Acidolysis of Wood in Ionic Liquids

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Three wood species including *Eucalyptus grandis* (E. grandis), Southern pine (S. pine), and Norway spruce thermomechanical pulp (N. spruce TMP) were dissolved in the ionic liquid (IL) 1-allyl-3-methylimidazolium chloride ([Amim]Cl), and then they were pretreated with small amounts of hydrochloric acid, as a function of time. The materials regenerated from the IL solutions were determined to contain significantly higher amounts of lignin than the original wood. Detailed analyses of the recovered IL revealed the presence of typical wood degradation compounds, such as 5-hydroxymethylfurfural, furan-2-carboxylic acid, catechol, methylcatechol, methylguaiacol, acetoguaiacone, and acetol. The acidic pretreatment of these wood species in IL resulted in not only the near-complete hydrolysis of cellulose and hemicelluloses but also in a significant amount of lignin degradation. Aqueous reactions (under identical acid concentrations) showed a remarkably lower efficiency, demonstrating that ILs offer a unique environment for the acid-catalyzed dehydration chemistry, which is known to occur when polysaccharides and/or wood are subjected to an acid treatment.

Introduction

Ever-growing energy demands and environmental concerns have prompted increasing amounts of work toward developing convenient and efficient biorefinery platform technologies for converting biomass to biofuels, valuable chemicals, and biomaterials.[1] Currently, major advancements have been made in this field by biological and chemical approaches, which are initiating a promising route for the creation of a new domestic biobased industry.[2] For example, Dumesic and co-workers reported on a pathway for the production of dimethylfuran from fructose, which can be obtained directly from renewable biomass.[3] However, the conversion of wood to low-molecular-weight chemicals is difficult, because of its compact structure and its poor solubility in most known solvents.[4] Therefore, the development of efficient pretreatment protocols for lignocellulosic materials is becoming increasingly important.[5−9]

Over the past several years, a renewed interest into ionic liquids (ILs) is evident, as initiated by their special properties over traditional solvents.[10] ILs are defined as compounds that are composed entirely of ions and are liquids at temperatures of <100 °C. Recently, societal drivers, based on green chemistry and environment protection, have caused ILs to receive much attention as green and tunable solvents. The negligible vapor pressures and high thermal stability of ILs have caused them to be regarded as excellent reaction media for high-temperature durable processes.[11] Furthermore, the solvating capabilities offered by ILs, which cause the uncommon stabilization of transition states, is thought to lead to higher conversion and better stereoselectivities, as far as functional group transformation chemistry is concerned. As early as 1934, Graenacher[12] disclosed his findings of cellulose dissolution in pyridine-based ILs; this was followed by the report of Swatloski et al.,[13] who showed that cellulose may also dissolve in 1-methyl-3-butyl imidazolium chloride. Both accounts can be considered to be responsible for the creation of a novel processing platform for cellulose.[12,13]

ILs are thought to be capable of disrupting the hydrogen bonds between different polysaccharide chains. This interaction was determined to decrease the crystallinity of cellulose and made the carbohydrate fraction more susceptible to acid hydrolysis. Recently, Jones et al. reported data, confirming these effects, whereby the acid-catalyzed conversion of loblolly pine wood in the IL 1-butyl-3-methyl imidadzolium chloride was studied.[14] They were able to convert almost the entire carbohydrate fraction of the starting material into water-soluble products under milder conditions than those reported for reactions in the aqueous phase. Complete conversion of the carbohydrate fraction into water-soluble products was observed at 120 °C, which is much lower than the temperatures typically applied for aqueous-phase hydrolysis. Moreover, unlike aqueous phase reactions, the presence of the lignin matrix did not hinder the hydrolysis process, because it remained as a solid residue and complete sugar−lignin fractionation was achieved. The water-soluble products included monosaccharides, oligosaccharides, furfural, and 5-hydroxymethylfurfural (HMF); however, the selectivity of the reactions still needs to be improved.

Another report, by Zhao et al., demonstrated that the presence of acid in ionic liquids is an efficient system for hydrolysis of lignocellulosic materials with improved total reducing sugars (TRS) yield under mild conditions.[15] These workers hydrolyzed corn stalk, rice straw, pine wood, and bagasse in C_4mimCl in the presence of 7 wt % hydrogen chloride at 100 °C under atmospheric pressure within 60 min. The corresponding TRS yields were increased by up to 66%, 74%, 81%, and 68%, respectively, for the different species. Furthermore, Rainers et al. reported that cellulose in lignocellulosic materials can be simply transformed to 5-hydroxy-methylfurfural (HMF) at 48% yield in a system of $CrCl_3$−HCl−DMA−LiCl−[Emim]Cl at 140 °C for 1 h.[16] HMF is a versatile intermediate between biomass-based carbohydrate chemistry and petroleum-based industrial organic chemistry.[17] HMF and its derivatives could potentially replace extensively consumed petroleum-based building blocks, which are currently used to make plastics and fine chemicals.[18]

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Zhang and co-workers investigated the catalytic conversion of sugars to HMF under low temperature (100 °C) IL-based thermolysis conditions.[19] It was determined that metal halides in 1-alkyl-3- methylimidazolium chloride can effectively catalyze the conversion of glucose to HMF. Particularly, the use of chromium(II) chloride as a catalyst was observed to be highly effective, leading to the conversion of glucose to HMF with ~70% yield. A wide range of metal halides were observed to catalyze the conversion of fructose to HMF. Most importantly, the reactions were very selective, because only a negligible amount of byproducts such as levulinic and formic acids were formed in these reactions. These byproducts are typically created in current acid-catalyzed processes that produce HMF, thus increasing the cost of product purification.

In our earlier work, we reported that softwood such as Norway spruce TMP (N. spruce TMP) can be dissolved in some ILs, including 1-butyl-3-methyl- and 1-allyl-3methyl-imidazolium chlorides ([Bmim]Cl and [Amim]Cl) with high wood regeneration yield.[20] The enzymatic hydrolysis of the regenerated wood was determined to produce higher conversions of cellulose to glucose than that of untreated wood. Our studies revealed that the recycled ILs from the pretreatment of wood contain carboxylic acids from the dissolved hemicelluloses.[21] When these ILs were used for additional wood pretreatment cycles, it was observed that the hydrolysis rate of cellulose increased, accompanied by lignin degradation.[21] As such, it became of interest to investigate the effect of small amounts of acid in ILs on wood degradation and its hydrolytic conversion during such a pretreatment stage.

In this communication, we have compared three wood species pretreated with dilute hydrochloric acid in water and in [Amim]Cl. The lignin contents of the regenerated wood were determined, and the components that remained in the recycled IL were examined by quantitative nuclear magnetic resonance (NMR) and detailed gas chromatographic−mass spectroscopic (GC-MS) analyses.

Materials and Methods

Eucalyptus grandis, southern pine, and Norway spruce thermomechanical pulp were the species examined and sampled, as per our earlier accounts.[20−22] (These components are abbreviated hereafter as E. grandis, S. pine, and N. spruce TMP, respectively.) All wood samples were kept in a vacuum oven at 50 °C for 24 h prior to use. An ionic liquid (IL), 1-allyl-3-methylimidazolium chloride ([Amim]Cl), was synthesized by a modified literature method.[22,23]

Synthesis of 1-Allyl-3-methylimidazolium chloride ([Amim]Cl). This ionic liquid was synthesized by the reaction of allyl chloride with an excess of 1-methylimidazole to avoid the formation of possible acid impurities. A freshly distilled allyl chloride (0.95 equiv) was added dropwise to the solution of freshly distilled methyl imidazole (1 equivalent) in dry acetone, and the mixture was allowed to heat at 55 °C overnight under nitrogen atmosphere. After cooling to room temperature, the acetone phase was separated and the excess of methylimidazole was removed by the acetone extraction as follows. The crude product was added dropwise to acetone and the resulting mixture was stirred for 5 h at 40 °C, followed by the removal of the acetone layer. This purification step was repeated five times. The IL layer was separated and condensed by the rotary evaporator to remove the remaining residues of organic solvent. The crude product was then decolorized with active carbon in boiling methanol. After the filtration and condensation, the final product was dried under vacuum at 40 °C for 48 h before use. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (3 H, s), 4.73 (2H, d, ^3J = 6.3 Hz), 5.10−5.20 (2H, m), 5.65−5.79 (1H, m), 7.30 (1H, s), 7.54 (1H, s), 10.10 (1H, s).

