



Utilization of inorganic salts as adjuvants for ionic liquid–water pretreatment of lignocellulosic biomass: enzymatic hydrolysis and ionic liquid recycle

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Abstract

Pretreatment of lignocellulosic biomass with ionic liquids (ILs) for the large-scale biorefinery remains challenging due to its high price. This study focused on the utilization of inorganic salts as adjuvants for ionic liquid–water pretreatment to improve the tolerance to water and the reusability of the ILs. After the pretreatment of rice straw by the mixture of 40% 1-ethyl-3-methylimidazolium chloride ([C₂mim]Cl) + 53% water + 7% K₂CO₃ at 110 °C for 1 h, the residues became highly susceptible to enzymatic hydrolysis; 93.70% of lignin was removed, and 92.07% sugar yield was achieved. [C₂mim]Cl–K₂CO₃ aqueous biphasic system was formed at room temperature when K₂CO₃ concentration increased to more than 30%, and the [C₂mim]Cl recovery of 94.32% was achieved. The results indicate that the addition of inorganic salts to IL aqueous solutions can significantly reduce the cost of IL pretreatment, while maintaining an efficient enzymatic hydrolysis of lignocellulosic biomass.

Keywords Lignocellulosic biomass · Pretreatment · Ionic liquid · Inorganic salt · Recycle

Introduction

Lignocellulosic biomass is one of the most abundant and beneficial renewable materials suitable for conversion into biofuels (Elgharbawy et al. 2016). However, the presence of lignin in the plant cell wall, the limited surface area of cellulose, and their complex bonding protect the cellulose and hemicellulose from enzymatic hydrolysis (Jönsson and Martín 2016). Therefore, a number of pretreatment technologies have been developed as the essential and central starting points to make biomass susceptible to saccharification (Chen et al. 2018; Liu et al. 2018).

Ionic liquids (ILs), a group of organic electrolytes with melting points below 100 °C, have attracted considerable attention as substitutes for conventional organic solvents (Silva et al. 2017; Zhang et al. 2017). After the report of Swatloski et al. (2002) on cellulose dissolution using imidazolium-based ILs, many ILs have been tested as novel solvents for biomass pretreatment (Aid et al. 2016; Chang et al. 2017). ILs have tunable capability to dissolve lignocellulosic biomass, resulting in reduced lignin content, increased surface area, and improved saccharification (Elgharbawy et al. 2016; Zhang et al. 2014). However, IL pretreatment is costly due to its considerably high prices compared with commercial solvents; this factor remains one of the main obstacles for their large-scale application in lignocellulose pretreatment (Zhang et al. 2017).

To minimize IL usage, aqueous solutions of ILs have been the subject of numerous investigations (Niazi et al. 2013). However, many ILs were sensitive to water (Niazi et al. 2013). For example, the maximum solubility of dissolved cellulose for 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl) in presence of 7% water was only 8.75% at 95 °C (Mazza et al. 2009). Moreover, high water content resulted in minimal improvement in glucose yield of the regenerated biomass (Brandt et al. 2012). Ren et al. (2016)

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utilized seawater (25%) as an alternative to freshwater for IL pretreatment, but the sugar yields were only 54–72%. Therefore, improvement the tolerance of ILs to water is required.

Moreover, the economic efficiency of biofuel production can be improved by recycling and reuse of ILs (Dibble et al. 2011). Extraction of ILs at room temperature by forming aqueous biphasic system (ABS) with inorganic salts has been investigated and suggested as a viable approach (Gao et al. 2013). Nevertheless, the effect of residual inorganic salts in the recycled IL on the sugar yield is an unresolved challenge. In this work, rice straw was pretreated by imidazolium-based IL/water/inorganic salt mixtures at 110 °C for 1 h, and the ABS composed of the ILs and the inorganic salts was formed at room temperature to recover the ILs from the waste water. The effect of inorganic salts on the biomass dissolution, lignin removal, crystalline structure, surface morphology, enzymatic hydrolysis, and the IL recovery was evaluated.

Materials and methods

Materials

Rice straw (*Oryza sativa*, RS) was collected from a farmland near Zhanjiang City in China. The dry material was ground and placed through a sieve plate with 0.15-mm particle size. The ILs 1-ethyl-3-methylimidazolium chloride ([C₂mim]Cl), [C₄mim]Cl, 1-hexyl-3-methylimidazolium chloride [C₆mim]Cl, and 1-octyl-3-methylimidazolium chloride [C₈mim]Cl, with purity of 99%, were provided by the Lanzhou Institute of Chemical Physics. Six inorganic salts, namely, KCl (99.5%), K₂SO₄ (99%), K₂HPO₄ (99%), KH₂PO₄ (99%), K₃PO₄ (99%), and K₂CO₃ (99%), and cellulase *Trichoderma reesei* (Celluclast 1.5 L, Product #C27 30–50 mL) were all purchased from Aladdin Ltd. (Shanghai, China).

