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COMMUNICATION

Lignin extraction from biomass with protic ionic liquids

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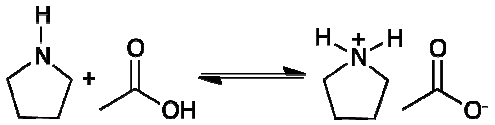
A highly effective method has been developed for the simple extraction of lignin from lignocellulosic biomass using a potentially inexpensive protic ionic liquid (PIL). After the lignin-extraction step, the PIL is easily recovered using distillation leaving the separated lignin and cellulose-rich residues available for further processing. Biopolymer solubility tests indicate that increasing the xylan (i.e., hemicellulose) solubility in the PIL results in greater fiber disruption/penetration, which significantly enhances the effectiveness of the lignin extraction.

Developing an economically-viable, integrated multiproduct biorefinery is necessary to accelerate biomass fractionation routes for the complete utilization of lignocellulosic biomass.[1-5] This could sustainably displace a substantial portion of the fossil fuel-based chemicals that are consumed within the transportation sector and chemical industry. Current techniques utilized for processing lignocellulosic materials (e.g., for the paper and pulp industry) are based on product streams that contain separated polysaccharides in which the cellulose is processed into materials (e.g., paper or fibers) or further processed into bio-based products or cellulosic bioethanol.[1,6-8] Other residues, including the lignin and hemicelluloses, are usually combusted to generate power.[6-10] In order to sustain a biorefinery's viability, the total process of material/biofuel production—including pretreatment (lignin removal and/or plant fiber disruption),[11-14] solvent and by-product recovery, and the production of derivatives from the by-products—needs to be optimized to minimize waste generation and resource underutilization.

Effectively partitioning lignocellulosic biomass into its various fractions is thus essential for the implementation of a biofuel/biorefinery-based economy. In particular, an efficient, low-cost technique for the removal and recovery of lignin, the component that largely renders biomass intractable,[15-21] is necessary to facilitate easier access to the polysaccharides and the production of valuable side-product streams based on lignin.[9,22-27] Lignin fractionation from biomass has been demonstrated with conventional ionic liquids (ILs),[28-30] but this typically requires high temperature processing (≥ 100 °C), extracts only a modest fraction of the lignin in the biomass (< 50%) and, most problematic, results in the buildup of soluble residuals (extractants, sugars, soluble lignin derivatives, etc.) in the ILs during their recovery and reuse. In addition, the high cost of the ILs necessitates the recoup of the ILs in their entirety, which is difficult to achieve due to small IL losses during processing and minor amounts of thermal degradation of the ions which occurs during the handling of ILs at elevated temperatures for long time periods.



Scheme 1 Reversible formation of [Pyrr][Ac] PIL from Pyrr and HAc reagents.

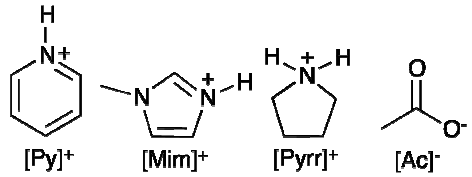


Fig. 1 PIL ions and their abbreviations: pyridinium $[Py]^+$, 1-methylimidazolium $[Mim]^+$, pyrrolidinium $[Pyrr]^+$ and acetate $[Ac]^-$.

Here it is demonstrated that protic ionic liquids (PILs)—salts formed in a one-step reaction from low cost acid (acetic acid) and base (amine) reagents, which typically melt below ambient temperature (Scheme 1)[31]—can be used at a relatively low temperature (< 100 °C) as an alternative to conventional (chemically intensive) lignin removal methods for biomass processing. The low cost of these reagents (acid and base), as well as the simplicity of the PIL synthesis method, indicate that the production of the PILs will be much simpler and more economical than for their aprotic IL counterparts. Furthermore, by taking advantage of the reversible exothermic reactions for PIL synthesis (Scheme 1) and the large difference in volatility between the PIL reagents and lignin, a procedure for the facile recovery/recycling of the PIL is available (i.e., once the lignin has been extracted from the biomass using a PIL, further separation *via* simple distillation is employed to recover the PIL leaving the non-volatile extracted lignin available for further processing).