Pretreatment of Wood in an Ionic Liquid: Dissolution, Wood Regeneration, and Recycling of the Ionic Liquid. The ionic liquid was charged into a 100-mL dried flask that was equipped with a mechanical stirrer, under an inert atmosphere of argon. The temperature of the dissolution process was controlled by an oil bath. The wood sample (particle size = 0.1−2 mm) was then added quickly into the IL (wood/IL 8 wt %), and the mixture was kept at 120 °C for 5 h with mild mechanical stirring, resulting in a transparent yellow to brown solution. The wood regeneration was performed as follows: The wood/IL solution was gradually added into an excess of rapidly stirred regeneration solvent (deionized water, methanol, or ethanol). The precipitated bulky material was then filtered off using a Büchner funnel and washed thoroughly with the regeneration solvent. A small sample of the regenerated wood was used to determine its solids content. The sample was dried overnight at 110 °C and then the regenerated wood yield was calculated using eq 1:

$$\text{regenerated wood yield (\%)} = \left(\frac{\text{Wt}_{\text{wood regenerated}}}{\text{Wt}_{\text{wood input}}}\right) \times 100 \tag{1}$$

The recycling process of ILs was performed as follows: The filtrate was condensed by rotary evaporator and then dried overnight under vacuum at 40 °C, to remove the residues of the regeneration solvent.

Pretreatment of Wood by Dilute Acid in Water. The wood sample (particle size = 0.1−2 mm) was added into the dilute acid (hydrochloric acid) solution (wood:H_2O 8 wt %), and the flask was sealed, placed in a commercial pressure cooker, and heated for 5 h (2 atm, 120 °C). After cooling to room temperature, the wood sample was collected by filtration and washed with deionized water until the pH of the filtrate measured 7. The solid wood residue was then dried overnight under vacuum at 40 °C, followed by the determination of the lignin content. The neutral filtrate was condensed and the obtained solid residues were dried overnight in a vacuum oven at 40 °C. The solid materials from the condensation of the filtrates were characterized by ^{31}P NMR, using the following procedure.

Thirty to thirty-five milligrams (30−35 mg) of the above sample, obtained from the filtrate, was dissolved in 0.2 mL of dimethyl formamide (DMF) and 500 μL of a prepared mixture of pyridine/$CDCl_3$ (1.6/1 ratio). Next, 200 μL of the internal standard, endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (e-HNDI) solution (63.2 mM, 11.32 mg/mL in 3/2 pyridine/$CDCl_3$) was added in one portion. Then, 50 μL of previously prepared solution of chromium(III) acetylacetonate ($Cr(acac)_3$) in $CDCl_3$ (10 mg/mL) was added. The mixture was subjected to a vortex for 30 s, then 100 μL of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane [PR(II)][24] was added in one portion and the mixture was further subjected to a vortex until it was visibly homogeneous (30 s). The final solution was transferred to a NMR tube and quantitative ^{31}P NMR spectra were acquired immediately, using a Bruker 300 MHz spectrometer equipped with a Quad probe dedicated to ^{31}P, ^{13}C, ^{19}F, and ^{1}H acquisition. A total of 256 scans was acquired for each sample with the relaxation delay time (d_1) of 5.0 s.[24,25]

Pretreatment of Wood by Dilute Acid in an Ionic Liquid: Dissolution, Wood Regeneration, and Recycling of the Ionic Liquid. The ionic liquid was charged into a 100-mL dried flask that was equipped with a mechanical stirrer,

Table 1. Concentrations of the Different Hydroxyl Functional Groups Present within the Recycled ILs Calculated from the ^{31}P NMR Analyses[a] (the Compositions of the Original Woods Are Also Listed)

		Concentration of Hydroxyl Group (μmol/g of IL)			Composition of Original Wood (%)		
	wood species	[Aliphatic −OH] (150−144 ppm)	[Phenolic −OH] (144−137 ppm)	[−COOH] (136−134 ppm)	hemicellulose	cellulose	total lignin
1	S. pine (clean IL treated)	40	0	38	29.4[b]	40.9[b]	29.1[b]
2	N. spruce TMP (clean IL treated)	12	0	30	25.7[c]	45.5[c]	28.3[c]
3	E. grandis (clean IL treated))	72	0	10	26.3[d]	44.7[d]	25.8[d]
4	E. grandis (recycled IL treated, third reuse cycle)	163	61	14	26.3[d]	44.7[d]	25.8[d]

[a] Data were the average value of three duplicate experiments, with a deviation of <5%. [b] Data obtained from ref 37. [c] Data obtained from ref 36. [d] Data obtained from ref 35.

under an inert atmosphere of argon. The temperature of the dissolution process was controlled by an oil bath. The wood sample (particle size = 0.1−2 mm) was then added quickly into the ionic liquid (wood/IL 8 wt %), and the mixture was kept at 120 °C for 3 h with mild mechanical agitation. After cooling to room temperature, the required amount of concentrated hydrochloric acid (HCl) was added and the mixture was homogenized at room temperature for 2 h. It was then heated up to 120 °C for 5 h, resulting in a black solution. The wood solution finally was gradually added into an excess of rapidly stirred water. The precipitated bulky material was then filtered using a Büchner funnel and washed thoroughly with deionized water. A small sample of the regenerated wood was used to determine its solids content. The sample was dried overnight at 110 °C, and then the wood-regenerated yield was calculated using eq 1.

The recycling of ILs was performed as follows: The filtrate was condensed in a rotary evaporator and then dried overnight under vacuum at 40 °C, to remove the residues of the regeneration solvent.

Determination of the Lignin Content. Klason lignin (acid insoluble) and the acid-soluble lignin contents of the regenerated wood samples were measured according to the method reported by Yeh et al.[26]

^{31}P NMR Analysis of the Recycled Ionic Liquid. Recycled IL (0.5 g) was placed in a 5-mL vial, then 150 μL of pyridine was added and the mixture was subjected to a vortex until it was visibly homogeneous. Next, 200−400 μL of the PR(II) reagent[24] was added and the resulting mixture was subjected to a vortex to form a yellow paste. After adding 500 μL of the Cr(acac)$_3$ solution in CDCl$_3$ (1 mg/mL), the mixture was further subjected to a vortex until a clear solution was formed. Then, 200 μL of the internal standard endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (e-HNDI) solution (63.2 mM, 11.32 mg/mL in 3/2 pyridine/CDCl$_3$) was added, followed by another 500 μL portion of the Cr(acac)$_3$ solution in CDCl$_3$ (1 mg/mL). Seven hundred microliters (700 μL) of the final solution were placed in a NMR tube, and the ^{31}P NMR spectrum was acquired immediately using a Bruker 300 MHz spectrometer.[24,25]

Extraction of the Recycled Ionic Liquid with Ethyl Acetate (EtOAc). A mixture of recycled IL (15 g) and deionized water (50 mL) was extracted three times with ethyl acetate (3 × 100 mL). The combined organic layers were dried over calcium chloride (CaCl$_2$), and, finally, the solvent was removed using a rotary evaporator. Prior to analysis, the residuals were dried overnight under vacuum at 40 °C.

^{31}P NMR Analysis of the Extracted (EtOAc) Materials. Ten to twenty milligrams (10−20 mg) of the extracted material was dissolved in 500 μL of pyridine/CDCl$_3$ (1.6/1), followed by the addition of 200 μL of the internal standard endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (e-HNDI) solution (64.3 mM, 11.52 mg/mL, in 3/2 pyridine/CDCl$_3$). Next, 50 μL of the Cr(acac)$_3$ solution in CDCl$_3$ (10 mg/mL) was added. The mixture was subjected to a vortex for 30 s, then 100 μL of the PR(II) reagent[24] was added and the mixture was further subjected to a vortex until it was visibly homogeneous (30 s). The solution was placed in an NMR tube, and ^{31}P NMR spectra were acquired immediately using a Bruker 300 MHz spectrometer.[24,25]

GC-MS Analysis of the Extracted (EtOAc) Materials. Two milligrams (2 mg) of the extracted material was dissolved in 5 mL of dichloromethane, followed by the addition of *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide (1 mg) as a silylation reagent. The GC-MS spectra were acquired using a Polaris Q GC-MS system that was equipped with a Hewlett−Packard Model HP-1 GC column and ion trap detector. The temperature program used was as follows: 40−250 °C, at a rate of 5 °C/min; hold for 5 min; 250−310 °C, at a rate of 10 °C/min; and hold for 5 min. The injector temperature was 230 °C, the ion source temperature was 200 °C, and the carrier flow gas was helium at a flow rate of 1.5 mL/min.