Phase diagrams

Phase behavior of IL/water/inorganic salt system was determined at the temperature range of 25–110 °C by the cloud point titration method (Gutowski et al. 2003). The aqueous solutions of KCl, K₂SO₄, K₂HPO₄, KH₂PO₄, K₃PO₄, and K₂CO₃ at 20–40 wt% and aqueous solutions of [C₂mim]Cl, [C₄mim]Cl, [C₆mim]Cl, and [C₈mim]Cl at 60 wt% were prepared. Subsequently, we carried out repetitive drop-wise addition of the aqueous inorganic salt solution to each IL aqueous solution until the detection of a cloudy and further biphasic solution, followed by the drop-wise addition of ultrapure water until a monophasic region is detected. Further details on the experimental procedure can be found elsewhere (Gao et al.

2017; Louros et al. 2010). The compositions were determined by the weight quantification of all components.

Pretreatment and regeneration of rice straw

We prepared 5% (w/w) rice straw mixture by combining 2.0 g of rice straw with 40 g of IL/water/inorganic salt solution. The mixture was stirred with a magnetic stirrer at 500 r/min and heated at 110 °C for 1 h. We used an inverted microscope (Leica DMI4000B, USA) to observe the dissolution processes. After the pretreatment, rice straw material was regenerated by adding 40 mL of water and then centrifuged at 8000 r/min for 10 min. Then, we collected the supernatant for the IL recovery and washed the precipitates to neutral and then dried in an oven at 60 °C for 24 h. To compare different pretreatment methods, rice straw was pretreated by pure [C₂mim]Cl, pure water, [C₂mim]Cl/water (mass ratio=0.5:0.5), K₂CO₃/water (mass ratio=0.2:0.98), and [C₂mim]Cl/water/K₂CO₃ (mass ratio of 0.5:0.48:0.02) at 110 °C for 1 h, respectively. We performed all pretreatments in triplicate.

Enzymatic hydrolysis of the regenerated rice straw

In a typical enzymatic hydrolysis reaction, we added 20 mg of the regenerated rice straw to 30 mL of acetate buffer (50 mM, pH 4.8) and incubated at 50 °C for 72 h with shaking at 120 rpm. We also added cellulase at a loading of 20 FPU/g of cellulose for each reaction. Dinitrosalicylic acid method was employed to measure the total reducing sugars derived from enzymatic hydrolysis. Sugar yield from the regenerated rice straw was calculated as follows (Li et al. 2009):

$$\text{Sugar yield (\%)} = \frac{\text{Reducing sugars weight}}{\text{Regenerated rice straw weight}} \times 100. \quad (1)$$

Recovery and reuse of ionic liquid

After the pretreatment and regeneration of rice straw, we removed the supernatant mainly containing IL and inorganic salt. Then, the corresponding inorganic salt of 40.0 g was added into the solution, and the mixture was vibrated by a vortex mixer (XW-80A, Jingke, Inc., China), and placed at 25 °C overnight. ABS of a IL-rich phase and an inorganic salt-rich phase was formed. After careful separation of both phases, the IL amounts in each phase were quantified via high-performance liquid chromatography (LC-20A, Prominence, Japan). The IL recovery was calculated (Gao et al. 2013):

$$\text{IL recovery (\%)} = \frac{x_T \times m_T}{x_T \times m_T + x_B \times m_B} \times 100, \quad (2)$$

where x_T and x_B are the mass fraction of IL in the top phase and bottom phase, and m_T and m_B are the mass of the top and

bottom phases, respectively. The experimental design of this study is summarized in Fig. 1.

Analysis methods

The lignocellulosic composition of biomass materials was measured according to the National Renewable Energy Laboratory procedure (Sluiter et al. 2008). An automatic moisture analyzer (HX204, Mettler-Toledo, Switzerland) was used to measure the water content in all samples. We also determined the ash content in accordance with the AOAC standard method 942.05 (Hongkulsup et al. 2016). Error bars show the standard deviation of triplicate measurements. The rice straw samples contained 33.16% cellulose, 29.80% hemicelluloses, 23.83% lignin, 3.3% ash, and 7.8% moisture. The surface morphology of the rice straw materials was characterized via scanning electron microscopy (SEM, Hitachi-S4800, Japan). Images were obtained at magnification of 2000 \times . Subsequently, we examined the crystalline structure of the rice straw samples using an X-ray diffractometer (D8 Advance, Bruker Inc., Germany) at 40 kV and 30 mA voltage. Samples were scanned over 2θ angles ranging from 5 $^\circ$ to 45 $^\circ$ with a step size of 0.02 $^\circ$. Scanning type was a continuous scanning. Crystallinity index (CrI, %) of each sample was (Gao et al. 2018):

$$\text{CrI (\%)} = \frac{I_{002} - I_{\text{am}}}{I_{002}} \times 100, \quad (3)$$

where I_{am} is the intensity of the background scatter at $2\theta = 18.2^\circ$, and I_{002} is the intensity of the peak at $2\theta = 22.4^\circ$.

Results and discussion

Phase behavior of IL/water/salt systems

Many imidazolium-based ILs have exhibited excellent solvating power for cellulose (Nazari et al. 2017) and lignocellulosic biomass (Hou et al. 2017). However, their solvation properties strongly depend on their miscibility with water (Kohno et al. 2012). The ILs could form ABS with kosmotropic salts at different temperatures (Freire et al. 2012; Mourão et al. 2012). Therefore, our work started with the measurement of the effect of IL, salt, and temperature on the phase equilibrium of the IL/water/inorganic salt ternary systems.

