

Cost-Effective Processing of Carbon-Rich Materials in Ionic Liquids: An Expeditious Approach to Biofuels

Sadia Naz, Maliha Uroos,* and Muhammad Ayoub

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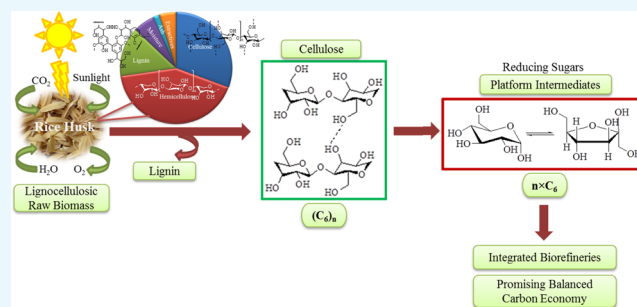
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ABSTRACT: This work presents a cost-effective approach for processing of renewable carbon-rich biomass using pyridinium-based Lewis acidic ionic liquids (LAILs). Rice husk as carbon-rich lignocellulosic waste was pretreated with a series of neutral and Lewis acidic ionic liquids to yield valuable intermediate platform monosaccharides. Novelty in the work lies in direct conversion of lignocellulosic carbohydrates into reducing sugars without their further conversion into 5-hydroxymethylfurfural or any other platform chemicals that are fermentation inhibitors for bioethanol production. The unconverted cellulose-rich material (CRM) is regenerated as a delignified material by the simultaneous addition of antisolvents. CRM and recovered lignin obtained after pretreatment were analyzed via scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and Fourier transform infrared (FTIR) spectroscopy. The process was optimized with respect to a high yield of platform sugars and the quantity as well as quality of recovered CRM and lignin contents. Various reaction parameters involving the molecular structure of ionic liquids (ILs), Lewis acidic strength of ILs, biomass loading into IL, time, temperature, and biomass particle size were screened thoroughly. From all of the tested ILs, unsymmetrical 3-methylpyridinium IL having *N*-octyl substitution and chloroaluminate anion showed a greater conversion efficiency at 100 °C for 1.5 h. FTIR and SEM analyses of recovered CRM justify >90% lignin removal from rice husk. From all of the removed lignin, 60 wt % of original lignin content was recovered. The Lewis acidic system possessed recycling ability up to 3 times for subsequent treatment of rice husk without a significant loss of efficiency.



1. INTRODUCTION

Lignocellulosic biomass is the only abundant and renewable carbon-rich material that has been expected to be the most potent and low-cost source for biofuels and fine chemicals.¹ The only barrier to the direct conversion of lignocellulosic biomass into renewable energy and valuable products is its recalcitrant nature due to the compact and rigid structure and the strong bonding present in its constituents. Thus, the highly intertwined constituents, cellulose, hemicellulose, and lignin, are first to be separated for further biorefinery applications. Traditionally, various methods like physical,² biological,³ chemical,⁴ physicochemical, or their combination/s are applied to separate the biomass components. But the problem is harsh conditions like high temperature and pressure associated with those methods.

Ionic liquids (ILs) are the most attractive pretreatment solvents to overcome biomass recalcitrance. They efficiently deconstruct the biomass and transform it into value-added chemicals. These are highly green, designed, and degradative solvents, possessing high dissolution ability even for polymeric compounds. Their adjustable striking features involve polarity, viscosity, as well as hygroscopicity that can be tuned accordingly.⁵ Various ILs have been reported for pretreatment, hydrolysis, deconstruction, and fine chemicals conversion of various biomasses, to date. The most explored ILs for biomass

processing are the imidazolium ones with a variety of anions. 1-Butyl-3-methylimidazolium chloride ([C₄C₁IM]Cl) is reported for the pretreatment and deconstruction of various biomasses like wheat straw,⁶ rice straw,⁷ sugarcane bagasse,⁸ bamboo biomass,⁹ sago waste,¹⁰ oil palm empty fruit bunch,¹¹ and many more. Most reported anions with this cation other than chloride are hydrogen sulfate,¹² acetate, and tetrafluoroborate.⁷ Some other widely explored cations for biomass include triethylammonium,¹³ phosphonium,¹⁴ and pyrrolidinium.¹⁵

Besides the green profile of ILs and their biomass processing efficiencies, the only problem in their bulk scale usage is the high cost of ILs due to their expensive starting reagents. A solution to this problem lies in exploring low-cost starting materials and to use the resultant ILs in biomass processing.¹⁶ Recently, various research groups have reported low-cost ILs for biomass pretreatment and processing. Yang and co-workers reported

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Table 1. Effect of Different ILs on One-Pot Saccharification and Delignification of Rice Husk

Rice husk (250 μm) + IL		(i) 100 °C, 1 h (ii) Acetone, H ₂ O		CRM + Lignin + TRS
sr., no.	IL	TRS (%)	% conversion ^a	% lignin recovery ^b
1	[C ₄ Py]Cl	15	43	
2	[C ₈ Py]Cl	18	43	
3	[C ₄ C ₁ Py]Cl	14	06	
4	[C ₈ C ₁ Py]Cl	58	79	<1
5	[C ₄ C ₁ IM]Cl	12	06	
6	[C ₈ C ₁ IM]Cl	32	04	
7	[C ₈ C ₁ Py]Br	32	04	
8	[C ₈ C ₁ Py]I	12	02	
9	[C ₈ C ₁ Py]BF ₄	31	04	
10	[C ₈ C ₁ Py]PF ₆	30	04	
11	[C ₈ C ₁ Py]NaCl ₂	07	>1	
12	[C ₈ C ₁ Py]KCl ₂	13	>1	
13	[C ₈ C ₁ Py]CrCl ₄	37	18	4
14	[C ₈ C ₁ Py]FeCl ₄	54	41	36
15	[C ₈ C ₁ Py]CoCl ₃	33	16	4
16	[C ₈ C ₁ Py]AlCl ₄	60	43	40
17	[C ₈ C ₁ Py]BiCl ₄	10	>1	<1
18	[C ₈ C ₁ Py]CdCl ₃	37	32	1

^aAll reactions were done with 10 wt % rice husk loading into IL, percentage conversion of whole carbohydrate content (cellulose and hemicellulose) of rice husk calculated by the difference between original and recovered content³¹ (moles of reacted cellulosic content/moles of initial cellulosic content) × 100%. ^bWith respect to the original lignin present in untreated rice husk,³² recovered lignin content (wt %) = (mass of extracted lignin/mass of lignin in raw biomass) × 100.

the extraction of cellulose-rich material (90 wt %) from corn straw using low-cost 2-hydroxy-*N*-(2-hydroxyethyl)-*N*-methyl-ethanaminium methanesulfonate at 140 °C for 6 h.¹⁷ Similarly, triethylammonium hydrogen sulfate ([TEA]HSO₄) is reported for the pretreatment of *Miscanthus* by Gschwend et al.¹⁸ Lignin was removed at high temperatures (150–180 °C), and the recovered CRM was subjected to enzymatic hydrolysis for sugar production. The same IL was used for the pretreatment of rice, wheat, and sugarcane agricultural biomasses by the same research group¹⁹ in 2019 but again at elevated temperatures. Also, the sugars were obtained in two steps: pretreatment by IL to recover CRM and then enzymatic saccharification.