Results and Discussion

^{31}P NMR Analysis of the Wood Components Remaining in Recovered Ionic Liquids (ILs), Using Water as the Regeneration Solvent (without Additional Acid in Pretreatment Procedure). Three wood species (*Eucalyptus grandis*, Southern pine, and Norway spruce TMP) were pretreated with [Amim]Cl at 120 °C for 5 h and then regenerated in an aqueous environment. The recovered ILs were characterized using quantitative ^{31}P NMR spectrometry. Under our experimental conditions, the aliphatic hydroxyls, phenolic hydroxyls, and carboxylic acid groups showed signals at different regions, as shown in Figure 2 (shown later in this work). The amounts (expresed in units of μmol/g IL) of the different hydroxyl groups present in the recycled ILs were calculated from the integrations of the selected signals against an internal standard.[22] The corresponding values are listed in Table 1. From the data of Table 1, it can be seen that hemicelluloses and cellulose are the main components present in the recycled IL after the wood pretreatment. This is reasonable because hemicelluloses are polar and water-soluble and, as such, they are known to possess good solubility in polar ILs. No signals due to aromatic moieties were apparent in the ^{31}P NMR spectra, possibly indicating that lignin remains intact during the pretreatment in neutral IL. It is also worth mentioning here that, despite the relatively similar hemicelluloses content of the different wood species, the recycled ILs contained variable amounts of dissolved carboxylic acids (see Figure 1). More specifically, it was found that the recycled ILs from the softwood species (S. pine and N. spruce TMP) contained significantly higher amounts of carboxylic acids than the corresponding IL from hardwood (E. grandis). This is not surprising when density considerations of softwoods and hardwoods are taken into account (i.e., the more-compact structure of hardwood can diminish the rate of the hemicelluloses hydrolysis reaction).

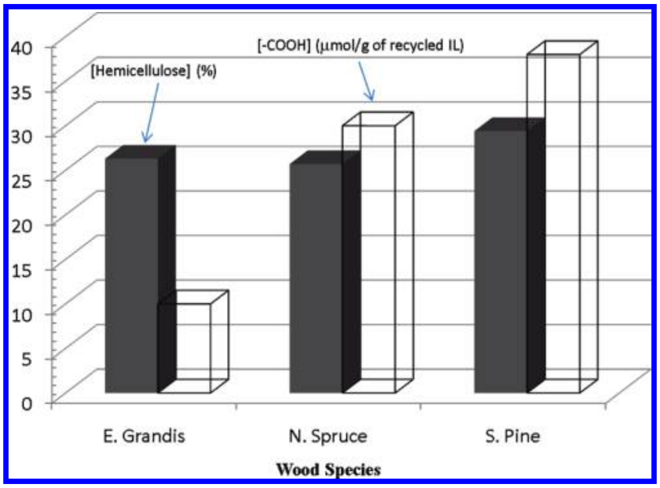

Figure 1. Carboxylic acid functional group concentrations (clear bar) present within the recycled ILs versus the hemicellulose content (dark bar) for three wood species (E. grandis, S. pine, and N. spruce TMP).

^{31}P NMR Analysis of the Components Remaining in Recovered Ionic Liquids, Using Methanol as the Regeneration Solvent (without Additional Acid in the Pretreatment Procedure). Among the various attractive features of ILs is their recycling ability. In this part of our work, we have investigated the recycling potential of the IL after various dissolution/regeneration cycles of wood. Our data show that the amount of lignin remaining within the IL increases after each reuse cycle. Figure 2 shows the ^{31}P NMR spectra of recovered ILs after the pretreatment of E. grandis with a fresh (used once) IL and with a recycled IL (after three reuse cycles). The absence of signals in the 144−137 ppm region indicates that the once-used IL does not contain significant amounts of lignin. However, the ^{31}P NMR spectrum of the recycled IL reveals obvious signals in the typical lignin region that are responsible for phenolic hydroxyl groups (∼61 mmol/g of IL). Subsequently, the NMR signal intensities in the aliphatic hydroxyl and carboxylic acid regions are elevated in the recycled IL, indicating that a variety of wood components (including hemicelluloses and other carbohydrates) accumulate within the IL during the recycling process. These findings indicate that the use of IL as a solvent for wood dissolution may also be accompanied by some degradation of the woody components. This is not totally surprising, however, because wood hemicelluloses contain a reasonable amount of carboxylic acid moieties that may conceivably induce such degradation reactions. Moreover, previous accounts have shown that small amounts of acidic moieties are generated when ILs are in contact with moisture, especially when exposed at elevated temperatures.[27] Thus, it is reasonable to assume that traces of acid generated during the various dissolution/regeneration cycles of wood within the IL may induce the observed decomposition. It is also important to mention that ILs themselves are known to display some catalytic action under acidic conditions. It is widely recognized that, for chloride-based imidazolium ILs, the proton present on the 2-position of the imidazole ring acts as a hydrogen-bond donor, and the associated chloride acts as a hydrogen-bond acceptor. This can effectively activate the hydroxyl groups of cellulose or of sugars dissolved in ILs.

It has been reported that the addition of an acid in the IL during the wood dissolution process can effectively cleave cellulose and hemicelluloses to smaller fractions.[15,16] Such an effect may provide an efficient pathway for the production of valuable chemicals from wood. Overall, the use of acids in conjunction with ILs has mainly been considered in the literature as a route for the deconstruction of cellulose and hemicelluloses. However, the possibility to degrade lignin in similar systems, with the objective of producing a valuable chemical stream, has not been considered.

Optimization of Wood Acid Pretreatment Conditions in the Ionic Liquid: Effect of Temperature and Time. As discussed previously, small amounts of acid in ILs may play an important role in the wood dissolution process. Zhao et al. investigated the presence of acids in ILs aimed at corn-based lignocellulose hydrolysis.[15] For example, in [Amim]Cl, a total reducing sugar (TRS) yield of 65% for corn stalk was obtained within 90 min at 100 °C in the presence of 2.0 mmol of hydrochloric acid/g lignocellulosic material (0.04 g of 37% HCl for 0.2 g of corn stalk). Another study reported conversion yields of >90% for hemicelluloses (xylans) after the pretreatment of corn stover at 190 °C under 12 atm for 2 min in the presence of sulfuric acid (1.1 wt % of concentrated H_2SO_4, 30 wt % of corn stover; acid concentration = 0.74 mmol of [H^+]/g corn stover).[5]

Because most of the recent studies in this area have examined lignocellulosic materials that do not represent wood biomass, and because of the inherent complexities of wood biomass, our work has been focused on it. More specifically, in our investigations, hardwood (E. grandis) was selected for being optimized toward an acidic IL pretreatment. The pretreatment time and temperature were optimized using an identical acid concentration (0.8 mmol of HCl/g wood). The plots of wood-regenerated yields versus pretreatment time and temperature are shown in Figures 3A and 3B, respectively. The data of Figure 3A shows that, after 5 h of pretreatment, the regenerated wood yield decreased as the temperature increased from 80 °C to 120 °C. At lower temperatures (80−100 °C), the regenerated wood yield was much higher (>90%) than those at temperatures of 120 °C and beyond (those exhibited yields of only 64.6%). The decrease in the regenerated wood yields observed at higher temperatures is most likely due to kinetic considerations of the hydrolysis, allowing greater amounts of cellulose and hemicelluloses to be degraded per unit time, resulting in higher overall weight losses. Figure 3B shows the time dependency of the regenerated wood yields at 120 °C. The results show that the main phase for the degradation of wood starts after a 2-h-long pretreatment and then rapidly proceeds, until it eventually levels off after 4 h of treatment. Here, note that the wood degradation rate reached its maximum in the pretreatment interval of 2−3 h. During this interval, ∼20% of the original mass of wood was deconstructed while longer pretreatment periods (3−4 h) offered only an additional 5%−6% wood mass reduction. At this point, it can be concluded that, under the selected reaction conditions, at least 4 h of pretreatment are needed to reach the maximum degradation of E. grandis wood.

Effect of Acid Concentration for Three Wood Species Pretreated in the Ionic Liquid at 120 °C for 5 h. Based on the optimization study described in the previous section, the effect of acid concentration on wood pretreatment yields was investigated next for three wood species in an IL. For comparative purposes, the same acid pretreatments were also performed in aqueous media. The plots of regenerated wood yield, as a function of the acid concentration, are shown in Figures 4A, 4B, and 4C).

