromatic skeletal vibrations (1610, 1510, and 1460 cm^{-1}) which are characteristic peaks of lignin (Figure 3)[30,50-53].

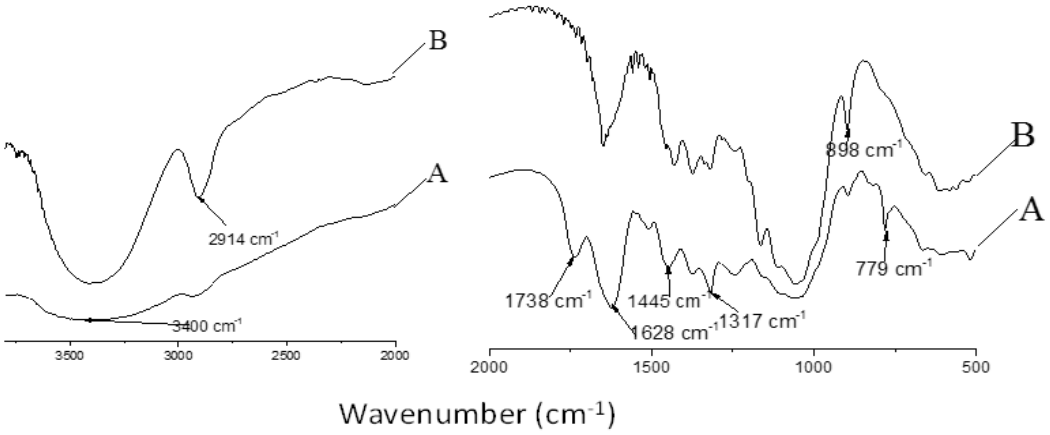


Figure 3: FTIR spectra for native Eucalyptus bark (A) and SIL treated Eucalyptus bark (B).

The FTIR spectra of both the native Bamboo and SIL treated sample represent more or less similar trends as indicated in Figure 4. Both distinctive and broad O-H stretching as well as C–H stretching absorption bands are observed at around 3406 and 2941 cm^{-1}, respectively. In the finger print region between 800 and 1800 cm^{-1}, the non-conjugated C=O stretch (in hemicellulose) is observed at 1739 cm^{-1} in spectra native bamboo while this is absent in the spectra for the SIL treated Bamboo. Analogous results were obtained by Sun et al. [13] and it could be attributed to the removal of hemicellulose during the SIL treatment. Comparing the spectra of native Bamboo bark and the SIL treated sample, the characteristic peaks for lignin at 1604, 1510, and 1465 cm^{-1}, respectively, are not observed in the spectra for SIL treated Bamboo. The absence of lignin characteristic peaks confirmed the delignification of the SIL treated Bamboo. The peaks which appear at around 1328, 1159, 1037, 1056 and 896 cm^{-1}, respectively, are mainly attributed to the carbohydrates which are present in both spectra [54]. Bamboo lignin contains high proportion of syringyl residues which can be observed by an intense single peak at 832 cm^{-1} and more intense peaks at 1128 and 1320 cm^{-1} in the FTIR spectrum for the native Bamboo [55].

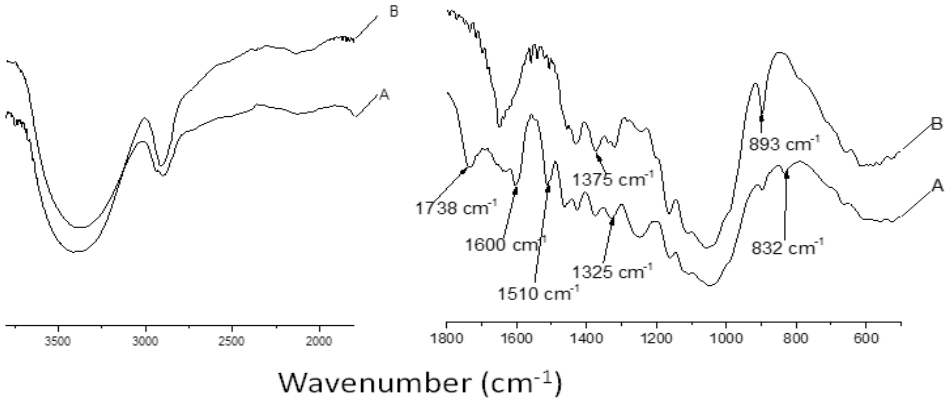


Figure 4: FTIR spectra for, native Bamboo (A) and SIL treated Bamboo (B).