Another tactic to boost the process efficiency for industrial application is to develop one-pot protocol by employing cost-effective ILs. This one-pot strategy reduces the operating and capital costs to a reasonable extent.²⁰ To date, various traditional methods and ILs have been reported for the effective deconstruction of biomass as well as the efficient conversion of its carbohydrate constituents (cellulose and hemicellulose). But most of them focus either only on conversion or on deconstruction. To our knowledge, there exist only a limited number of reports for the simultaneous delignification and conversion of delignified biomass. Recently, we reported [C₄C₁Py]CoCl₃ for the one-pot deconstruction of wheat straw and simultaneous conversion of its carbohydrate contents at a low temperature (100 °C) and 2 h reaction time.²¹ Lignin recovery was 67%, and carbohydrate conversion was 32%, accounting for the generation of 70% total reducing sugars (TRS). Another recent paper by the research group of Lopez reported acidified water and methyl isobutyl ketone (MIBK) for one-pot delignification and carbohydrates conversion of *Eucalyptus globulus* wood (non-IL method).²² Lignin recovery was reported 17.4 g per 100 g of wood used. Carbohydrates of wood were converted into various chemicals like furfural,

levulinic acid, formic acid, and acetic acid at high temperatures 180 or 190 °C but at short reaction times, 70 min.

In this context, this work aims to develop an economical, one-pot protocol for the deconstruction of rice husk and simultaneous conversion of its cellulosic components into monosaccharides. Pyridinium-based ILs are used that are 4 times cheaper compared to the most widely explored imidazolium ILs for biomass processing. Method of synthesis and process cost are also almost the same as those of imidazolium ones.²³ It is suggested that structural variations in pyridinium skeleton should be tested for the sustainable design of IL.²⁴ Our former research justified the dissolution power of pyridinium-based ILs for cellulose²⁵ and deconstruction efficiency for lignocellulosic biomass.²⁶ This work presents their effectiveness for the simultaneous conversion and delignification of compact biomass. Pyridinium cations, with and without 3-methyl substitution, and butyl or octyl side chains were tethered with different anions. It is suggested that the toxicity of ILs tends to decrease by ring methylation. Couling et al. reported the following order of toxicity for pyridinium-based ILs: 1-butyl-3,5-dimethylpyridinium bromide ([C₄C₁²Py]Br) < 1-butyl-3-methylpyridinium bromide ([C₄C₁Py]Br) < 1-butylpyridinium bromide ([C₄Py]Br).²⁷ Also, the good biodegradability is reported to be associated with a long unbranched alkyl side chain or side chain bearing some polar group.²⁸ Studies also reveal that 1-butyl-3-methylpyridinium bromide ([C₄C₁Py]Br), 1-hexyl-3-methylpyridinium bromide ([C₆C₁Py]Br), and 1-octyl-3-methylpyridinium bromide ([C₈C₁Py]Br) could be mineralized completely by microbial community, but the only readily biodegradable IL among all is [C₈C₁Py]Br.²⁹

2. RESULTS AND DISCUSSION

2.1. Characterization of ILs.

All of the synthesized ionic liquids (ILs) were characterized via FTIR (Figures S1 and S2)

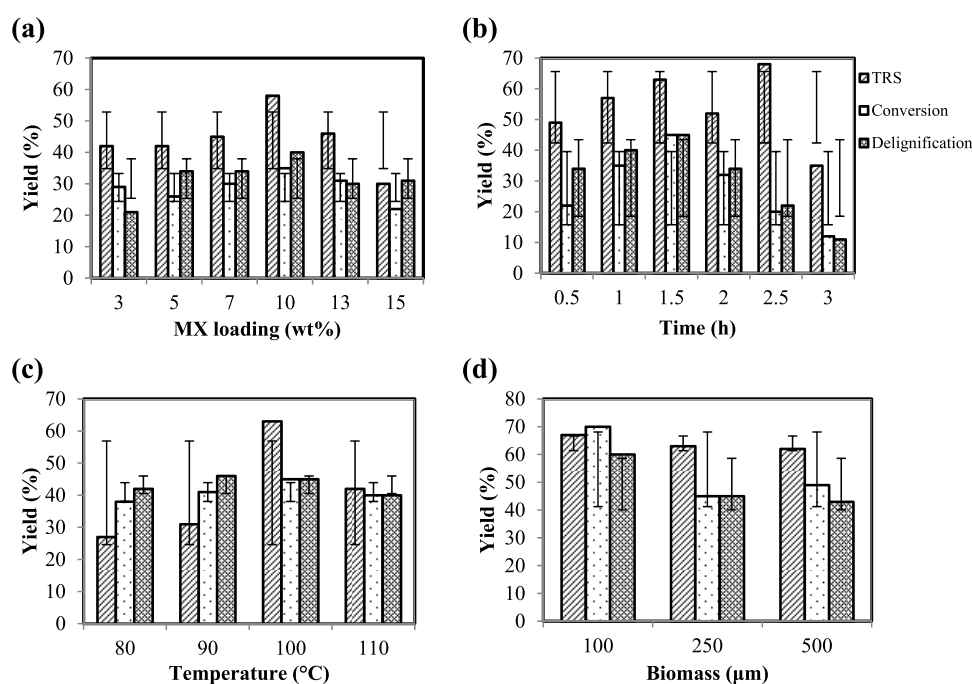


Figure 1. Optimization of (a) Lewis acidic character of $[\text{C}_8\text{C}_1\text{Py}]\text{AlCl}_4$, (b) time, (c) temperature, and (d) biomass particle size.