It seems that, for the measurements conducted in dilute acid aqueous conditions, the weight losses occurring as a result of the pretreatment can be correlated with the hemicellulose content of the individual wood species. Notably, for such control experiments, where the highest acid concentration was used (1.5 mmol of HCl/g wood), the weight loss of softwoods was in

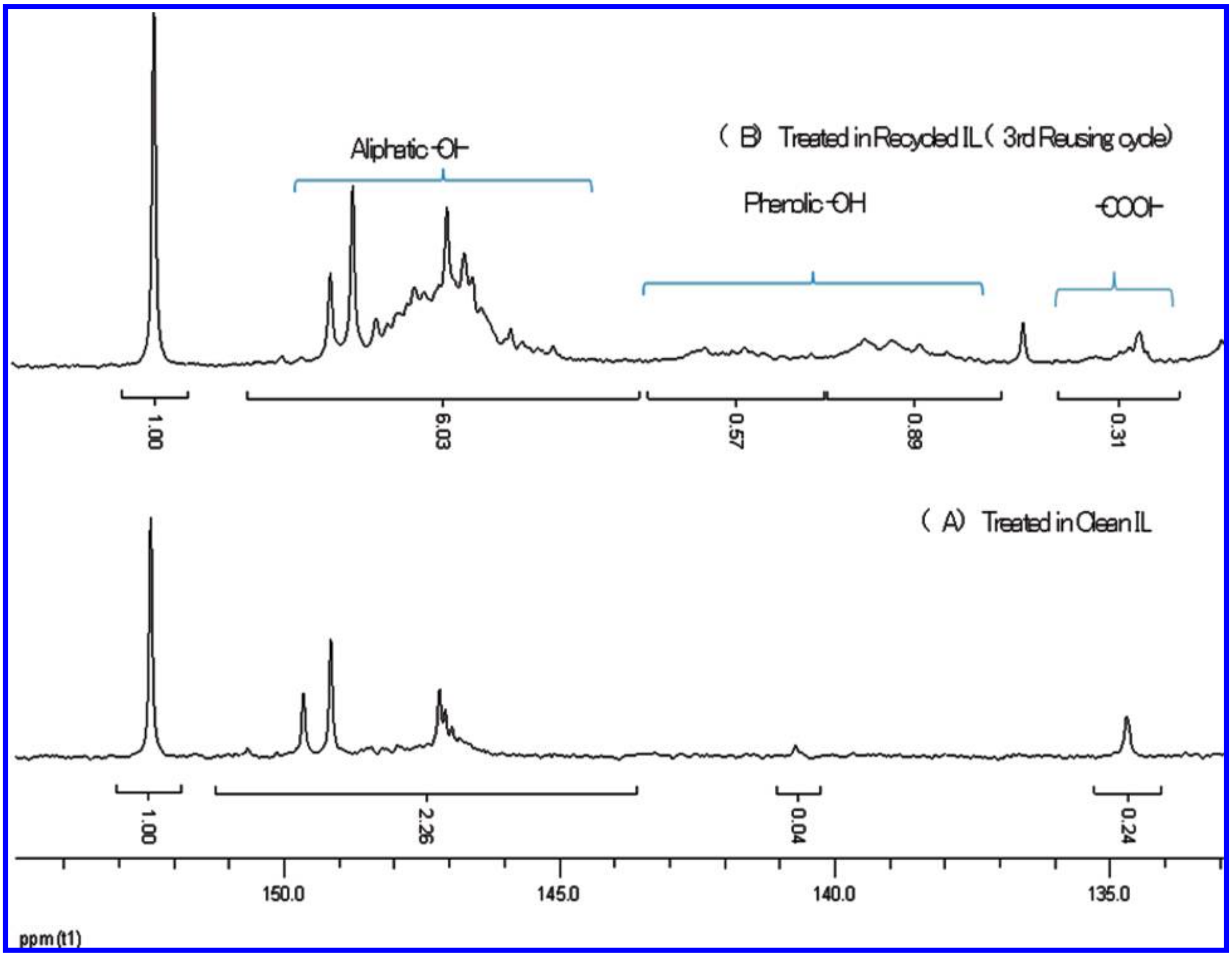

Figure 2. ^{31}P NMR spectra of the IL recovered from the pretreatment of E. grandis with clean and recycled [Amim]Cl, using methanol as a regeneration solvent.

close proximity to the total hemicellulose content of the wood species used. This is not totally surprising, since earlier work has shown that, under mild aqueous acidolysis conditions, only the noncrystalline hemicellulose fraction is susceptible to degradation.[8,28] Hardwood (Figure 4A), as opposed to softwoods (Figures 4B and 4C), showed a more pronounced resistance toward acid hydrolysis, which may be due to the more-compact structure of the hardwood, as was postulated earlier and in accordance with our earlier observations.[21]

Overall, for the three wood species examined, the regenerated wood yields decreased as the acid concentration increased. When the control experiments conducted in water are compared to those conducted in ILs, it becomes clear that the weight loss of the wood is significantly higher in the latter. This is most likely due to the fact that both hemicellulose and crystalline cellulose are hydrolyzable in the IL media, because of the ILs' capability to disrupt the hydrogen bonds between the different polysaccharide chains.[17,22] This interaction decreases the crystallinity of cellulose and makes the carbohydrate fraction more susceptible to acid hydrolysis.

The acidic IL pretreatments showed significant differences between the hardwoods and softwoods, especially at lower acid concentrations. More specifically, the hardwood (E. grandis) was determined to be more difficult to hydrolyze than either of the two softwoods (S. pine and N. spruce TMP) when the acid concentration was <0.6 mmol of HCl/g wood. For example, at 0.4 mmol of HCl/g wood, the regenerated wood yield for N. spruce TMP was determined to be 58%, while the regenerated wood yield for the E. grandis hardwood remained >90%. However, when the acid concentration was increased to 1.4−1.5 mol of HCl/g wood, the regenerated wood yield for E. grandis decreased drastically, down to 34%, while the regenerated wood yields for S. pine and N. spruce TMP were 53% and 42%, respectively. By considering the sum of total carbohydrates present in the various species (hemicellulose and cellulose) to be 64% for E. grandis, 70% for S. pine, and 71% for N. spruce TMP, it can be concluded that almost all of the carbohydrate components of E. grandis have been acid-hydrolyzed (assuming the weight loss is solely derived from the hydrolysis of cellulose and hemicelluloses). Similar calculations, however, for the softwoods revealed that only 67%−82% of the total carbohydrates were hydrolyzed, indicating that some of the softwood carbohydrates remained intact during the pretreatment.

Lignin Contents Present in the Wood Regenerated from the Acid Pretreatments. Gravimetric measurements allowed the amount of the degraded lignin to be estimated using eq 2:

$$\text{lignin degraded yield (\%)} = \frac{\text{lignin content}_{\text{orig. wood}} - (\text{yield}_{\text{regenerated wood}} \times \text{lignin content}_{\text{regenerated wood}})}{\text{lignin content}_{\text{orig. wood}}} \times 100 \qquad (2)$$

For example, the amount of the lignin degradation during the acid IL pretreatment of E. grandis (120 °C, 5 h, 1.5 mmol of HCl/g wood) was calculated to be ∼10%.

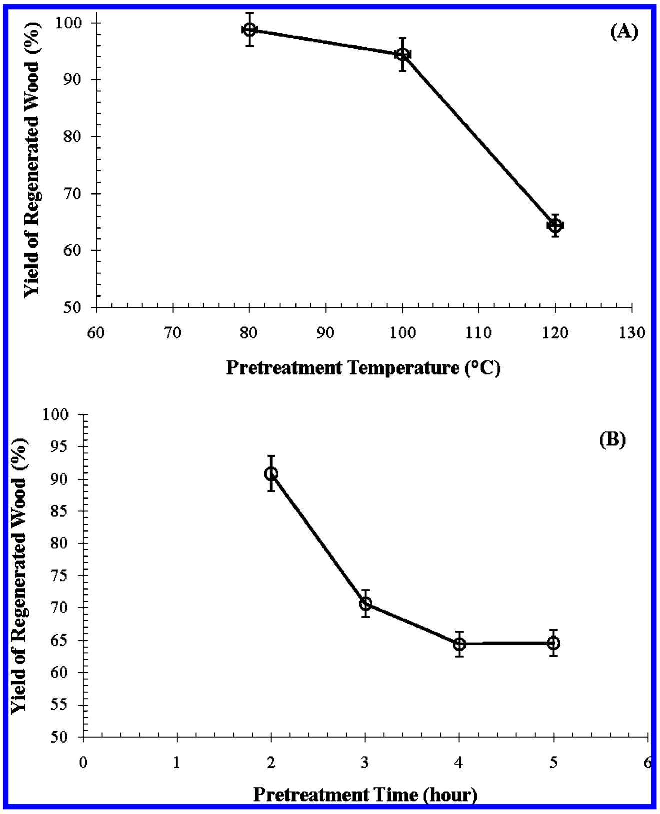

Figure 3. Optimization of (A) the pretreatment temperature (the pretreatment time is 5 h) and (B) the pretreatment time (the pretreatment temperature is 120 °C) in the presence of 0.8 mmol of HCl/g wood (with E. grandis as the wood sample and water as the regeneration solvent).