Crystallinity Analysis

The changes in crystallinity of the biomass samples before and after treatment with SIL were analyzed by means of FTIR according to crystallinity indices proposed by O'Connor et. al. [44,45]. This method has been successfully applied to characterize the structure of cellulose-based biopolymers composed of either crystalline cellulose I or II as well as their mixtures [44,45,56,57]. The crystallinity study focuses mainly on determining the absorption ratios of the bands at 1375/2902 and 1420/893 cm^{-1}, thus giving the Total Crystallinity (TCI) and Lateral Order Indices (LOI), respectively. In such processes, a decrease in the crystalline index should occur, hinting conversion of cellulose I structure to cellulose II. The broad absorption signal observed at 3400 cm^{-1} can be assigned to the –OH intra- and intermolecular stretching modes, whereas the band at 2910 cm^{-1} it originates from the C-H stretching. Likewise, the band at 1377 cm^{-1} can be assigned to the C-H bending, 1423 cm^{-1} to the CH_2 symmetric bending and 898 cm^{-1} to the C-O-C in plane symmetric stretching [44,45,56,57]. The higher index value represents the material has a higher crystallinity and ordered structure. As shown in (Table 3), after the SIL treatment, the LOI of Wheat straw increased from 0.75 to 1.0, and the TCI of Wheat straw significantly decreased from 0.26 to 0.04. On the other hand, the LOI of Eucalyptus bark decreased vastly from 2.5 to 0.5, and the TCI decreased from 1.6 to 0.7. Analogously, the LOI of bamboo decreased from 1.2 to 0.53, while the TCI of bamboo showed a slight increase from 0.47 to 0.58. This indicated that the crystalline cellulose has to a large extent been transformed into amorphous form.

Sample	TCI (1377/2910 cm^{-1})	LOI (1423/898 cm^{-1})
Native Bamboo	0.47 ± 0.005	1.2 ± 0.003
SIL treated Bamboo	0.58 ± 0.003	0.53 ± 0.001
Native Eucalyptus Bark	1.6 ± 0.009	2.5 ± 0.002
SIL treated Eucalyptus Bark	0.7 ± 0.009	0.5± 0.001
Native Wheat straw	0.26 ± 0.009	1.12 ± 0.003
SIL treated Wheat straw	0.04 ± 0.01	0.69 ± 0.009

Table 3: IR crystallinity indexes data of the SIL treated and non-treated biomass.

Nuclear magnetic resonance spectroscopy (^{13}C NMR) of the processed wood (non-dissolved fraction)

^{13}C CP/MAS NMR spectra of the undissolved material after SIL treatment in different biomass types were compared against each other's native untreated counterpart. Signals from cellulose appear in the region between 63 and 106 ppm for all samples, annotated C1-C6 in Figure 5A. The signal at 89 ppm originates from C-4 of the highly ordered cellulose of the crystallite interiors while the broader upfield signal at 84 ppm is assigned to the C-4 of disordered cellulose [58,59]. The signals at 21 and 173 ppm, marked Ac and C=O in Figure 4A, assigned to the methyl and carbonyl carbons of acetyl groups attached to hemicelluloses are clearly visible in the native untreated sample of all biomass types. Lignin peaks usually appear in the region of 125 - 160 ppm with

the exception of the methoxy peak which is located at 56 ppm. Comparing the peak intensities for the untreated and treated samples, it is clear that lignin and hemicellulose fractions have been almost completely depleted after the SIL treatment, leaving only the cellulose peaks as the dominating features of the spectra (Figure 5). The barely visible peaks observed between 145 - 185 ppm in the treated samples can be attributed to very small amounts of residual lignin but also to spinning side-bands originating from the intense cellulose peaks. Even though the NMR data only should be considered semi-quantitative, the result can nevertheless be interpreted as to reflect the nearly complete removal of lignin as well as hemicellulose from the biomass samples.

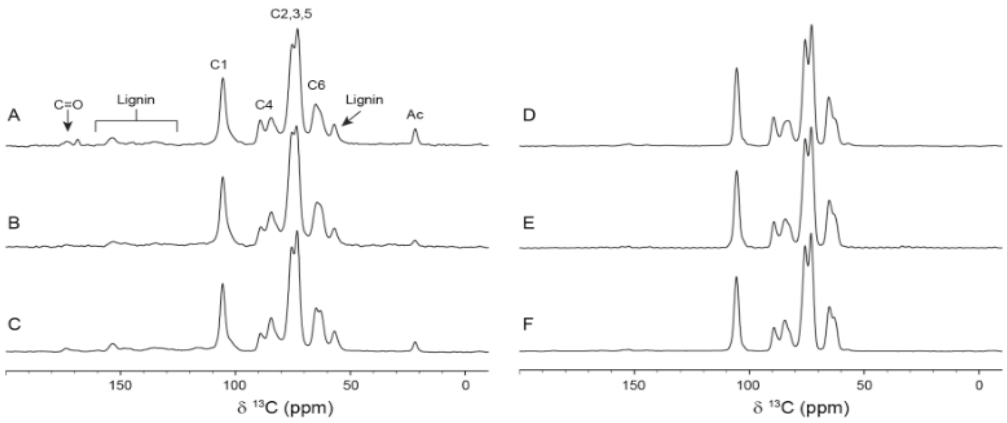


Figure 5: ^{13}C CP/MAS spectra of untreated and SIL treated biomass samples. A-C Untreated Eucalyptus bark, Wheat straw and Bamboo, respectively. D-F Corresponding samples after SIL treatment.