and proton nuclear magnetic resonance (^1H NMR) spectroscopies (Figures S3–S6). FTIR peaks are detailed in Section 4. ^1H NMR spectra of 1-butylpyridinium-based ILs exhibited a doublet at 8.81 ppm with a coupling constant of 6.0 Hz and two triplets at 8.49 and 8.03 ppm with coupling constants of 7.6 and 6.0 Hz, respectively, corresponding to all five protons of pyridinium ring. Protons of butyl side chain are justified by the appearance of a triplet at 4.56 ppm, two multiplets at 1.90 and 1.27 ppm, and a triplet at 0.88 ppm. ^1H NMR peaks for unsymmetrical pyridinium cation of 1-butyl-3-methylpyridinium-based ILs appeared as a singlet at 8.62 ppm, two doublets at 8.56 and 8.27 ppm, and a triplet at 7.85 ppm. 3-Methyl substitution appeared as a singlet at 2.46 ppm. A triplet at 4.83 ppm with a J value of 7.2 Hz, two multiplets at 1.88 and 1.24 ppm, and a triplet at 0.85 ppm with a J value of 7.6 Hz justified the presence of butyl substitution. For 1-octylpyridinium-based ILs, protons of pyridinium exhibited a doublet and two triplets at 8.78, 8.50, and 8.05 ppm, respectively. Octyl substitution displayed a triplet at 4.53 ($J = 6$ Hz) and two multiplets at 1.92 and 1.09 ppm corresponding to seven CH_2 groups and a triplet at 0.75 ppm for CH_3 with $J = 5.6$ Hz. Similarly, for 1-octyl-3-methylpyridinium, the aromatic ring exhibited a singlet (8.62 ppm), two doublets (8.56 and 8.28 ppm), and a triplet (7.85 ppm). A singlet appeared at 2.47 ppm for 3-methyl substitution, while a triplet (4.46 ppm), two multiplets (1.89 and 1.09 ppm), and a triplet at 0.75 ppm appeared for octyl substitution.

2.2. One-Pot Deconstruction and Simultaneous Cellulose Conversion. **2.2.1. Effect of ILs.** Four different symmetrical/unsymmetrical pyridinium-based neutral ILs varying in their N -alkyl length were loaded with 10 wt % 250 μm rice husk based on their maximum loading capacity and best conversion results. Initially, the experiments were done at 100 $^\circ\text{C}$ for 1 h. Percentage yields of reducing sugars indicated that the unsymmetrical ILs are most effective. Of these unsymmetrical ones, 1-octyl-3-methylpyridinium chloride ($[\text{C}_8\text{C}_1\text{Py}]\text{Cl}$) led to the highest reducing sugars resulting in 79% conversion of the carbohydrate content of rice husk (Table 1).

The effect of cations and anions of IL was then studied by changing the cation of $[\text{C}_8\text{C}_1\text{Py}]\text{Cl}$ from pyridinium to imidazolium, and anion from chloride to bromide, iodide, tetrafluoroborate, and hexafluorophosphate. Results indicated the superiority of pyridinium core over the imidazolium one for carbohydrate conversion. It votes for this protocol to be the most economic and cost-effective. Among various anions, considerable results were that of chloride due to its strong interaction and hydrogen-bonding ability with cellulose and lignin content of lignocellulosics for dissolution as reported in the literature.

IL $[\text{C}_8\text{C}_1\text{Py}]\text{Cl}$ yielding best results was then made Lewis acidic by addition of 10 wt % of nine different metal chlorides: NaCl, KCl, CrCl₃, FeCl₃, CoCl₂, CuCl₂, AlCl₃, BiCl₃, and CdCl₂ to enhance the delignification, which was less than 1% by the above-reported neutral ILs. These Lewis acidic ILs are proposed to form interactions with biomass by disrupting the hydrogen-bonding network of cellulose as well as dispersive and ion-dipole interactions, and π - π and n - π conjugation for the dissolution of lignin.³⁰ AlCl₃ was found to be the most effective Lewis acid causing the highest saccharification as well as delignification. This may be attributed possibly to the greater coordination tendency of AlCl₃ with IL forming $[\text{C}_8\text{C}_1\text{Py}]\text{AlCl}_4$, which, in turn, has greater coordination ability with carbohydrate and lignin contents of rice husk biomass. FeCl₃, CrCl₃, and CoCl₂ also have considerable activities. Other metal chlorides like NaCl, KCl, and BiCl₃ did not work. An exception was CuCl₂, which failed to form any complex with IL.

2.2.2. Optimization of Different Process Variables. Encouraged by the best conversion and delignification results of $[\text{C}_8\text{C}_1\text{Py}]\text{AlCl}_4$, further experimentation was done to optimize different process variables like Lewis acidity of ILs, time, temperature, and biomass particle size systematically.

Different wt % amounts of AlCl₃ were added in $[\text{C}_8\text{C}_1\text{Py}]\text{Cl}$ to find its best catalytic loading in IL to set the Lewis acidity. A 10 wt % loading was found optimal with respect to TRS production and deconstruction, after which a sudden decrease in outcomes

was observed probably due to reduction in the coordination ability of IL (900 mg) used for the reaction and certain other side reactions due to excessive metal chlorides that tend to reduce the targeted products (Figure 1).

Time dependence of the system was then studied by carrying out the next batch reaction with 10 wt % AlCl_3 at 100 °C for 1 h (Figure 1). Analysis of produced reducing sugars was done after every 30 min. TRS was found to increase with an increase in time up to 1.5 h, at which maximum conversion and delignification was achieved.

After studying the influence of time on deconstruction and conversion rate, the effect of temperature was monitored by carrying out the batch experiments at 80, 90, 100, and 110 °C (Figure 1). The rate of deconstruction and depolymerization of rice husk was observed to be directly proportional to temperature up to an optimal limit. After optimum temperature, TRS was decreased sharply due to the initiation of some other side reactions. The acceleration of conversion and deconstruction rate with temperature is due to the decrease in viscosity of IL media with a high temperature, which in turn enhances the mass transfer rate, thus easing the depolymerization of the cellulosic network present in rice husk.³³ After optimal temperature, certain side reactions are accelerated, causing polymerization of sugars and also affecting the deconstruction rate.³⁴ Hence, the righteous temperature noted for this reaction with the optimized catalytic system and time is 100 °C. The possibility of formation of 5-hydroxymethylfurfural (5-HMF) via dehydration of sugars was checked at higher temperatures >100 °C, following our previously reported protocol.³⁵ Analysis was done using D-Star HPLC instrument with a UV–vis detector equipped with Discovery, HS C18 column; 5 μm particle size (25 cm \times 4.6 mm) using acetonitrile as mobile phase at 25 °C and a flow rate of 1.0 mL/min. 5-HMF (>0.1%) was detected with $[\text{C}_8\text{C}_1\text{Py}]\text{AlCl}_4$ even at 130 °C, but the recovered CRM was fully carbonized, suggesting that the main byproducts formed in the reaction are humins (insoluble carbohydrate degradation products). 5-HMF was observed to produce with the $[\text{C}_4\text{C}_1\text{Py}]\text{CrCl}_4$ catalytic system; 20% 5-HMF, 54% TRS, and 65% lignin extraction were obtained at 130 °C in 1 h (Figure S8). The yield of sugar is less due to the further dehydration reaction leading to 5-HMF. Also, the lignin recovery is enhanced under these conditions, but CRM is in completely decarbonized form.