Figure 5 shows the lignin contents of the regenerated E. grandis, being plotted as a function of the acid concentration for both the aqueous and the IL pretreatments. In both cases, it is apparent that the lignin content of the regenerated hardwood increases as the acid concentration is increased. This indicates that more carbohydrates can be hydrolyzed at higher acid concentrations. However, note that the increase in the lignin content was always observed to be higher for the woods regenerated from the IL pretreatment system. This can be explained by the solubility differences of the wood species within the two pretreatment processes, i.e., wood dissolves in [Amim]Cl, whereas in water, it remains insoluble. Therefore, the acid hydrolysis of the cellulose will be more efficient in ILs, because of the better accessibility of the acid into the crystalline regions of cellulose. For example, the regenerated material from the acidic IL pretreatment (120 °C, 5 h, 1.4 mmol of HCl/g wood) was determined to have a lignin content of 72%, whereas the E. grandis wood regenerated from the acid pretreatment in water possessed a lignin content of 31%, which is slightly higher than that of the original wood. Similar tendencies were also determined to operate for the two softwoods: N. spruce TMP and S. pine (data not shown).

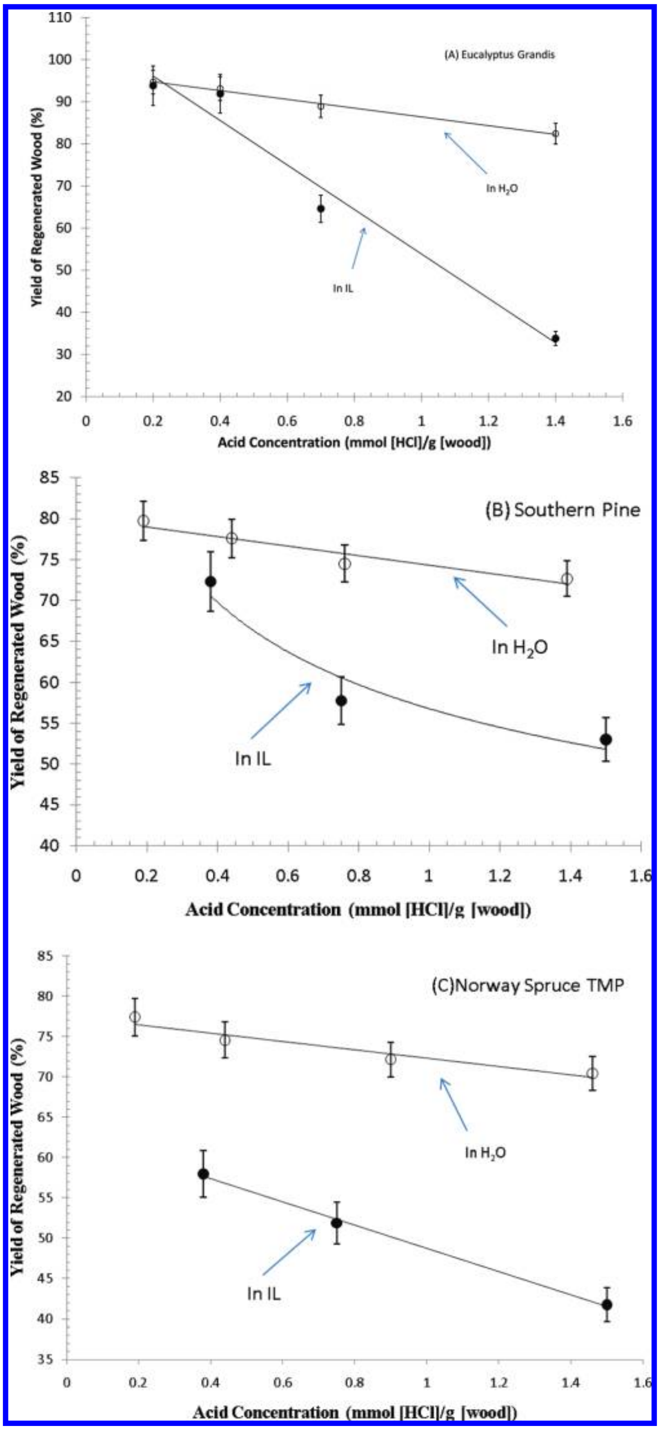

Figure 4. Regenerated wood yields of three wood species ((A) E. grandis, (B) S. pine, and (C) N. spruce TMP) pretreated with [Amim]Cl, in the presence of different concentrations of dilute acid.

^{31}P NMR Analyses of the Wood Components Solubilized during Aqueous Acid Pretreatments. After all aqueous pretreatments, the remaining wood was collected by filtration. The filtrate was then lyophilized and thoroughly vacuum-dried, and then the remaining residue was examined using quantitative ^{31}P NMR spectroscopy. The ^{31}P NMR spectra of Figure 6 show pronounced signals in the 150−144 ppm region, because of the presence of aliphatic hydroxyl groups, whereas signals due to free phenolic hydroxyl groups (144−137 ppm) and carboxylic acid groups (136−134 ppm) are almost absent. These data are in excellent agreement with literature accounts, where it is shown that the aqueous acidolysis of wood primarily causes the solubilization of the hemicellulose fraction.[8,25]

The actual concentrations ($[-\text{OH}]_{\text{in water}}$) for the different hydroxyl bearing functional groups present within the filtrates (Table 2) were calculated using eq 3, because the variable ($[-\text{OH}]_{\text{solid material}}$) can be obtained from the integration values of the corresponding signals in the quantitative ^{31}P NMR spectra.

$$[-\text{OH}]_{\text{in water}} = \frac{[-\text{OH}]_{\text{solid material}} \times \text{Wt}_{\text{solid material obtained}}}{\text{Wt}_{\text{aqueous solution used}}} \qquad (3)$$

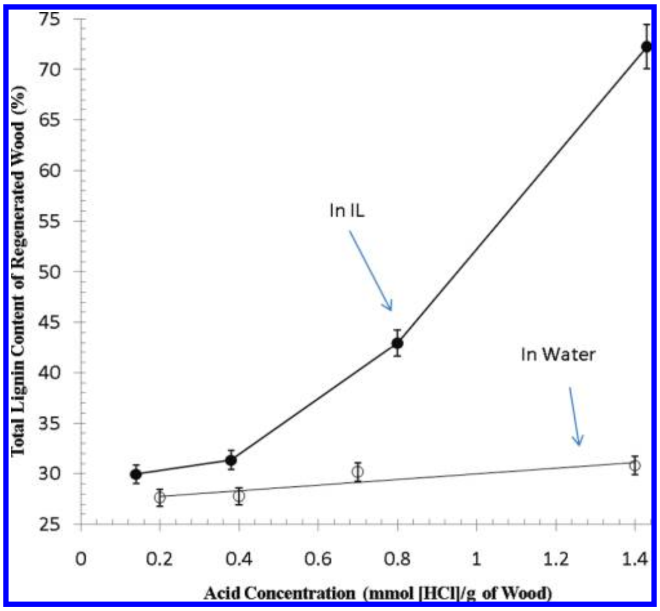

Figure 5. Lignin contents of the regenerated E. grandis pretreated with [Amim]Cl at 120 °C for 5 h, in the presence of different concentrations of dilute acid.