It was demonstrated that the salt abilities to induce the formation of IL-based ABS follow the Hofmeister series (Shahriari et al. 2012). As shown in Table 1, the IL aqueous solutions containing less than 20% of KCl, K_2SO_4 , or KH_2PO_4 maintained homogeneous phase at temperature ranging from 25 to 110 $^\circ\text{C}$. For the systems containing K_2HPO_4 , K_3PO_4 , or K_2CO_3 , low temperature was beneficial to phase split. For example, homogenous system of $[\text{C}_2\text{mim}]\text{Cl}/\text{water}/\text{K}_2\text{CO}_3$ (0.2:0.6:0.2) at 110 $^\circ\text{C}$ tended to form ABS when temperature decreased to 25 $^\circ\text{C}$ (Fig. 2). On the other hand, the significant influence of the salt concentration should not be ignored. When the IL content was approximately 50% in the mixture, the mass fraction of each salt should be controlled less than 10% to obtain a monophasic system during the pretreatment at high temperature. After the pretreatment, ABS was obtained at room temperature by increasing the salt content.

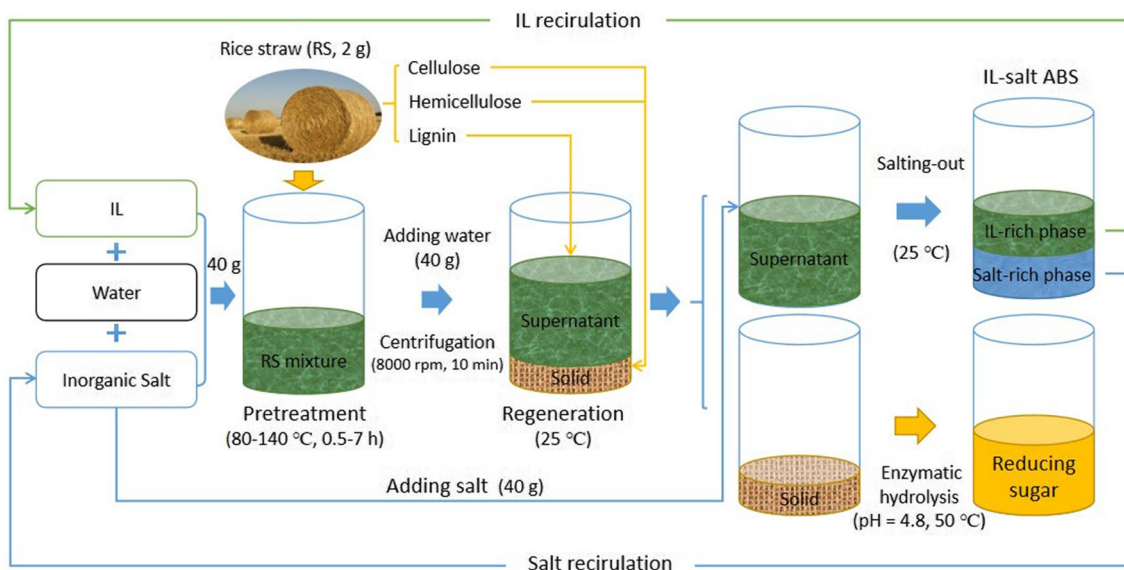


Fig. 1 Schematic of the cyclic process for the enhanced saccharification of rice straw pretreated by IL/water/inorganic salt

Table 1 Liquid–liquid equilibria of IL/water/inorganic salt systems at different temperatures

	KCl	K ₂ SO ₄	KH ₂ PO ₄	K ₂ HPO ₄	K ₃ PO ₄	K ₂ CO ₃
Mass ratio of IL/water/inorganic salt = 0.3: 0.6: 0.1, 25 °C						
[C ₂ mim]Cl	×	×	×	√	√	√
[C ₄ mim]Cl	×	×	×	√	√	√
[C ₆ mim]Cl	×	×	×	√	√	√
[C ₈ mim]Cl	×	×	×	√	√	√
Mass ratio of IL/water/inorganic salt = 0.3: 0.6: 0.1, 110 °C						
[C ₂ mim]Cl	×	×	×	×	×	×
[C ₄ mim]Cl	×	×	×	×	×	×
[C ₆ mim]Cl	×	×	×	×	×	×
[C ₈ mim]Cl	×	×	×	×	×	×
Mass ratio of IL/water/inorganic salt = 0.2: 0.6: 0.2, 25 °C						
[C ₂ mim]Cl	×	×	×	√	√	√
[C ₄ mim]Cl	×	×	×	√	√	√
[C ₆ mim]Cl	×	×	×	√	√	√
[C ₈ mim]Cl	×	×	×	√	√	√
Mass ratio of IL/water/inorganic salt = 0.2: 0.6: 0.2, 110 °C						
[C ₂ mim]Cl	×	×	×	×	√	√
[C ₄ mim]Cl	×	×	×	√	√	√
[C ₆ mim]Cl	×	×	×	√	√	√
[C ₈ mim]Cl	×	×	×	√	√	√