Rice husk loading was also altered by varying different particle sizes (Figure 1). Processing of lignocellulosic biomass necessitates small-sized biomass so that highly viscous IL can easily diffuse and penetrate inside the cell walls due to its complex construction. However, a high energy is required to reduce the particle size that also enhances the process cost. To check the effect of particle size, rice husk with three different sizes of 100, 250, and 500 μm was used. The dissolution, deconstruction, and conversion decreased with increasing size of lignocellulose particles as is obvious by less percent conversion and lignin recovery.

2.3. Biomass Fractionation. After the pretreatment process, lignocellulosic components cellulose and lignin were regenerated via antisolvents water and acetone (1:1) (Figure 2). Usually water, acetone, and alcohols or their binary mixtures are used for this purpose. Enzymatically hydrolyzed biomass requires water, while those pretreated with AILs require some organic solvent along with water for CRM and lignin retrieval.

Here, water disrupts the hydrogen bond formed between lignocellulose and IL during dissolution, thus regenerating the

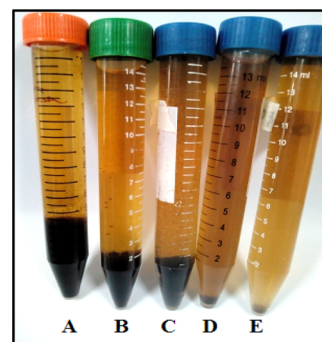


Figure 2. Retrieval of lignin by addition of antisolvents. Pretreatment systems: (A) $[\text{C}_8\text{C}_1\text{Py}]\text{AlCl}_4$, 100 μm rice husk, (B) $[\text{C}_8\text{C}_1\text{Py}]\text{AlCl}_4$, 250 μm rice husk, (C) $[\text{C}_8\text{C}_1\text{Py}]\text{FeCl}_4$, 250 μm rice husk, (D) $[\text{C}_8\text{C}_1\text{Py}]\text{CoCl}_3$, 250 μm rice husk, and (E) $[\text{C}_8\text{C}_1\text{Py}]\text{CrCl}_4$, 250 μm rice husk.

cellulose. Acetone added to the system dissolves all of the lignin, and then its evaporation resulted in the regeneration of lignin. CRM was collected via filtration, while lignin was recovered via centrifugation. The recovered lignin was about 60 wt % of original lignin content. As lignin is the main problem in the efficient conversion of lignocellulosic carbohydrate content,³⁶ its separation is important for developing integrated biorefineries. If successfully done, it improves the enzymatic hydrolysis of carbohydrates and thus cellulosic material of biomass can better be utilized.

UV–vis analysis of commercial and recovered lignin was also performed showing λ_{max} at 280 nm. Total phenolic content was determined using the lignin solution to check if further breakdown of lignin is happening due to ILs or intact biopolymer is recovered. No significant total phenolic percentage is observed using Folin's reagent.

2.4. Mass Balance. Mass balance was calculated on the basis of recovered masses of lignin and regenerated CRM. Starting from 100 mg of biomass, 42, 43, 50, 61, and 62 mg of CRM were obtained by $[\text{C}_8\text{C}_1\text{Py}]\text{AlCl}_4$, $[\text{C}_8\text{C}_1\text{Py}]\text{FeCl}_4$, $[\text{C}_8\text{C}_1\text{Py}]\text{CdCl}_2$, $[\text{C}_8\text{C}_1\text{Py}]\text{CrCl}_4$, and $[\text{C}_8\text{C}_1\text{Py}]\text{CoCl}_3$, indicating 43, 41, 32, 18, and 16% conversions of the carbohydrate content of rice husk (250 μm), respectively. Talking about optimized conditions, 22 mg of CRM was obtained, leading to 70% conversion of carbohydrates. On the other hand, 15 mg of mass was that of lignin fraction.

2.5. Characterization of CRM and Lignin Samples.

2.5.1. FTIR Analysis. Untreated as well as deconstructed rice husk was analyzed via Fourier transform infrared (FTIR) spectroscopy (Figure 3). Untreated rice husk exhibits various peaks related to cellulose as well as lignin. The region beyond 1800 cm^{-1} is not of much interest, as it contains similar –OH stretching vibrational band (3322 cm^{-1}) and C–H stretches (2920 cm^{-1}) in untreated as well as treated biomass. The peak at 1639 cm^{-1} in original and IL-treated rice husk also corresponds to methylene and methyne groups, while diaryl C–O stretch and alkyl–aryl (R–O) stretch are observed at 1100 and 1032 cm^{-1} , respectively.³⁷ Contrarily, the IR spectrum of lignin contains characteristic peaks in the aromatic region (Figure 3c). Peaks at 1585 and 1504 cm^{-1} are responsible for aromatic skeletal vibration breathing with C=O stretching, whereas aromatic skeleton C–C stretching is obvious at 1252 cm^{-1} .³⁸ Delignification can clearly be seen by comparing the FTIR spectra of original rice husk with that of regenerated CRM; the peak intensities at 1585 and 1504 cm^{-1} are clearly decreased in