Table 2. Concentrations of Different Hydroxyl Functional Groups Present within the Recycled Solvents Calculated from the ^{31}P-NMR Analysis (1.4 mmol HCl/g wood)[a]

		Concentration (μmol/g of solvent)		
group	wood species	[Aliphatic −OH] (150−144 ppm)	[Phenolic −OH] (144−137 ppm)	[−COOH] (136−134 ppm)
1	S. pine (in water)	152	3.8	3.7
2	N. spruce TMP (in water)	177	7.0	3.4
3	E. grandis (in water)	183	20	9.7
4	S. pine (in IL)	110	130	9.6
5	N. spruce TMP (in IL)	130	170	23
6	E. grandis (in IL)	670	34	1.2

[a] Data shown are the average value of three duplicate experiments, with a deviation of <5%. The concentration data of the different hydroxyl groups in water were calculated using eq 3.

As can be seen from the data of Table 2, the concentrations of aliphatic hydroxyl groups (predominantly arriving from carbohydrates) present within the pretreatment filtrates are very similar for the three wood species examined, in the range of 150−180 μmol/g of water. However, the concentrations of the phenolic hydroxyl functional groups (mainly arising from the solubilized lignin) were determined to be significantly lower (3−20 μmol/g of water). Therefore, under aqueous conditions, the hydrolysis products seem to be mainly originating from hemicellulose, whereas most of the lignin and cellulose remained intact.

^{31}P NMR Analyses of Wood Components Present within Recycled Ionic Liquids after Acid Pretreatments. In contrast to the relatively simple ^{31}P NMR data obtained when aqueous

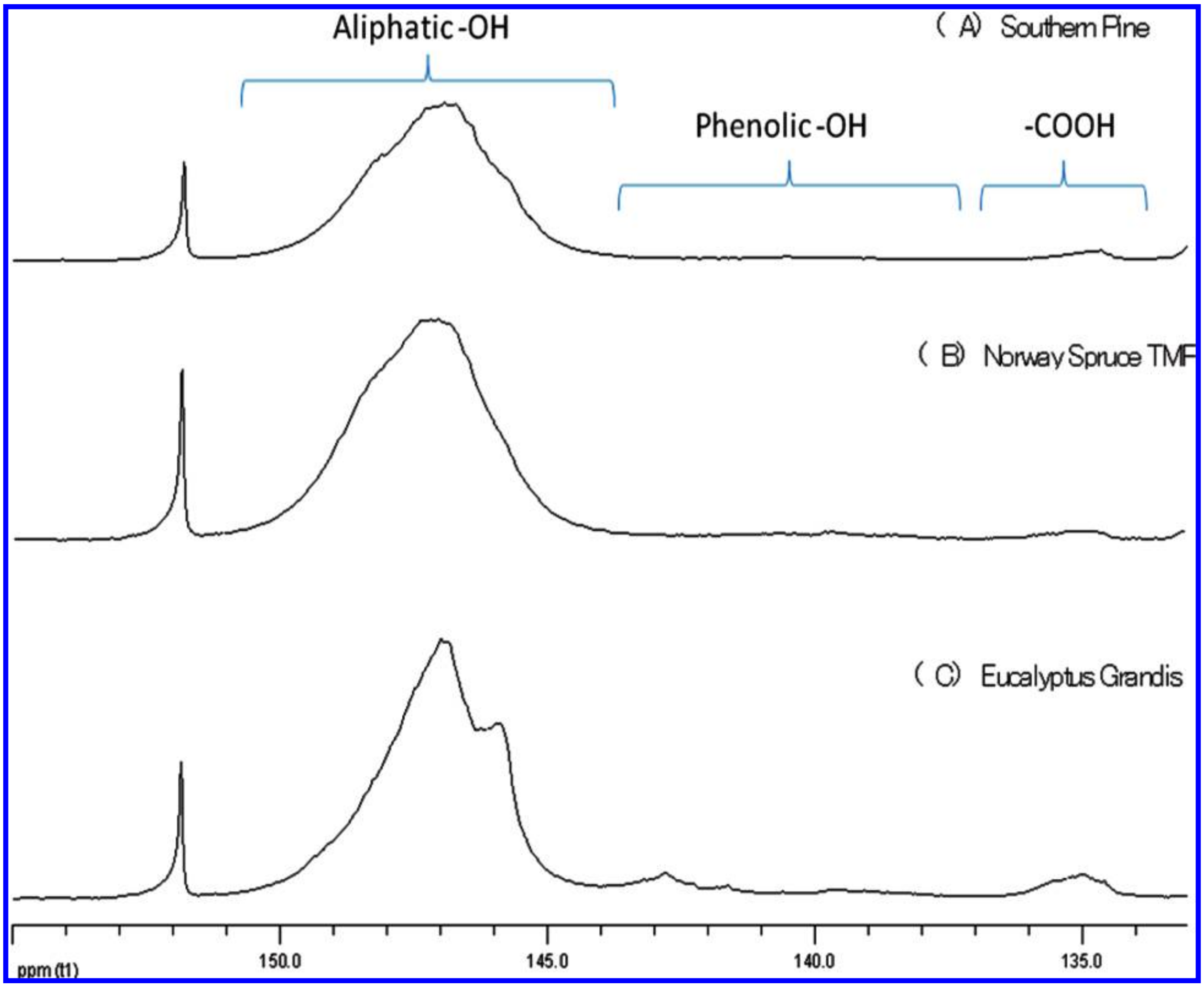

Figure 6. ^{31}P NMR spectra of the solid materials obtained from the filtrates of dilute acid (1.5 mmol of HCl/g wood) treatments for the three wood species in water at 120 °C for 5 h.

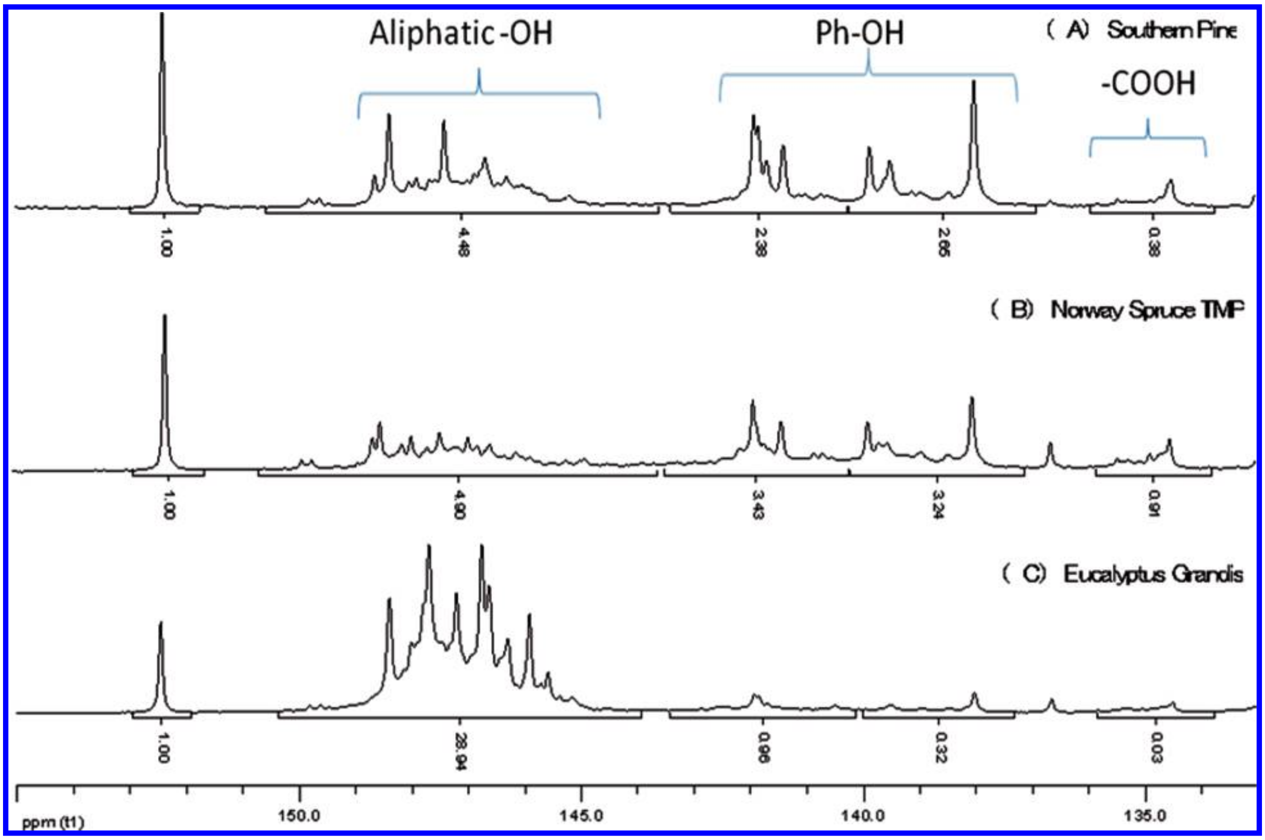

Figure 7. ^{31}P NMR spectra of the recycled ILs from the pretreatment of the three wood species ((A) S. pine, (B) N. spruce TMP, and (C) E. grandis) with [Amim]Cl, in the presence of acid (1.5 mmol of HCl/g wood) at 120 °C for 5 h.