√ indicates ABS was formed, × indicates ABS could not be formed

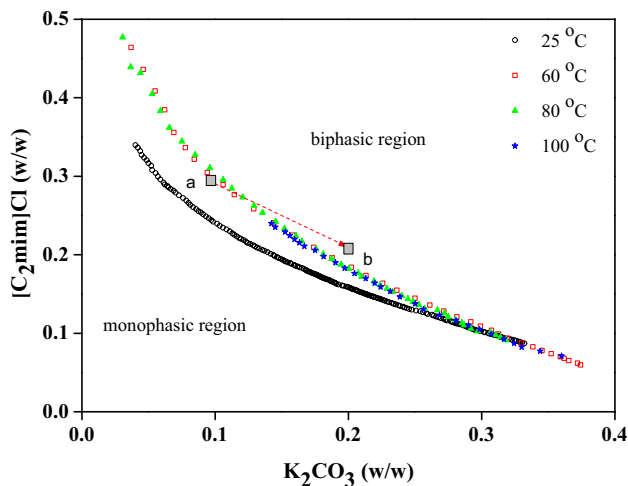


Fig. 2 The mutual coexistence curves for the [C₂mim]Cl/water/K₂CO₄ system: **a** mass ratio of [C₂mim]Cl/water/K₂CO₄ = 0.3:0.6:0.1; **b** mass ratio of [C₂mim]Cl/water/K₂CO₃ = 0.2:0.6:0.2

Dissolution of rice straw

The dissolving process of rice straw in pure water, pure [C₂mim]Cl, [C₂mim]Cl/water, water/K₂CO₃, and [C₂mim]Cl/water/K₂CO₃ at 110 °C for 1 h was compared, and the micrographs are shown in Fig. 3. Compared with untreated rice straw, water-treated samples displayed no significant

changes on the structural properties, whereas the rice straw samples mixed with pure [C₂mim]Cl, 50% [C₂mim]Cl + 50% water, or 98% water + 2% K₂CO₃ became more homogeneous and loosening. Li et al. (2009) demonstrated that 4% (w/w) of wheat straw can be totally dissolved in [C₄mim]Cl at 100 °C for 1 h. Notably, a large amount of fibers was separated and exposed in 50% [C₂mim]Cl + 48% water + 2% K₂CO₃ system, and this rice straw dissolution tended to be complete after incubation at 110 °C for 1 h.

Lignin removal

Lignin is a hydrophobic heteropolymer, which has been proven as a major factor hindering enzymatic hydrolysis of lignocellulosic biomass (Cheng et al. 2018). We measured the lignin content in the regenerated rice straw samples pretreated by the above five solvents, and the results of lignin removal are shown in Fig. 4. Pure water pretreatment revealed no effective impact on the lignin removal. The lignin removal after pretreatment by 50% [C₂mim]Cl + 50% water (21.43%) was lower than that of the pure [C₂mim]Cl pretreatment (26.47%), because water molecules compete with the [C₂mim]⁺ for hydrogen bond formation and consequently interrupt the biomass dissolution (Elgharbawy et al. 2016). The pretreatment with 50% [C₂mim]Cl + 48% water + 2% K₂CO₃ at 110 °C for 1 h can achieve the most obvious lignin removal (74.36%). The changes were consistent with the observation during dissolution, suggesting that

Fig. 3 Micrographs of the rice straw samples dissolving in different solvents at 110 °C for 1 h: **a** untreated; **b** water; **c** [C₂mim]Cl; **d** 50% [C₂mim]Cl + 50% water; **e** 2% K₂CO₃ + 98% water; **f** 50% [C₂mim]Cl + 48% water + 2% K₂CO₃