Three PILs with different cations (Fig. 1) were utilized to demonstrate the method and explore how ion structure influences the lignin extraction. PIL synthesis occurs *via* proton exchange. The extent of this proton transfer (i.e., ion formation) has been linked to the difference in the pK_a of the reagents (ΔpK_a)—the greater the difference, the more the reaction is driven to the right in Scheme 1.[32] Given that the pK_a values for the reagents are Py 5.14, Mim 7.50, Pyrr 11.27, and HAc 4.76,[33,34] this suggests that

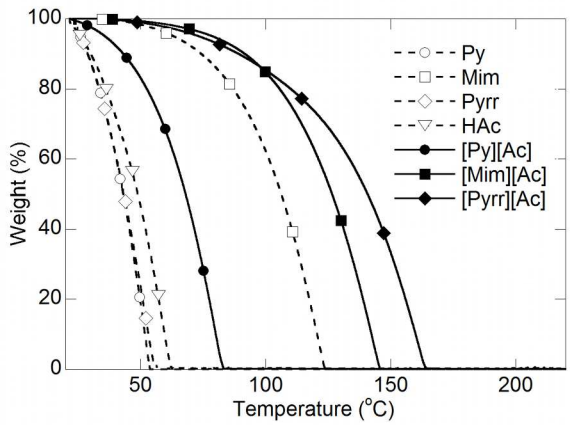


Fig. 2 Variable-temperature TGA heating traces (5 °C min^{-1}) of reagents and PILs.

Table 1 Solubility of Kraft lignin, cellulose and xylan (% w/w) in the reagents and PILs (after heating/stirring at 90 °C for 24 h)

	lignin	cellulose	xylan
Py	> 50	0.10 ± 0.00	0.02 ± 0.02
Mim	> 50	0.24 ± 0.02	6.34 ± 0.17
Pyrr	7.98 ± 0.10	0.63 ± 0.00	1.44 ± 0.07
HAc	0.7	0.07 ± 0.01	0.90 ± 0.04
[Py][Ac]	> 50	0.12 ± 0.03	0.82 ± 0.00
[Mim][Ac]	> 50	0.20 ± 0.05	5.60 ± 0.77
[Pyrr][Ac]	> 50	0.79 ± 0.04	> 15[a]

[a] Solubility limited by viscosity.

the ionicity (fraction of amine-acid mixture present as ions) should increase in the order:

[Py][Ac] < [Mim][Ac] << [Pyrr][Ac]

This conclusion is well supported by a Walden plot (ESI-Fig. S5),[32,35-37] as well as the thermal stability trends for the PILs (Fig. 2). Mass loss at elevated temperature for the PILs occurs due to the formation and subsequent loss of volatile reagents (i.e., the reversal of the proton exchange reaction forming ions - Scheme 1). For the [Py][Ac] and [Mim][Ac] PILs, this occurs at temperatures only modestly higher that for the amines from which the salts are formed. For the [Pyrr][Ac] PIL, however, mass loss does not occur until a substantially higher temperature than for the highly volatile pyrrolidine (Pyrr) (Fig. 2) confirming that both proton transfer to the amine is largely complete and that the N-H bond formed is quite stable.

The solubility of biomass components in the PILs was determined initially using commercially available model biopolymers: lignin (Kraft lignin-Indulin AT), cellulose (microcrystalline cellulose) and hemicellulose (xylan from beech wood). The PILs, as well as the amine reagents used to synthesize them, are able to dissolve large amounts of Kraft lignin (Table 1) with the exception of Pyrr. Furthermore, a negligible solubility of cellulose in the reagents and PILs is noted. Xylan (the principal component of corn stover hemicellulose),[38] on the other hand, has widely varying solubility in the different reagents and PILs (Table 1). Notably, xylan is largely insoluble in Py, Pyrr, HAc, and [Py][Ac]; is moderately soluble in Mim and [Mim][Ac]; and has a relatively high solubility in [Pyrr][Ac]. Given that [Pyrr][Ac] is more "ionic" than the other PILs, this suggests that the xylan and lignin solubility in this PIL may originate from interactions with the salt ions (as the solubility of the biopolymers in both Pyrr and HAc is quite low). These results provide verification that PILs are able to dissolve large amounts of (Kraft) lignin, but little to no cellulose, which is necessary for the selective extraction (partitioning) of lignin for lignocellulosic biomass fractionation. These results, however, do not indicate that a PIL is a much more favorable lignin extraction agent than the reagents, but this will be demonstrated below for lignin extraction from corn stover (CS).