Table 3. Compounds Identified from the EtOAc Extracted Fraction from the Recycled Ionic Liquid after the Acidic Pretreatment of *Eucalyptus grandis* (Using Retention Times and Characteristic Ions)

	product[a]	retention time, RT (min)	characteristic ions (*m*/*z*)	E. grandis	S. pine	N. spruce TMP
1	dihydrofurfural alcohol (TMS)	10.2	173, 145, 129, 95, 75	yes	yes	yes
2	furan-2-carboxylic acid (TMS)	10.3	184, 169, 145, 125, 95, 75	yes	yes	yes
3	5-hydroxymethylfurfural (5-HMF)	12.1	126, 97, 69	yes	yes	no
4	5-HMF (TMS)	13.1	198, 183, 139, 97	no	yes	yes
5	catechol (TMS)	14.8	183, 155, 139, 111, 99, 81	yes	yes	yes
6	4-vinyl-2-methoxyphenol	21.0	151, 123, 108	no	yes	no
7	methylguaiacol (TMS)	22.3	212, 184, 166, 139, 112, 84	yes	yes	yes
8	tetrahydro-5-HMF (TMS)	22.9	203, 185, 157, 129, 115, 111, 87, 69	yes	yes	yes
9	methylcatechol (TMS)	26.2	268, 253, 225, 197, 185, 170, 155, 143	yes	no	yes
10	4-allyl-2-vinylphenol (TMS)?[b]	26.3	232, 204, 176, 137, 109, 95, 81, 53	no	yes	no
11	acetoguaiacone	27.1	167, 149, 121, 105	yes	yes	no
12	2,5-dihydyoxymethylfuran (TMS)	27.6	272, 257, 229, 201, 187, 173, 145, 131	yes	yes	yes
13	unknown	33.1	285, 159, 131, 111, 95, 75	yes	yes	no
14	1-hydroxy-2-propanone (acetol) (TMS)	36.9	147, 129, 111, 83, 55	yes	yes	yes
15	di(ethylbutylphenol-2-yl)methane?[b]	38.2	368, 312, 297, 256, 191, 178, 163, 135, 119, 91	yes	yes	yes

[a] TMS represents the trimethylsilylated derivatives. [b] The question marks mean that the corresponding proposed products are just possible structures.

extracts were examined, such analyses performed on recycled ILs (obtained from three wood species) were much more complex (see Figure 7). More specifically, the spectra from the aqueous pretreatments show only broad signals in the aliphatic region (148−144 ppm) of the ^{31}P NMR, while the spectra from the IL pretreatments contain several well-defined sharp signals present in both the aliphatic and the phenolic regions (144−137 ppm) of the ^{31}P NMR spectra. The actual concentrations of the different hydroxyl functional groups, because of the solubilized wood components present within the recycled ILs, are listed in Table 2.

Interestingly, the IL recovered from the acid pretreatment of E. grandis contained 5−6 times more aliphatic hydroxyl groups (mainly due to solubilized carbohydrates) than the ILs recovered from the pretreatments of the softwoods. However, the ILs that were recovered from the acid pretreatments of softwoods were determined to contain higher concentrations (4−5-fold) of phenolic hydroxyl functional groups (mainly arising from solubilized lignin components) than the IL recovered from the pretreatment of the E. grandis hardwood. It is apparent that the concentrations of the various hydroxyl functionalities, present in the solubilized material, are dependent on the wood species (hardwood versus softwood) and the pretreatment conditions (aqueous versus IL).

Hardwood lignin possessing a higher ratio of syringyl/guaicyl (S/G) units invariably shows a high β-O-4 (alkyl aryl ether) bond content, which is known to result in a relatively linear structure.[29] In contrast, softwood lignin, containing mainly guaiacyl (G) phenolic units, is of lower β-O-4 bond content with a higher abundance of branched structures, making it more cross-linked. Therefore, it is not surprising that the dilute acid pretreatment of

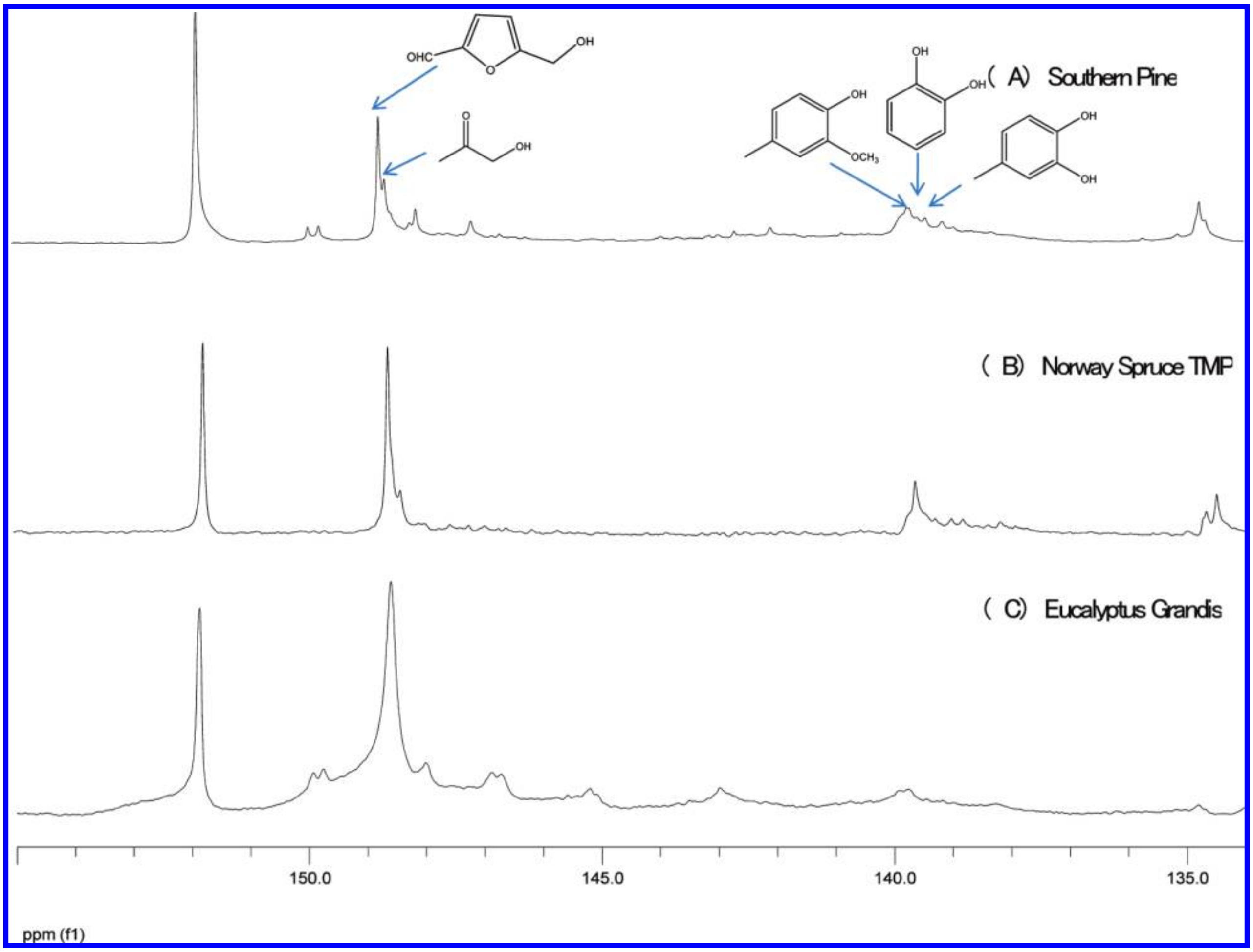

Figure 8. ^{31}P NMR spectra of the EtOAc extracted materials from the recycled ILs from the pretreatments of the three wood species with [Amim]Cl in the presence of acid (1.5 mmol of HCl/g wood) at 120 °C for 5 h.