Recovered material from spent SIL on biomass

After the SIL treatment of the biomass materials, addition of methanol to the spent SIL, induced precipitation of the dissolved materials. The precipitates were washed with methanol several times to ensure the removal of the SIL, followed by drying and analysis using acid methanolysis followed by GC analysis to qualify the hemicellulose fraction of the material. The main component found in the recovered material was hemicellulose and lignin, accounting for about 80 wt-% of the total material.

The solid precipitated material was analyzed using FTIR and the results unravel the absence of the characteristic peaks for cellulose at 1035 cm^{-1} (C-O stretching vibration characteristic for cellulose) and at 1161cm^{-1} (the C-O asymmetric band). Moreover, the changes at 1376cm^{-1} (bending of C-H) and 1320 cm^{-1} (C-C and C-O skeletal vibrations), 1437cm^{-1} (CH_2 scissoring motion) confirmed that the recovered materials from the spent SIL were mainly lignin and hemicelluloses. Furthermore, signals appearing at the fingerprint region for both lignin and hemicelluloses at 1240, 1460, 1510, 1590, 1627, and 1730 cm^{-1}, respectively, have a rather strong signal which is an indication that the recovered material is rich in both lignin and hemicellulose but no extraction or dissolution for cellulose took place during the SIL treatment of the biomass (Figure 6).

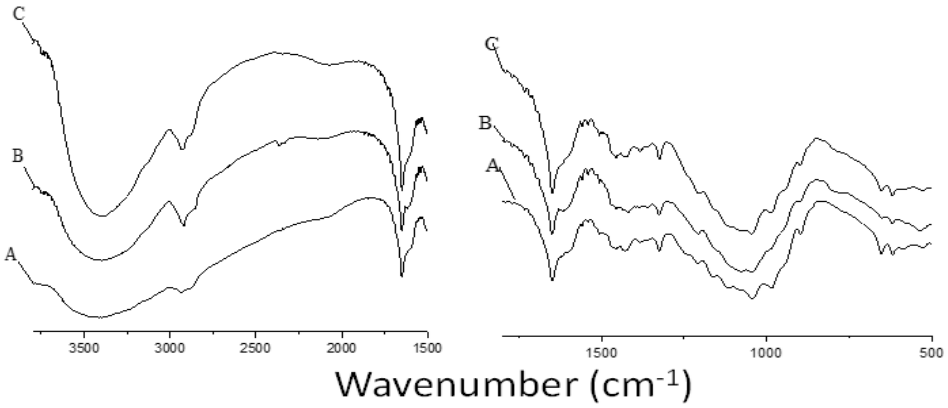


Figure 6: FTIR of the recovered materials from spent SIL; Eucalyptus bark (A) Wheat Straw (B) and Bamboo (C).

Conclusions

We have herein demonstrated that switchable ionic liquids, specifically of the SO_2 switched DBU MEASIL can also be used to fractionate other lignocellulose than soft or hard wood. Consequently, grass, agricultural residues and eucalyptus bark were treated successfully. In most literature cases when ionic liquids are used to process biomass, milling of the biomass sample into smaller particles has been performed. This will, consequently, reduce the mass transfer limitations whereas our SIL process uses big chunks for material (chips), thus reducing the energy demands of this process step. The SIL treatment for Eucalyptus bark resulted in 48 wt-% as the non-dissolved fraction (of which 89.2 wt-% was glucan, 7.3 wt-% hemicelluloses and 1 wt-% lignin), while also in case of Bamboo 49 wt-% of the biomass remained in the non-dissolved fraction (of which 73.7 wt-% was glucan, 9 wt-% hemicelluloses and 9 wt-% lignin). Still, in the case of Wheat straw, again 50 wt-% remained in the non-dissolved fraction (of which 67 wt-% was glucan, 11 wt-% hemicelluloses and 13 wt-% lignin).

Approximately 77.9 wt-% of the dissolved material was recovered from the spent SIL upon addition of an anti-solvent. The non-dissolved biomass obtained as the result of the SIL treatment, contains cellulose-rich material with similar FTIR spectra as that of pure cellulose. During SIL treatment, the crystalline form of cellulose changed from cellulose I to cellulose II. The NMR analysis results confirmed the production of lignin and hemicellulose free pulp using SIL as solvent of fast growing biomass types. Furthermore, SEM images support the conclusion that the structure has and morphology of biomass changed resulting into a more homogeneous macrostructure. The fractionation procedure introduced herein provides an alternative to enrich and extract useful biomass fractions usable in further processing to chemicals and fuels.

Highlights

- Deconstruction of Fast growing biomass and pulping residuals
- Switchable ionic liquid aided delignification of fast growing biomass
- Production of lignin free pulp
- Valorization of poorly explored biomass types as potentially valuable raw materials
- Verifying the suitability Short Time High Temperature (STHT) procedure for other types of lignocellulosic materials

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