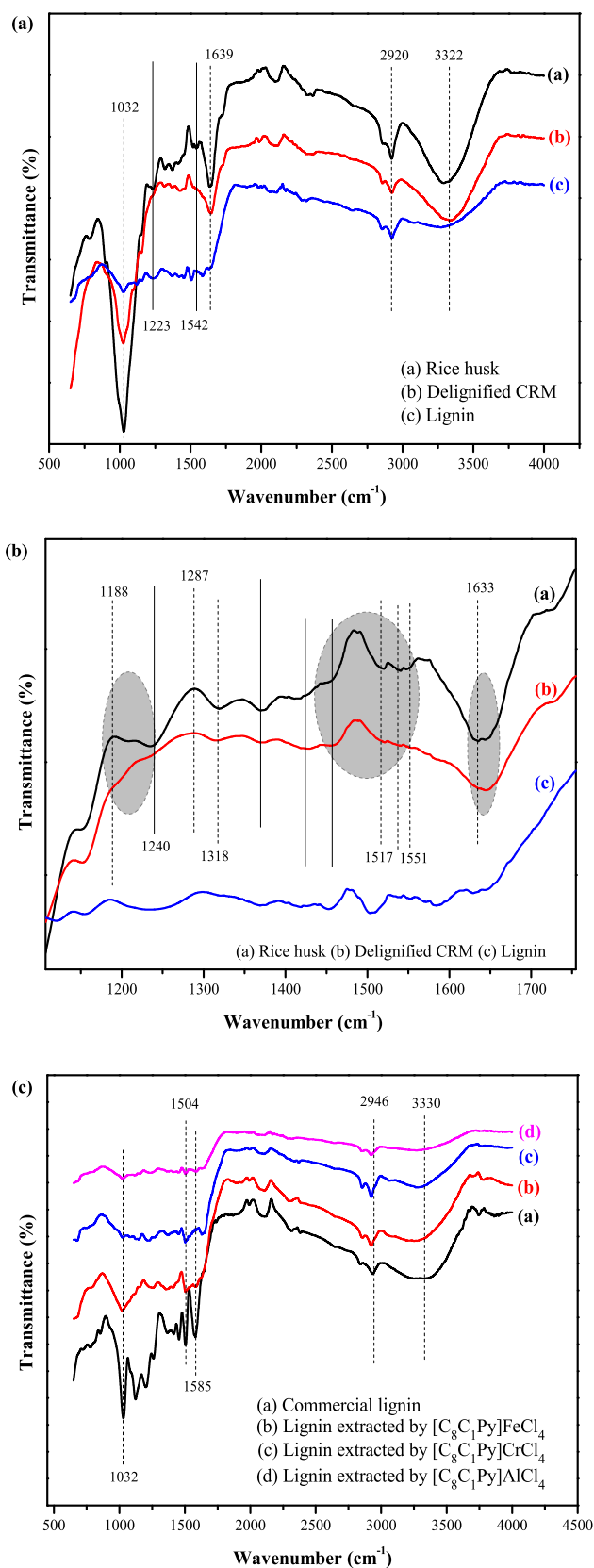


Figure 3. (a) FTIR spectra of rice husk before and after processing, (b) hydrogen-bond disruption in CRM and transformation of cellulose I to cellulose II after IL treatment, and (c) comparison of extracted lignin samples with commercial alkaline lignin (TCI).

CRM obtained after IL treatment. The hydrogen-bond disruption in CRM and the transformation of cellulose I to cellulose II are obvious by peak shifts in the areas 1510–1570 and 1180–1280 cm⁻¹, respectively (Figure 3b).³⁹ For lignin, a comparison is provided for commercial lignin and recovered lignins using [C₈C₁Py]FeCl₄, [C₈C₁Py]AlCl₄ and [C₈C₁Py]-CrCl₄. The aromatic peaks at 1585 and 1504 cm⁻¹ are more intense for lignins recovered by [C₈C₁Py]FeCl₄ and [C₈C₁Py]-CrCl₄, while the peak area for alkyl–aryl (R–O) stretch is greater in [C₈C₁Py]FeCl₄ compared to the remaining two, suggesting the more intact lignin recovery by this catalytic system (Figure 3c).

2.5.2. SEM Analysis. Changes in the morphology and structure of rice husk after delignification were checked via scanning electron microscopy images (Figure 4). Previous studies show an obvious change in surface morphology of the polysaccharide–lignin network.⁴⁰ SEM images were taken at 12 000, 3000, and 1600× magnifications, all showing a clear change in the morphology of rice husk after IL treatment. Untreated original rice husk appeared as a highly compact and rigid structure. This complexity is due to the lignin and its strong binding with cellulose via hemicellulose interlinking. Contrarily, the delignified CRM appeared as a highly porous flat sheet with a rough surface, confirming the reduced crystallinity after IL pretreatment. Images having 12 000 and 3000× magnifications exhibit fade rough surfaces of pretreated samples, verifying the penetration of IL molecules into the fiber network. This is in agreement with literature reports.^{40,41}

2.5.3. TGA Analysis. Thermogravimetric analysis of original and treated rice husk was done to check the composition and stability change of biomass due to IL. Two plateaus can be seen from the thermograph curves of untreated rice husk and regenerated CRM (Figure 5). The first one is due to the removal of moisture from biomass, and the other is due to the degradation of biomass.⁴² In general, the thermal decomposition of biomass is described in three steps: water evaporation from biomass (room temperature to 150 °C), hemicellulose decomposition (>190 °C), and decomposition of cellulose (290–370 °C). In contrast, lignin shows a wide thermal decomposition range (280–500 °C) overlapping partially with that of hemicellulose.⁴³

Three different thermal decomposition regions can be seen from the TGA profiles of original as well as IL-treated rice husk (Figure 5): 20–260, 260–347, and 347–800 °C. Thermographs show less stability of CRM compared to compact biomass that is due to the decrease in its crystallinity after IL treatment. The onset temperature of untreated biomass for water evaporation is 218 °C, whereas for regenerated CRM, it is 257 °C. The main weight loss is observed in the second region that is attributed to the cellulose and hemicellulose decomposition region. A remarkable weight loss of 45% is observed from 250–348 °C for original rice husk. However, in the treated sample, only 27% weight is lost from 257 to 334 °C that approves the conversion/saccharification of the remaining cellulose during processing. Subsequently, the third region shows the weight loss due to lignin and then the straight line exhibits ash contents.

2.6. Recycling Experiments. Lewis acidic ionic liquid [C₈C₁Py]AlCl₄ showed 82% recovery after being used up in pretreatment reaction. A two times recycling ability is also observed to be associated with this system. Most of the IL systems used for biomass pretreatment and deconstruction are usually reported with a three times recycling ability.⁸ This