A second important consideration for a pretreatment step is the ease of the separation/recyclability of the PIL after the lignin extraction. To demonstrate this, mixtures of the PILs with Kraft lignin were made and then separated using vacuum distillation. The PILs were readily recovered (Fig. 3) and the leftover lignin maintains its thermal stability characteristics (implying that the lignin was largely unmodified), while exhibiting some changes in its physical appearance due to the precipitation from solution (ESI-Figs. S15, S16 and S22). Analogous recyclability experiments carried out with cellulose in the PILs confirmed that the recovered cellulose largely maintains its cellulose-I crystal structure due to the low solubility of cellulose in the PILs (ESI-Fig. S17).

The structure and properties of Kraft lignin differ markedly from that of biomass lignin. The PILs were therefore then employed to pretreat extractive-free corn stover (EF-CS). After heating and stirring the EF-CS in the PILs (90 °C for 24 h), the

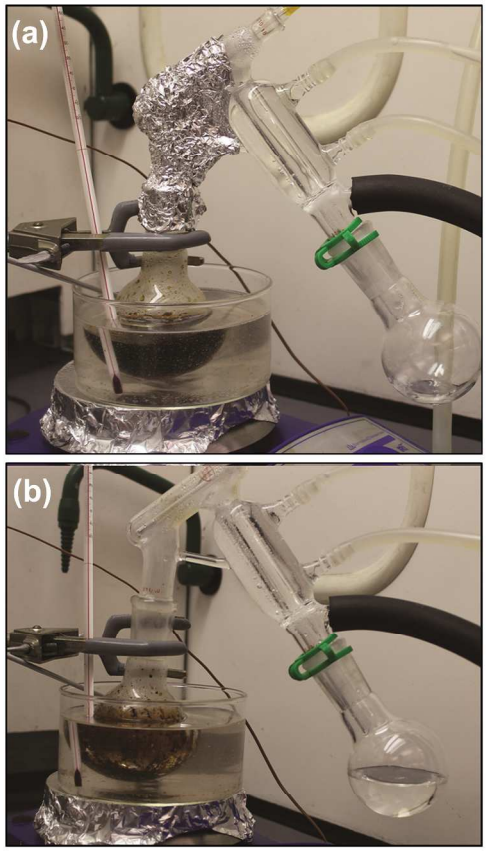
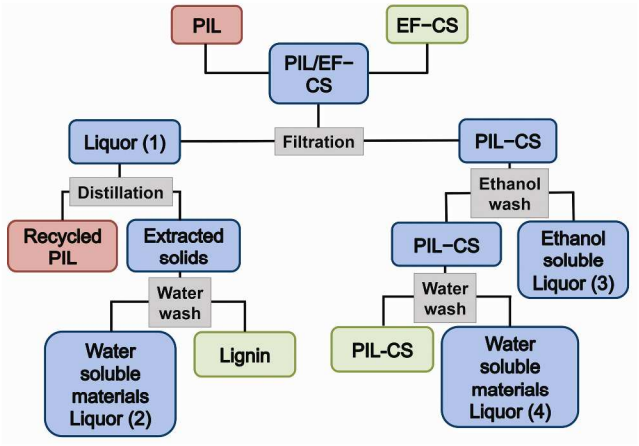


Fig. 3 Distillation apparatus used to separate the PILs from lignin showing: (a) initial setup and (b) after completed collection of the distillate (PIL).