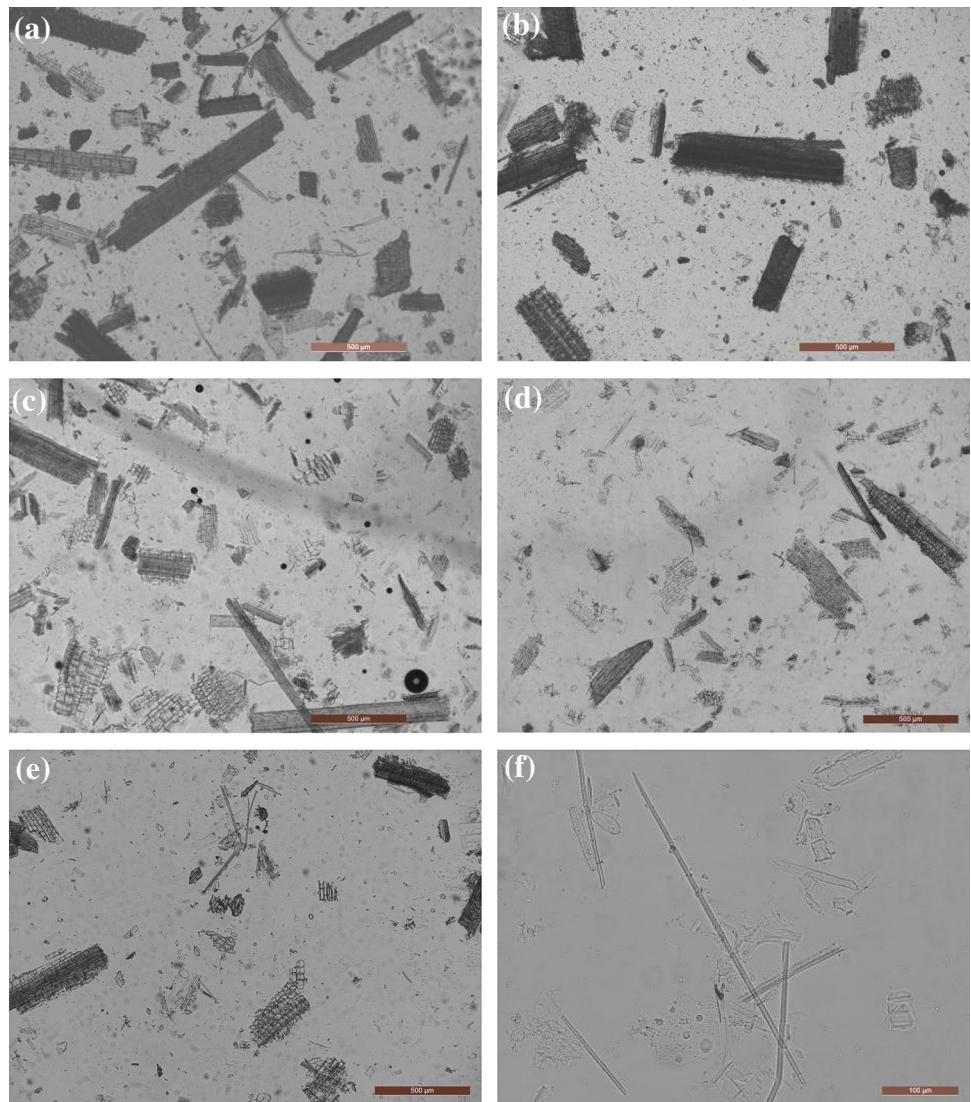
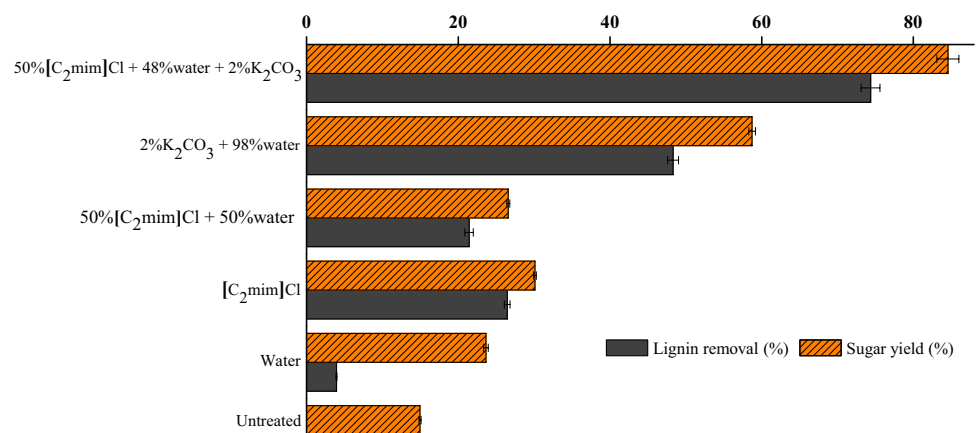


Fig. 4 The lignin removal and sugar yields of the RS pretreated by different solvents at 110 °C for 1 h



adding a small amount of K_2CO_3 to the $[C_2mim]Cl$ -water mixture can significantly break up the compact structure of rice straw.

Structural properties of the regenerated rice straw

As shown in Fig. 5, the main peaks of all the samples were located at approximately 22.4° and 18.2° , which indicates the stable crystalline structure of α -cellulose. The XRD pattern of untreated rice straw exhibited a broad peak, which was the characteristic of the amorphous structure. The intensity of the peak at $2\theta = 22.4^\circ$ significantly decreased for the sample pretreated by 50% $[C_2mim]Cl$ + 48% water + 2% K_2CO_3 , and consequently CrI value was slightly reduced after the pretreatment, which is consistent with the results after alkalization (Pan et al. 2017). Earlier studies also demonstrated that the CrI value of regenerated cotton stalks treated by $[C_2mim]Cl$ was lower than untreated samples (Bahcegul et al. 2012; Haykir et al. 2013). It is many because the mixture of 50% $[C_2mim]Cl$ + 48% water + 2% K_2CO_3 dissolved hemicellulose of rice straw. The solution of 98% water + 2% K_2CO_3 shows similar alkaline pH. However, the CrI increased after pretreatment by 98% water + 2% K_2CO_3 . For these results, it should be clear that the structural changes of lignocellulosic biomass cannot be solely predicted from the XRD crystallinity index.