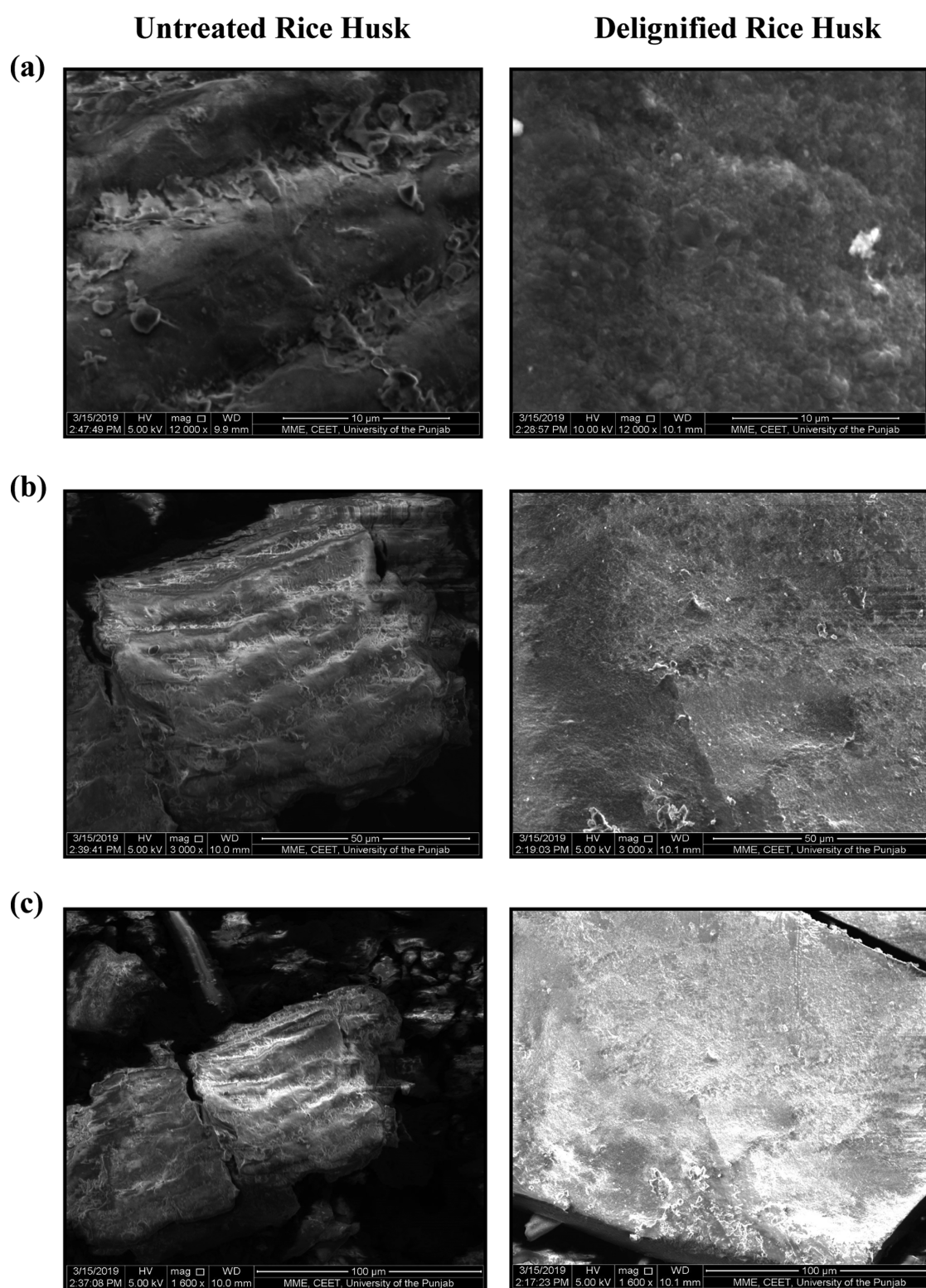


Figure 4. SEM images of rice husk and extracted CRM at (a) 10 μm , (b) 50 μm , and (c) 100 μm .

system was also recovered for the third cycle, but due to 18% weight loss in three consecutive cycles, it was not tested for further reusability. The regenerated IL system was confirmed via FTIR and ^1H NMR analyses (Figures 6 and S9) and recycled by adding fresh rice husk into it (Figure 7).

3. CONCLUSIONS

A one-pot protocol is developed for the deconstruction and simultaneous sugar formation from the waste of locally abundant agricultural feedstock. In contrast to widely reported imidazolium ILs, 4 times cheaper pyridinium-based ILs are reported with efficient processing abilities. A 10 wt % loading of rice husk in 1-octyl-3-methylpyridinium chloroaluminate IL resulted in a

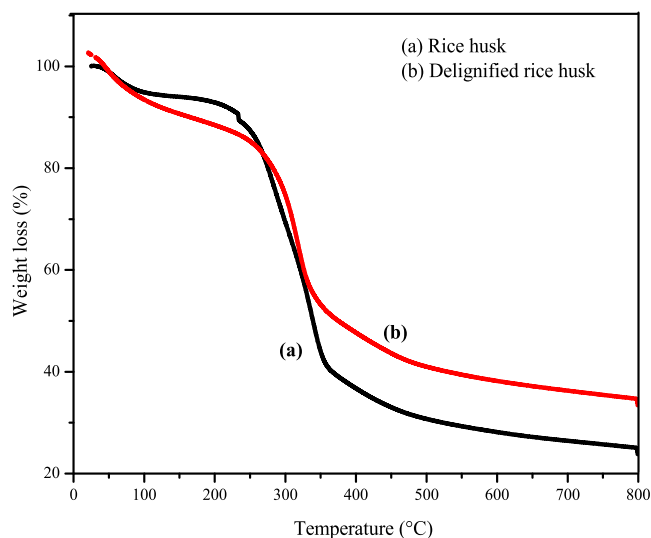


Figure 5. TGA of rice husk and extracted CRM.

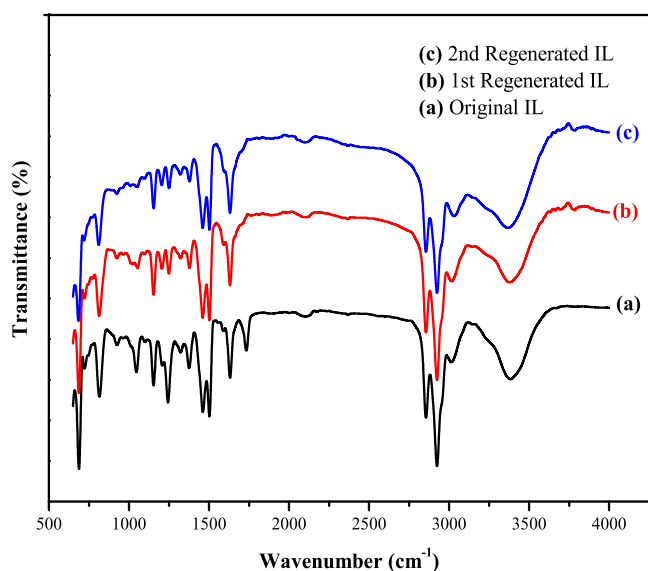


Figure 6. FTIR spectra of regenerated ILs.

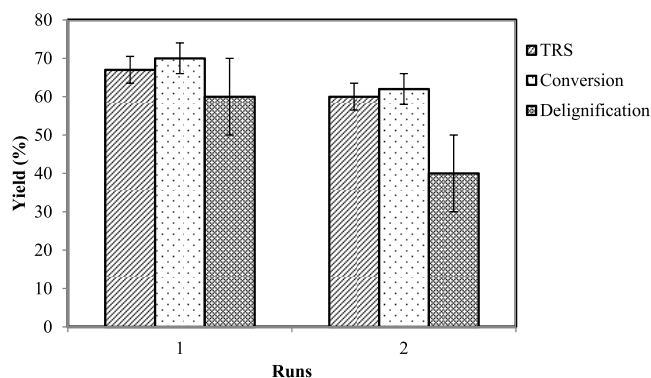


Figure 7. Recycling experiments.

60 wt % lignin recovery and an overall 70% carbohydrate conversion when processed at 100 °C for 1.5 h. Under these conditions, sugars are not converted further into any other platform chemical such as 5-hydroxymethylfurfural (5-HMF) that is also a well-known fermentation inhibitor. Thus, the sugars

can be separated and further converted into bioethanol or may be used for any other purpose. Cellulose-rich material (CRM) obtained under these conditions is also of reduced crystallinity and refined properties. At higher temperatures and prolonged reaction times, yield of sugars is decreased due to the formation of insoluble humins and brown soluble carbonized products. By switching the anion to chlorochromate, 5-HMF is formed in 20% overall yield based on the total carbohydrate components of original untreated rice husk at 130 °C temperature in 1 h. The lignin recovery is up to 65% under these conditions, but the CRM is fully carbonized. Thus, one can choose optimum conditions based on the desired end product; whether the focus is on reducing sugars or the target product is 5-HMF. The pyridinium-based LAIL catalytic system seemed to be green and sustainable due to its considerable recycling ability. As biomass is a contributor to the natural carbon cycle, balanced carbon economy is also promising. In short, the process is benign and feasible with respect to a low-cost processing medium (IL), less reaction time and temperature, high recycling efficiencies, and balanced carbon economy.