Scheme 2 Lignin-extraction process for CS using a PIL with labelled process streams.

Table 2 Composition (% w/w) of EF-CS and PIL-CS after pretreatment (90 °C for 24 h)

	EF -CS	[Py][Ac] -CS	[Mim][Ac] -CS	[Pyrr][Ac] -CS
lignin	16.6	15.7	14.3	6.2
glucan	38.2	42.6	44.5	52.8
xylan	20.0	20.8	22.1	22.0
arabinan	2.5	1.3	1.8	2.9
galactan	1.1	0.9	0.8	0.8
mannan	0.1	0.0	0.2	0.2
ash	0.9	1.1	2.0	0.4
total	61.9	65.6	69.4	78.7

insoluble solids (i.e., PIL-CS) were separated by filtration from the liquid PIL filtrate (i.e. Liquor 1) (Scheme 2). Compositional analysis of the solids (Table 2) revealed that the lignin extraction efficiency increased in the order:

[Py][Ac] < [Mim][Ac] << [Pyrr][Ac]

The PILs were then recovered from the filtrate mixture containing the extracted materials (lignin with a lesser amount of hemicellulose and other components) (Liquor 1) using vacuum distillation. The recovered PILs were characterized using ^{1}H-NMR analysis (Fig. 4). The [Py][Ac] and [Mim][Ac] PILs were recovered as essentially pure PILs (ESI-Figs. S18 and S19), but the [Pyrr][Ac] PIL contained some amide impurity (ESI-Figs. S20 and S24-S27)[39] due to the extensive pretreatment time at elevated temperature. Note that the shift in the peak associated with the protons bonded to the cation nitrogen atom was verified to be due to the presence of small amounts of water (ESI-Fig. S28).

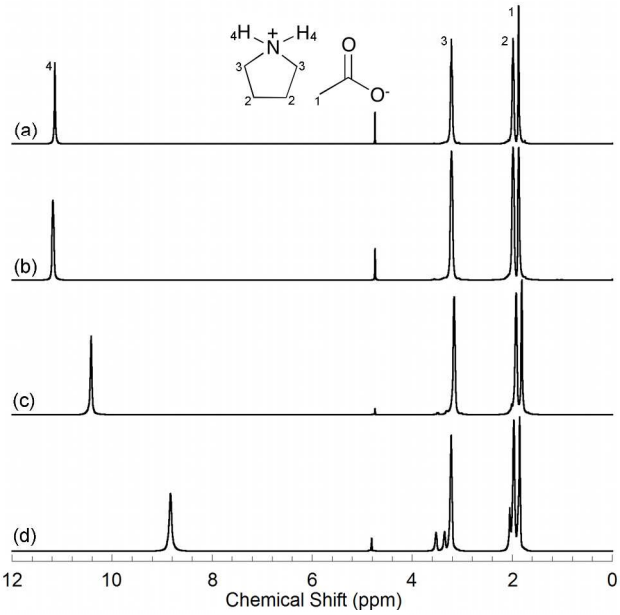


Fig. 4 ^{1}H-NMR spectra (δ_{solv} = 4.75 ppm for D_2O-external lock) of the PIL ([Pyrr][Ac]): (a) after synthesis, (b) after distillation (no Kraft lignin or EF-CS), (c) after distillation (from Kraft lignin mixture after heating at 90 °C for 0.5 h) and (d) after distillation (from lignin filtrate—"Liquor (1)"—after heating at 90 °C for 24 h with EF-CS).