SEM was used to examine the surface morphology of the rice straw samples. As shown in Fig. 6, the surface of each regenerated materials displayed a rough texture compared with native rice straw, implying an increase in the surface area (Gao et al. 2018; Haykir et al. 2013). In general, the changes in the structure were minimal for the samples

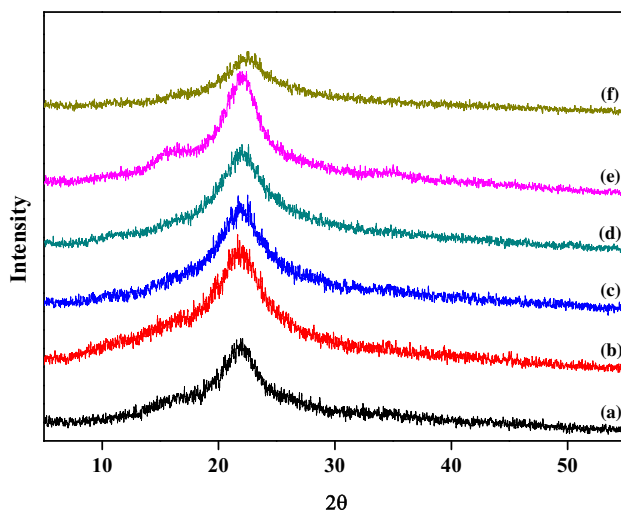


Fig. 5 X-ray diffraction patterns of the regenerated RS samples pretreated by different solvents at $110^\circ C$ for 1 h: **a** untreated; **b** water; **c** $[C_2mim]Cl$; **d** 50% $[C_2mim]Cl$ + 50% water; **e** 2% K_2CO_3 + 98% water; **f** 50% $[C_2mim]Cl$ + 48% water + 2% K_2CO_3

pretreated via pure water or 50% $[C_2mim]Cl$ + 50% water, wherein the appearance of the surfaces almost resembled that of the untreated rice straw. Fish scale-shaped surfaces were observed for $[C_2mim]Cl$ -pretreated rice straw. Many separated cellulose fibers were randomly distributed on the surface after the pretreatment by 50% $[C_2mim]Cl$ + 48% water + 2% K_2CO_3 , possibly due to the lignin dissolution during pretreatment.

Sugar yield of the regenerated rice straw

The enzymatic hydrolysis of rice straw samples was compared in terms of sugar yield obtained for each sample pretreated via five different solvents. All the pretreated rice straw samples exhibited a higher sugar yield compared with the untreated rice straw as shown in Fig. 4. Sugar yield for $[C_2mim]Cl$ -pretreated rice straw sample was 30% but decreased to 26% when water content was 50% in $[C_2mim]Cl$. Among the five pretreatments, the highest sugar yield was obtained via the pretreatment of 50% $[C_2mim]Cl$ + 48% water + 2% K_2CO_3 at $110^\circ C$ for 1 h. This yield was 86% at 72 h of enzymatic hydrolysis, which was almost 5.5-fold greater than that of the untreated rice straw.

Combined with the significant lignin dissolution, the disrupted structure, and the improved sugar yield of the regenerated rice straw, we can conclude that adding a slight amount of K_2CO_3 efficiently improved the $[C_2mim]Cl$ tolerance to water and provided ideal pretreatment environment to enhance the saccharification of lignocellulosic biomass.

Optimization of pretreatment conditions

To evaluate the influence of alkyl side chain length of ILs and the IL content, the chloride anion was kept, and $[C_2mim]^+$, $[C_4mim]^+$, $[C_6mim]^+$, and $[C_8mim]^+$ were selected. The mass fraction of the ILs was varied from 10 to 60%. All these pretreatments were performed at $110^\circ C$ for 1 h. Then, IL- K_2CO_3 ABS was produced at room temperature to recover the ILs. The lignin removal, sugar yield, and IL recovery are listed in Table 2.

Increasing the alkyl side chain of the imidazolium cation decreased the lignin removal and sugar yield. The highest IL recovery of 88% was observed for $[C_8mim]Cl$ due to its high hydrophobicity (Ventura et al. 2012). However, the lignin removal of the rice straw sample pretreated by 50% $[C_8mim]Cl$ + 48% water + 2% K_2CO_3 was only 5%. The 40% $[C_2mim]Cl$ + 58% water + 2% K_2CO_3 pretreatment resulted in a significant sugar yield and IL recovery of 85.39% and 88.53%, respectively. The results suggested that the $[C_2mim]Cl$ aqueous solution containing K_2CO_3 was effective to break down the structure of lignocellulosic biomass at water content of approximately 60%.