4. MATERIALS AND METHODS

Pyridine (Sigma-Aldrich), 3-methylpyridine (Merck-Schuchardt), 1-methylimidazole (Sigma-Aldrich), 1-chlorobutane (Fischer Scientific), 1-chlorooctane (Aldrich), 1-bromooctane (Aldrich), sodium tetrafluoroborate (Sigma-Aldrich), potassium hexafluorophosphate (Aldrich), 3,5-dinitrosalicylic acid (Sigma-Aldrich), 5-hydroxymethylfurfural (Sigma), standard sugars, and metal chlorides were purchased of analytical grade and used as such. Ethyl acetate and *n*-hexane were purchased and used after distillation. Commercial alkaline lignin (Tokyo Chemical Industries) was purchased for a comparative study of extracted lignin.

Rice husk as carbon-rich lignocellulosic waste was collected from a local farm in Lahore, Punjab, Pakistan. It was washed, dried, ground, and meshed to particular sizes of 100, 250, and 500 μm . Before processing, any possible moisture present in prepared biomass was removed by oven drying at 70 °C for 48 h. The composition of rice husk was found to be 15% lignin, 44% hemicellulose, 32% cellulose, 4% moisture, 2% ash, and 4% extractives as investigated according to the TAPPI method.⁴⁴

4.1. Synthesis of Ionic Liquids (ILs). A series of ILs having pyridine/3-methylpyridine/1-methylimidazole core with C₄ or C₈ alkyl chain varying in their counter anion X = Cl, Br were prepared via *N*-alkylation reactions, as reported in our previous research (Figures S1 and S3–S6).²⁵

4.1.1. 1-Butylpyridinium Chloride [C₄Py]Cl. Yield (89%), mp 103 °C, FTIR (cm⁻¹): 3037 (Ar–H stretching), 2959, 2935 (C–H stretching of alkanes), 1632 (C=N), 1486 (C=C), 1169 (C–N). ¹H NMR (400 MHz, D₂O) δ (ppm): 0.88 (3H, t, *J* = 7.2 Hz, CH₃), 1.27–1.34 (2H, m, CH₂), 1.90–1.97 (2H, m, CH₂), 4.56 (2H, t, *J* = 7.2, CH₂), 8.03 (2H, t, *J* = 6, Ar–H), 8.49 (1H, t, *J* = 7.6, Ar–H), 8.81 (2H, d, *J* = 6, Ar–H).

4.1.2. 1-Butyl-3-methylpyridinium Chloride [C₄C₁Py]Cl. Yield (85%), mp (95–97 °C), FTIR (cm⁻¹): 3058 (Ar–H stretching), 2962 (C–H stretching of alkanes), 1633 (C=N), 1505 (C=C), 1157 (C–N). ¹H NMR (400 MHz, D₂O) δ (ppm): 0.85 (3H, t, *J* = 7.6 Hz, CH₃), 1.24–1.29 (2H, m, CH₂), 1.88–1.93 (2H, m, CH₂), 2.46 (3H, s, CH₃), 4.83 (2H, t, *J* = 7.2 Hz, CH₂), 7.85 (1H, t, *J* = 6.8 Hz, Ar–H), 8.27 (1H, d, *J* = 8 Hz, Ar–H), 8.56 (1H, d, *J* = 5.6, Ar–H), 8.62 (1H, s, Ar–H).

4.1.3. 1-Octylpyridinium Chloride [C₈Py]Cl. Yield (91%), mp (35 °C), FTIR (cm⁻¹): 3048 (Ar–H stretching), 2924, 2856

(C–H stretching of alkanes), 1632 (C=N), 1487 (C=C), 1170 (C–N). ¹H NMR (400 MHz, D₂O) δ (ppm): 0.75 (3H, t, *J* = 5.6 Hz, CH₃), 1.09–1.26 (10H, m, 5CH₂), 1.92–1.98 (2H, m, CH₂), 4.53 (2H, t, *J* = 6 Hz, CH₂), 8.05 (2H, t, *J* = 5.6 Hz, Ar–H), 8.50 (1H, t, *J* = 7.6 Hz, Ar–H) 8.78 (2H, d, *J* = 4.4 Hz, Ar–H).

4.1.4. 1-Octyl-3-methylpyridinium Chloride [C₈C₁Py]Cl. Yield (89%), mp (67 °C), FTIR (cm⁻¹): 3018 (Ar–H stretching), 2924, 2854 (C–H stretching of alkanes), 1632 (C=N), 1504 (C=N), 1482 (C=C), 1246 (C–N). ¹H NMR (400 MHz, D₂O) δ (ppm): 0.75 (3H, t, *J* = 5.6 Hz, CH₃), 1.09–1.24 (10H, m, 5CH₂), 1.89–1.95 (2H, m, CH₂), 2.47 (3H, s, CH₃), 4.46 (2H, t, *J* = 6 Hz, CH₂), 7.85 (1H, t, *J* = 6.8 Hz, Ar–H), 8.28 (1H, d, *J* = 6.4 Hz, Ar–H), 8.56 (1H, d, *J* = 5.2, Ar–H), 8.62 (1H, s, Ar–H).

From the synthesized ILs, 1-octyl-3-methylpyridinium bromide [C₈C₁Py]Br was subjected to ion metathesis reactions to yield [C₈C₁Py]BF₄ and [C₈C₁Py]PF₆. To 1 equiv of hydrophilic IL [C₈C₁Py]Br, aqueous solution of equimolar salt (sodium tetrafluoroborate or potassium hexafluorophosphate) was added and shaken well. Oily layers of hydrophobic ILs containing BF₄⁻ and PF₆⁻ anions were observed to form immediately. The aqueous layer was then separated, and the remaining mixture was kept unagitated until sodium/potassium bromide salts were deposited at the bottom of the flask. IL as a thick yellow liquid was transferred and stored in an oven-dried vial (Figure S2).⁴⁵

4.1.5. 1-Octyl-3-methylpyridinium Tetrafluoroborate [C₈C₁Py]BF₄. Yield (80%), FTIR (cm⁻¹): 3016 (Ar–H stretching), 2915, 2850 (C–H stretching of alkanes), 1630 (C=N), 1504 (C=N), 1482 (C=C), 1248 (C–N). 825 (BF₄ stretch). ¹H NMR (400 MHz, D₂O) δ (ppm): 0.75 (3H, t, *J* = 5.6 Hz, CH₃), 1.09–1.24 (10H, m, 5CH₂), 1.89–1.95 (2H, m, CH₂), 2.47 (3H, s, CH₃), 4.46 (2H, t, *J* = 6 Hz, CH₂), 7.85 (1H, t, *J* = 6.8 Hz, Ar–H), 8.28 (1H, d, *J* = 6.4 Hz, Ar–H), 8.56 (1H, d, *J* = 5.2, Ar–H), 8.62 (1H, s, Ar–H).