The [Pyrr][Ac] PIL was able to extract greater than 70% of the

Table 3 Composition of corn stover components after pretreatment with [Pyrr][Ac]—amount recovered, g (% w/w of initial component in EF-CS)

	lignin	glucan	xylan	arabinan	galactan	mannan	ash
EF-CS	0.833 (100)	1.913 (100)	1.000 (100)	0.126 (100)	0.053 (100)	0.005 (100)	0.040 (100)
extracted solids from [Pyrr][Ac] (Lignin)	0.606 (72.81)	0.067 (3.50)	0.009 (0.85)	0.006 (5.00)	0.001 (1.00)	0.000 (6.00)	0.029 (71.25)
water wash-lignin (Liquor 2)	0.025 (3.00)	0.204 (10.66)	0.311 (31.07)	0.028 (22.55)	0.026 (49.18)	0.004 (77.84)	-
[Pyrr][Ac]-CS (PIL-CS)	0.185 (22.19)	1.572 (82.17)	0.656 (65.53)	0.087 (68.95)	0.023 (43.32)	0.001 (12.52)	0.010 (25.00)
ethanol wash-CS (Liquor 3)	0.010 (1.20)	~ 0	~ 0	~ 0	~ 0	~ 0	-
water wash-CS (Liquor 4)	0.005 (0.60)	~ 0	~ 0	~ 0	~ 0	~ 0	-
total	0.831 (99.80)	1.834 (96.33)	0.975 (97.45)	0.122 (96.50)	0.050 (93.50)	0.005 (96.00)	0.039 (96.25)
Liquor 2 + PIL-CS	0.210 (25.19)	1.776 (92.83)	0.967 (96.60)	0.115 (91.50)	0.049 (92.50)	0.005 (90.36)	0.010 (25.00)

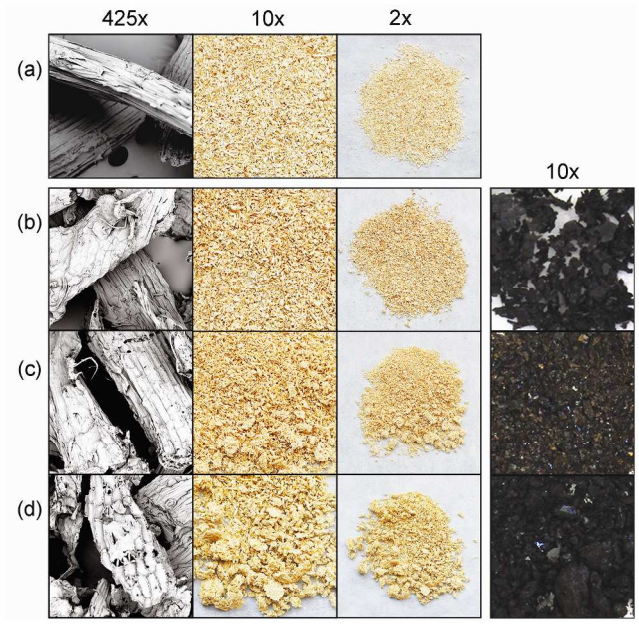


Fig. 5 Images depicting the CS fibers before and after PIL treatment and the recovered lignin from CS after PIL treatment: (a) EF-CS, (b) [Py][Ac]-CS, (c) [Mim][Ac]-CS and (d) [Pyrr][Ac]-CS.

lignin in the EF-CS, leaving a polysaccharide-rich stream (PIL-CS) (Tables 2 and 3). Despite the high Kraft lignin solubility in all three PILs (Table 1), the amount of CS-lignin extracted varied significantly for the three PILs (Table 2). The trend in lignin removal followed the trend in xylan solubility (Table 1). Using the same processing conditions (stirring at 90 °C for 24 h), the neat reagents were found to be ineffective at extracting lignin from corn stover—% lignin after pretreatment: Py (15.6%), Mim (13.9%), Pyrr (15.0%) and HAc (16.5%) (compare with results in Table 2). Note that the Mim reagent, which is able to dissolve some hemicellulose (xylan) (Table 1), is able to extract more lignin than the Py and Pyrr, but this reagents still does not extract a significant amount of the lignin from the CS. SEM analysis of the CS fibers before and after the PIL pretreatment confirmed that an increase in lignin removal does correspond with an increased disruption of the CS fibers (increase in the size of the fibers, as well as the formation of pores on the fiber surface - Fig. 5)—indicating that penetration of the CS fibers by the PILs has occurred as both more lignin and hemicellulose are removed. Lignin found in the outer plant cell wall accounts for only about 20% of the lignin in biomass.[40] In order to access the remainder of the lignin, one or more of the polysaccharides needs to be partially soluble in the PIL.