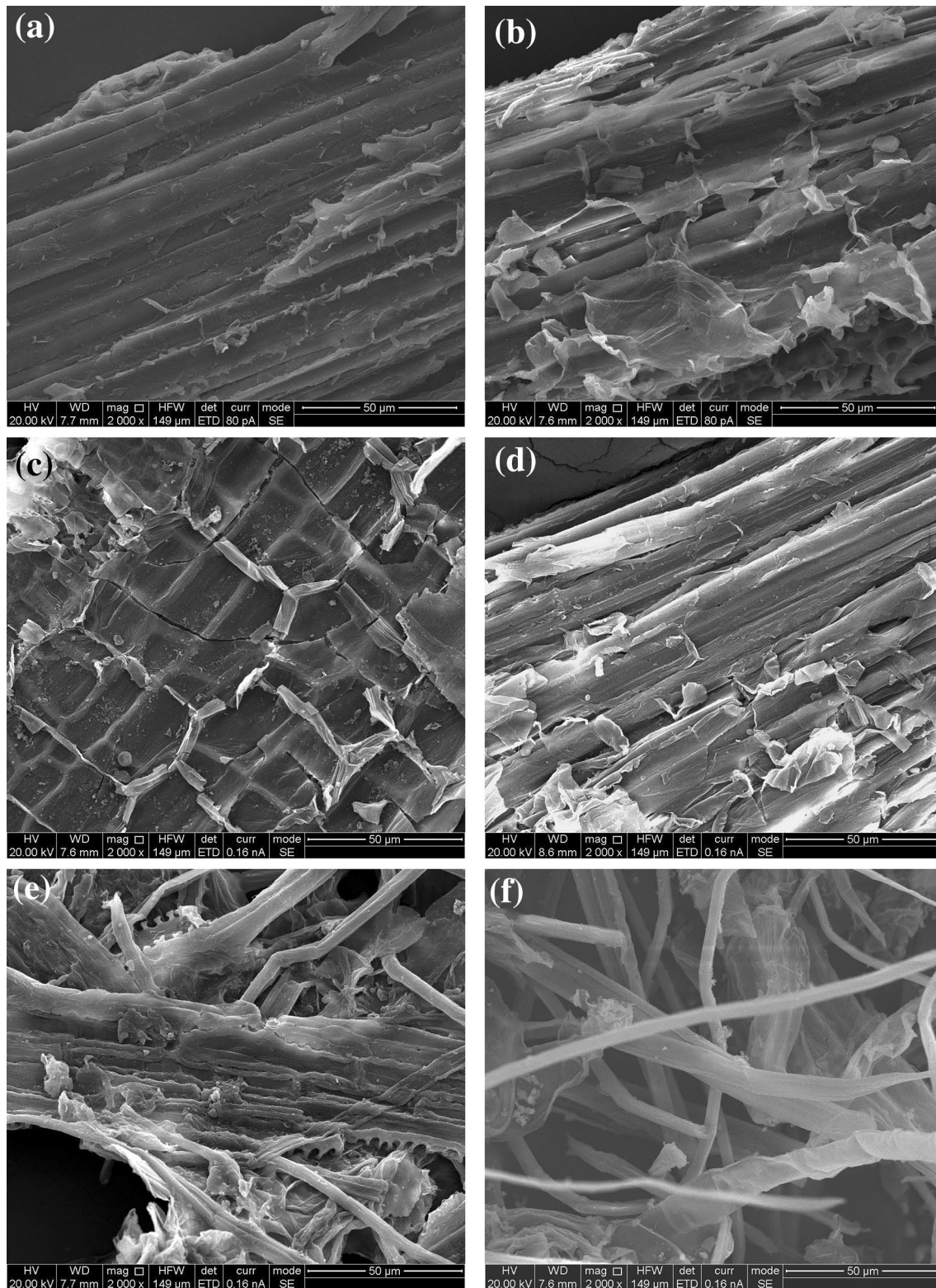


Fig. 6 SEM images (2000×) of the RS samples pretreated by different solvents at 110 °C for 1 h: **a** untreated; **b** water; **c** [C₂mim]Cl; **d** 50% [C₂mim]Cl + 50% water; **e** 2% K₂CO₃ + 98% water; **f** 50% [C₂mim]Cl + 48% water + 2% K₂CO₃

Table 2 Effect of ILs and their mass fractions on the IL/water/ K_2CO_3 pretreatment and IL recovery

IL	Mass fraction (%)	Solvent pH	Lignin removal (%)	Sugar yield (%) ^a	IL recovery (%)
[C ₈ mim]Cl	50	10.85	5.37 (±0.06)	32.57 (±0.96)	98.36 (±1.24)
[C ₆ mim]Cl	50	11.08	24.07 (±0.84)	36.11 (±0.35)	94.25 (±0.71)
[C ₄ mim]Cl	50	12.31	43.46 (±0.95)	60.97 (±1.21)	92.77 (±1.25)
[C ₂ mim]Cl	50	13.21	74.36 (±1.00)	86.25 (±0.05)	90.45 (±1.12)
[C ₂ mim]Cl	10	11.08	43.10 (±1.58)	74.27 (±1.20)	70.17 (±0.73)
[C ₂ mim]Cl	20	11.74	50.88 (±1.23)	76.54 (±0.34)	75.66 (±0.42)
[C ₂ mim]Cl	30	12.29	58.03 (±1.34)	78.48 (±0.88)	82.23 (±1.03)
[C ₂ mim]Cl	40	12.86	72.38 (±1.67)	84.99 (±0.51)	88.53 (±0.69)
[C ₂ mim]Cl	60	14.11	74.86 (±2.46)	86.67 (±1.23)	94.26 (±1.43)

Mass fraction of K_2CO_3 was 2%, pretreatment temperature was 110 °C, and pretreatment time was 1 h