4.1.6. 1-Octyl-3-methylpyridinium Hexafluorophosphate [C₈C₁Py]PF₆. Yield (83%), FTIR (cm⁻¹): 3022 (Ar–H stretching), 2923, 2856 (C–H stretching of alkanes), 1632 (C=N), 1509 (C=N), 1482 (C=C), 1249 (C–N). 1048 (PF₆ stretch). ¹H NMR (400 MHz, D₂O) δ (ppm): 0.75 (3H, t, *J* = 5.6 Hz, CH₃), 1.09–1.24 (10H, m, 5CH₂), 1.89–1.95 (2H, m, CH₂), 2.47 (3H, s, CH₃), 4.46 (2H, t, *J* = 6 Hz, CH₂), 7.85 (1H, t, *J* = 6.8 Hz, Ar–H), 8.28 (1H, d, *J* = 6.4 Hz, Ar–H), 8.56 (1H, d, *J* = 5.2, Ar–H), 8.62 (1H, s, Ar–H).

Eight different Lewis acidic ionic liquids (LAILs) were also prepared from [C₈C₁Py]Cl by heating it with chlorides of sodium, potassium, chromium, iron, cobalt, aluminum, bismuth, and cadmium. Metal chloride (10 wt %) was loaded in [C₈C₁Py]Cl and heated at 100 °C for 30 min at constant stirring until all of the metal chloride has been dissolved.

4.2. Lignocellulosic Biomass Processing. **4.2.1. General Processing Protocol.** In a glass vial immersed in an oil bath, 900 mg of oven-dried IL was taken and 10 wt % rice husk of particular mesh size (100–500 μm) was loaded into it. The reaction mixture was stirred at 100 rpm for a specific reaction time (0.5–3.0 h) at a particular temperature (80–110 °C). After completion of processing time, 20 mg of crude reaction mixture was withdrawn as the sample for analysis of produced sugars.

4.2.2. Total Reducing Sugar (TRS) Analysis. The percentage of TRS produced during the course of the reaction was measured by DNS assay.³⁵ Crude sample (20 mg) withdrawn from the pretreatment reaction mixture was diluted 150 times, and a 1 mL solution of dinitrosalicylic acid was added into it. It

was then boiled well for 15 min and subjected to photometric analysis at 540 nm using a UV–vis spectrophotometer (UVD-3500, Labomed, Inc.).⁴⁶

The concentration of reducing sugars was determined from the glucose calibration curve, while the percentage was calculated by this equation⁴⁷

$$Y_{\text{TRS}} = \frac{C_{\text{TRS}} \times M_2 \times 150}{M_b \times 1.11 \times \frac{M_2}{M_o}} \times 100\%$$

where *C*_{TRS} is the concentration of total produced sugars (g/L), *M*_o is the overall mass of reaction mixture (g), *M*₂ is the mass of crude sample withdrawn from the reaction mixture for sugars analysis (g), *M*_b (g) is the mass of original rice husk initially added to the reaction, 150 is the dilution factor, and 1.11 is the ratio of molecular weight of monomeric sugar to that of polymeric cellulose present in rice husk.

4.2.3. Deconstruction of Biomass. After pretreatment with IL, a 1:1 ratio of deionized water and acetone was added to the reaction mixture as antisolvents.⁴⁸ Cellulose is regenerated by the addition of water as it breaks down the hydrogen bonding between cellulose and IL by binding IL to itself. Lignin is separated by the action of acetone. Cellulose-rich material (CRM) was filtered and washed with deionized water. The remaining filtrate containing possibly the lignin dissolved in acetone, water, and IL was subjected to evaporation of acetone, to regenerate the lignin. It was then centrifuged for separation from the IL phase and washed with deionized water to remove any possible IL from it.

4.2.4. IL Recovery and Recycling. After the extraction of lignin from aqueous phase IL, water was evaporated to recover IL/IL–metal salt catalytic system. The percentage recovery of IL was calculated on the basis of the initial amount of IL added to the reaction

$$\text{recovered IL (\%)} = \frac{\text{weight of dried recovered IL}}{\text{weight of initially used IL for reaction}} \times 100$$

The recovered IL was then recycled for successive runs by adding fresh biomass under the same reaction conditions.

4.3. Characterization of Products. All of the synthesized ILs were characterized via ¹H NMR and FTIR spectroscopy analyses recorded via an Avance AV-400 MHz spectrometer and an Agilent Cary 630 FTIR spectrometer with a scanning range of 4000–400 cm⁻¹, respectively. Original biomass, regenerated CRM, extracted lignin, and regenerated IL samples were well dried and also submitted for FT-IR analyses. Thermogravimetric analysis for rice husk and delignified CRM was performed using LECO's TGA 701 from ambient to 600 °C with a 10 °C/min heating rate in flowing 175 Nitrogen gas at a 3.5 L/m (low) gas flow rate. SEM images for the original and treated biomasses were recorded by SEM (model VEGA TESCON) with variable pressure. Gold sputtering of samples was done, and images were taken at different magnifications.

4.4. Design of Experiments (DOE). All of the experiments were performed in triplicate, and the effect of all independent variables (rice husk loading into IL, type and wt % loading of IL and catalyst, reaction temperature and time, as well as particle size of biomass) on the response (TRS, delignification, and percentage conversion) was analyzed statistically to determine their mean using IBM SPSS statistics 21.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c04881>.

FTIR spectra of synthesized ILs, ^1H NMR spectra of all ILs used in this study, standard DNS curve for glucose concentration, HPLC chromatograms of standard 5-HMF and 5-HMF produced in IL-treated rice husk samples under different conditions, and ^1H NMR spectra of regenerated IL (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Maliha Uroos – Centre for Research in Ionic Liquids & Centre for Organic Chemistry, School of Chemistry, University of the Punjab, 54590 Lahore, Pakistan; orcid.org/0000-0001-8757-4151; Email: malihauroos.chem@pu.edu.pk

Authors

Sadia Naz – Centre for Research in Ionic Liquids & Centre for Organic Chemistry, School of Chemistry, University of the Punjab, 54590 Lahore, Pakistan; orcid.org/0000-0001-5290-3621

Muhammad Ayoub – Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Perak, Malaysia; orcid.org/0000-0003-1399-8423

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsomega.1c04881>

Notes

The authors declare no competing financial interest.

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