Previous reports have suggested that PILs can act as catalysts to depolymerize lignin from biomass through the cleavage of the β-O-4 bonds at high temperature (130-200 °C),[41-47] but there is no indication that this depolymerization of lignin occurs in the present study using neat [Pyrr][Ac] at a lower temperature. These previous works used considerably different processes from the one reported in the present manuscript. One group depolymerized lignin used PILs in dilute mixtures (2 mmol) with ethanol/water (50 mL) at 200 °C in a stainless steel autoclave.[41-44] Another group depolymerized lignin using a PIL with a small amount of water added at 110-150 °C.[45-47] It is noteworthy that, under these processing conditions, the PILs will be largely dissociated into the amines and acid (i.e., H_2SO_4 or HCl) reagents rather than existing as discrete ions, as noted in Fig. 2. These processes therefore resemble to some extent the well known organosolv pretreatment process with ethanol/water mixtures and the addition of the strong acid H_2SO_4 as a catalyst.[48-51] In particular, the lignin depolymerization process was found by these authors to be relatively ineffective at 110 °C (higher temperatures were necessary)[45-47] and the present process does not utilize the strong acids (pK_a values: HCl -8.0, H_2SO_4 -3.0/1.9 and HAc 4.8) necessary for lignin depolymerization. In addition, the high temperatures and acids employed by these other processes degrade the polysaccharides into a variety of chemicals,[52] whereas the reported process results in little to no degradation of the polysaccharides.

The results reported demonstrates that PILs are able to extract large amounts of lignin from biomass. The dissolution, to some extent, of one or more of the polysaccharides, however, is necessary to enable PIL penetration of the biomass fibers and full access to the lignin. Partial dissolution of xylan, the major hemicellulose component in CS, disrupts the fibers enough to attain a very high amount of lignin extraction. This preliminary work with three PILs suggests that the solubility of xylan in the PILs may be directly proportional to the salt ionicity. Further work systematically varying the structure of ions will confirm this.

Pure PILs can be recovered at yields approaching 100% using relatively mild distillation conditions (with a partial vacuum). For full PIL recovery, however, a careful selection of the anions/cations used to synthesize the PIL is necessary to avoid PILs that are susceptible to the formation of amide by-products due to thermal degradation.[39] This reaction is thought to be minimized by increasing the number of substituents on the amine group. This slight increase in steric hindrance on the cation could reduce the reactivity of the reagents and select for the lower energy state –the PIL.[39] PILs, which do not undergo this side reaction, but extract even greater amounts of lignin from CS have, however, been identified.[52]

The functionality/composition of the lignin extracted by the PILs appears to be largely retained. It is crucial to note that, after the PIL distillation step leaving the lignin-rich solids, the polysaccharides and sugars extracted by the PIL may be readily separated from the lignin by a simple water wash step (Liquor 2 in Scheme 2), as the lignin is insoluble in water. If this wash is then combined with the polysaccharide-rich solids, well over 90% of the polysaccharides/sugars may be recovered with removal of approximately 75% of the lignin in the EF-CS (Table 3). Therefore, the use of potentially inexpensive PILs to selectively extract lignin from lignocellulosic biomass, using simple processing conditions at a modest temperature and near atmospheric pressure, with high extraction efficiency and low waste generation is a quite promising means for the total utilization of lignocellulosic biomass—a necessary requirement for the implementation of a biofuel/biorefinery-based economy.

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Notes and references

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† Electronic Supplementary Information (ESI) available: NMR analysis, experimental details, distillation set up and additional characterization results. See DOI: 10.1039/b000000x/

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52 Preliminary work has found that PILs with significantly different ion structures from those reported here are very effective lignin extractants and fully recoverable (no significant thermal degradation occurs during biomass processing and distillation). These will be reported in a future publication.

TOC

A simple, highly effective method for lignin extraction from biomass is reported using PILs which can easily be distilled/recovered.