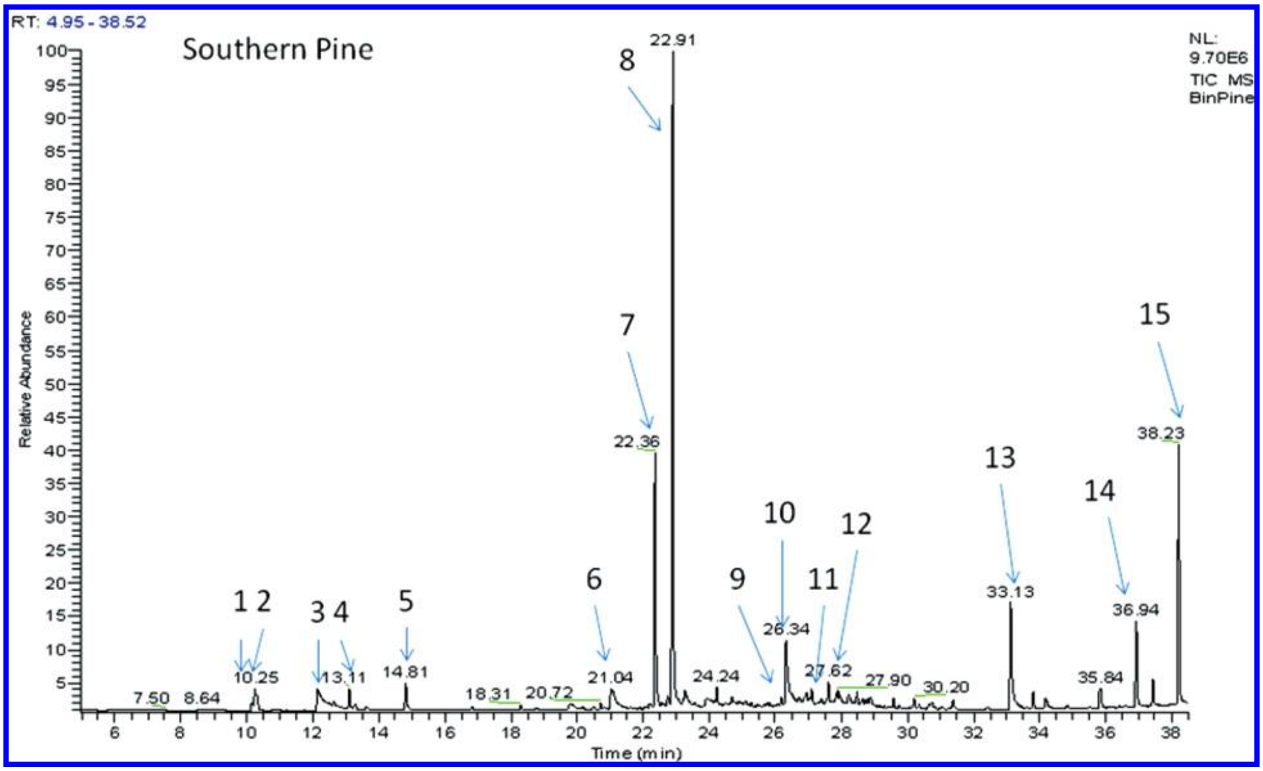

Figure 9. GC-MS spectrum of the EtOAc extracted materials from the recycled ILs from the pretreatment of S. pine with [Amim]Cl, in the presence of acid (1.5 mmol of HCl/g wood) at 120 °C for 5 h.

hardwood and softwood in ILs offered different results. With regard to the effect of the pretreatment media, it can be seen from the data of Table 2 that IL media are more effective toward wood acidolysis than aqueous media. For example, such a comparison between the pretreatments of E. grandis showed that the concentration of the aliphatic hydroxyls increased significantly (3.7 times) when an IL was used as the pretreatment medium. Similar comparisons between the pretreatments of the two softwoods in different media showed that the concentrations of the phenolic hydroxyls increased (24-fold for N. spruce TMP and 34-fold for S. pine) when an IL was used as a pretreatment medium. These data may be attributed to the fact that the dissolution of wood in ILs provides a better environment, allowing for greater accessibility of the acid to the wood components. In addition, the unique polar nature of the IL may also allow for the stabilization of the transient anomeric carbocations involved in the mechanism of carbohydrate acidolysis, facilitating fragmentation.

The ^{31}P NMR spectra of the recycled IL indicate the presence of a variety of sharp signals that are due to mobile degradation products of polysaccharides and lignin. The broad signals of Figure 6 (aqueous acid pretreatment) are indicative of less-mobile more-polymeric moieties. In our effort to further identify the chemical structures of the compounds solubilized within the IL acid treatment, the recycled IL from such pretreatment were subjected to ethyl acetate (EtOAc) extraction, followed by gas chromatography, mass spectrometry, and NMR.

Separation of the Hydrophobic Components Present within the Recycled Ionic Liquid Followed by ^{31}P NMR Analyses. The recycled ILs seemed to contain both hydrophilic sugars and more-hydrophobic compounds, such as furans and phenols. The latter can be extracted from an aqueous mixture of the IL using ethyl acetate. Apparently, the ^{31}P NMR spectrum (Figure 8) of the extracted material seems simpler than that of the original IL solution prior to the extraction (Figure 7). As anticipated, the extraction significantly reduced the intensity of the aliphatic signals present in the 148−144 ppm region, because of the hydrophilic carbohydrate components. Consequently, such NMR analyses of the ethyl acetate soluble fraction revealed the presence of 5-hydroxymethylfurfural (148.71 ppm), acetol (148.4 ppm), 2-methoxy-4-methylphenol (139.96 ppm), catechol (138.94 ppm), and acetic acid (134.58 ppm), which are known to originate from the acidolysis reactions of polysaccharides and lignin,[3,14−16,30,31] because these chemical shifts coincide well with those of identified compounds, as previously determined.[32,33] Moreover, certain substituted phenols might be deduced and assigned according to the literature methods.[34] However, detailed GC/MS analyses further confirmed our findings.

GC-MS Analyses of Wood Acidolysis Products Extracted from Ionic Liquids. Figure 9 shows a typical GC-MS chromatogram of the ethyl acetate extracted compounds produced during the acid IL pretreatment of S. pine, which was performed with 1.4 mmol of HCl/g wood, (signal identity listed in Table 3). Among the identified compounds, 5-hydroxymethylfurfural (HMF), 1-hydroxy-2-propanone (acetol), and other furan derivatives (including furan-2-carboxylic acid, tetrahydro-5-HMF, and 2,5-dihydyoxymethylfuran) are typical acidolysis products of polysaccharides, as documented in the recent literature.[3,15,16,16] Moreover, these GC-MS analyses showed the presence of some typical lignin degradation compounds such as catechol, methylcatechol, methylguaiacone, and acetoguaiacone.[30,31]

Conclusions

Three wood species—*Eucalyptus grandis* (E. grandis), southern pine (S. pine), and Norway spruce thermomechanical pulp (N. spruce TMP)— were dissolved in an ionic liquid (IL) ([Amim]Cl) and treated with dilute hydrochloric acid. For comparison, similar pretreatments were also conducted in aqueous media at equivalent acid concentrations. As anticipated, the aqueous hydrolysis conditions were effective only for the hemicellulose, whereas the acidic treatment in IL also caused the hydrolysis of cellulose. As a matter of fact, at the highest acid concentration investigated (1.4−1.5 mol of HCl/g wood), most of the carbohydrates were hydrolyzed (E. grandis, 95%; S. pine, 67%; and N. spruce TMP, 82%). Several low-molecular-weight hydrolysis products were identified from the recycled ILs including 5-hydroxymethyfurfural (HMF), furan-2-carboxylic acid, and 1-hydroxy-2-propanone. Analyses of the hydrolysis products also revealed typical lignin-derived compounds indicating that lignin was also degraded during the acidic IL pretreatment conditions. Therefore, it is evident that an IL-based acid pretreatment of wood may offer a potential platform for the efficient conversion of woody biomass to readily digestible carbohydrates and other valuable chemicals.

Note Added after ASAP Publication: The version of this paper that was published online March 4, 2010 contained errors in Figure 8. The corrected version was reposted March 10, 2009.

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