^aEnzymatic hydrolysis time was 72 h

In a previous study, [C₄mim]Cl–HCl pretreatment improves the cellulose conversion (Hegde et al. 2016). As seen in Table 3, the [C₂mim]Cl aqueous solutions with KCl, K_2SO_4 , and KH_2PO_4 were acidic (pH < 7) but hardly affected the rice straw. By contrast, the solutions containing K_2HPO_4 , K_3PO_4 , and K_2CO_3 were alkaline (pH > 7), resulting in high lignin removal and sugar yield. This result agreed with the finding that the enzymatic hydrolysis of lignocellulosic biomass was improved by combining IL with alkaline pretreatment (Uju and Kamiya 2016). When the mass ratio of [C₂mim]Cl/water/salt was 0.4:0.58:0.02, the effectiveness of pretreatment in the presence of different salts on enhancing the saccharification of rice straw followed the order of $K_2CO_3 > K_3PO_4 > K_2HPO_4 > KH_2PO_4 \approx K_2SO_4 \approx KCl$. Moreover, [C₂mim]Cl was difficult to be recovered by adding KCl, K_2SO_4 , and KH_2PO_4 due to their weak salting-out (Shahriari et al. 2012), whereas K_2HPO_4 , K_3PO_4 , and K_2CO_3 presented a strong salting-out ability. Therefore, addition of K_3PO_4 and K_2CO_3 could be used as effective adjuvants

of [C₂mim]Cl aqueous solutions to pretreat lignocellulosic biomass and recover [C₂mim]Cl from waste water.

Enzymatic hydrolysis of the regenerated rice straw seems to be significantly increased with the salt contents. Sugar yield of the rice straw increased to 92.07% with the increase of the mass fraction of K_2CO_3 to 7%. However, sugar yield appeared to be slightly lower at K_2CO_3 content of 9%. The results revealed that high salt content could lead to further IL decomposition in aqueous solutions.

Reusability of IL

Lignin co-precipitation unrecovered in the previous cycles could reduce its capability to dissolve lignocellulosic biomass in a new cycle (Chen et al. 2018). The recycling performances of the [C₂mim]Cl/water/ K_2CO_3 system are shown in Table 4. The sugar yield and IL recovery decreased slightly with the recycling times. Because, the residual inorganic salts in the recycled IL maintained the pH of the aqueous

Table 3 Effect of inorganic salts and their mass fractions on the [C₂mim]Cl/water/salt pretreatment and [C₂mim]Cl recovery

Inorganic salt	Mass fraction (%)	Solvent pH	Lignin removal (%)	Sugar yield (%) ^a	IL recovery (%)
KCl	2	4.31	2.02 (±0.04)	17.13 (±0.47)	–
K_2SO_4	2	5.36	2.44 (±0.13)	18.91 (±1.11)	–
KH_2PO_4	2	5.88	2.20 (±0.06)	19.55 (±0.54)	–
K_2HPO_4	2	9.91	13.94 (±1.18)	27.96 (±0.98)	71.25 (±1.24)
K_3PO_4	2	13.60	45.76 (±2.25)	64.33 (±2.64)	98.14 (±0.77)
K_2CO_3	2	12.86	72.38 (±1.67)	84.99 (±0.51)	88.53 (±0.69)
K_2CO_3	1	12.16	70.49 (±1.40)	75.17 (±2.20)	95.95 (±1.23)
K_2CO_3	3	12.97	78.94 (±0.78)	88.67 (±1.28)	96.28 (±2.51)
K_2CO_3	5	13.22	81.45 (±1.29)	80.32 (±1.37)	92.67 (±0.40)
K_2CO_3	7	13.46	93.70 (±2.43)	92.07 (±1.66)	94.32 (±0.44)
K_2CO_3	9	13.69	85.39 (±1.55)	90.61 (±0.72)	94.54 (±2.10)

Mass fraction of [C₂mim]Cl was 40%, pretreatment temperature was 110 °C, and pretreatment time was 1 h

^aEnzymatic hydrolysis time was 72 h

Table 4 The recycling performances of the [C₂mim]Cl/water/K₂CO₃ (mass ratio = 0.4: 0.53: 0.07)

Run	Sugar yield (%) ^a	[C ₂ mim]Cl recovery (%)
1	92.07 (± 1.51)	94.32 (± 0.44)
2	88.05 (± 1.37)	90.06 (± 0.36)
3	87.69 (± 0.42)	88.52 (± 0.58)
4	85.15 (± 1.84)	89.06 (± 1.07)
5	85.98 (± 0.26)	84.06 (± 0.79)

5% of rice straw was pretreated at 110 °C for 1 h

^aEnzymatic hydrolysis time was 72 h

solutions to the original solvent, boosting the effectiveness of enzymatic hydrolysis in a new cycle (85.98% sugar yield in 5th cycle). These findings demonstrated that aqueous solutions containing K₂CO₃ was recyclable and can be reused upon K₂CO₃ addition. The impurities carried over from the previous pretreatment cycles seemed to have little effect on its performance, suggesting that aqueous [C₂mim]Cl containing K₂CO₃ may partially do self-cleaning to avoid the build-up of lignin in the solution.

Conclusion

Addition of K₃PO₄ and K₂CO₃ could improve the IL pretreatment of lignocellulosic biomass at water content of 60%, and also enhance the reusability of IL in a new cycle. In particular, 93.70% of lignin removal and 92.07% of sugar yield of rice straw could be achieved after pretreatment using 40% [C₂mim]Cl + 53% water + 7% K₂CO₃ at 110 °C for 1 h. [C₂mim]Cl could be recovered by creating ABS when K₂CO₃ or K₃PO₄ mass fraction was increased to appropriately 30%. This cyclic process provided an efficient and low-cost approach for biomass refinery.

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Compliance with ethical standards

Conflict of interest The authors declare no competing financial interest.

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