

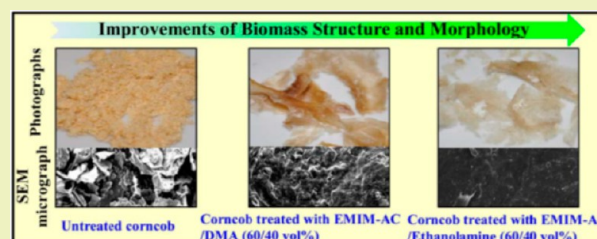
Effect of Organic Solvent in Ionic Liquid on Biomass Pretreatment

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ABSTRACT: Pretreatments of corncob and rice straw with cosolvents of ionic liquids and organic solvents were studied. The effects of the organic solvent type, organic solvent fraction in ionic liquid, and reaction temperature on product yield and properties were also examined. The mixtures of 1-ethyl-3-methylimidazolium acetate (EMIM-AC)/dimethylacetamide (DMA) at 40–60 vol % DMA added provided relatively similar values of sugar yield and conversion, extracted lignin content, and yield of regenerated biomass compared with those of EMIM-AC. However, the mixtures of EMIM-AC/ethanolamine (60/40 vol %) and 1-butyl-3-methylimidazolium chloride (BMIM-Cl)/ethanolamine (60/40 vol %) rendered greater enhancements of biomass pretreatment than their ionic liquids. It was also found that various benefits are gained with the use of ionic liquid/organic solvent as a cosolvent—low viscosity (giving eases of wash out and handle), more loading of cellulose, and high thermal stability (even operated at high temperature of 150 °C).

KEYWORDS: Biomass, Pretreatment, Ionic liquid, Hildebrand solubility parameter, Organic solvent



INTRODUCTION

Biomass has been known as a renewable source of energy and chemical feedstock.^{1,2} It is an essential resource influencing the development of industry and the world economy (concerning economic and environmental issues).³ Bioconversion has been acknowledged as a commercial process to convert biomass into energy and valuable chemical products, for example, ethanol, butanol, biogas, and hydrogen.^{4–8} However, the recalcitrance of biomass, which is very complex in composition, the chemical/biological resistance of lignin, and high crystalline cellulose could affect directly the efficiencies of biomass utilization for bioconversion processes.^{9,10} Biomass pretreatment is thus required for improving biomass properties, which can result in high yields in products from the bioconversion processes. A variety of physical, chemical, physicochemical, and biological pretreatment methods, such as, steam explosion, ammonia fiber explosion, acid hydrolysis, alkaline hydrolysis, irradiation, and organosolv, has been proposed.^{10,11} However, these methods have some drawbacks: problems with industrial scale applications, requirements of extreme conditions and high energy consumption, high toxicity, inhibition of fermentable sugars, and waste generation.¹² The pretreatment with an ionic liquid is well-known as a prospective process with great potential for lignin extraction and carbohydrate dissolution (by decreasing biomass crystallinity).^{10,13} The advantages of ionic liquids, which possess environmentally friendly molten salts, a high polarity, a low melting point, nonvolatility, and designability,^{14–16} lead to extensive studies to develop processes for commercial applications.

Ionic liquids play a role as a new class of solvent for biomass pretreatment. The physicochemical properties of ionic liquids, which depend on ionic liquid type, have been important factors for the pretreatment process, for example, viscosity, melting point, dipolarity, and hydrogen bond basicity.^{17–19} Some

literature suggested the features of the potential for ionic liquids to be used as a biomass pretreatment process, which are as follows:^{17,20} they dissolve biomass at low temperatures, possess low viscosity and chemical stability, do not decompose biomass, are easy to regenerate and recycle, are cost-effective, are easy to process, and are nontoxic to enzymatic and microbial fermentation. This indicates that several properties of the ionic liquids should be considered. The viscosity is an important factor in practical utilizations. Generally, ionic liquids possess relatively high viscosity, for example, 1-butyl-3-methylimidazolium chloride (BMIM-Cl) has been known as an effective ionic liquid to render excellent dissolution of cellulose but it has high viscosity (142 mPas at 80 °C) being in the form of a solid at room temperature.^{17,21–23} Thus, this factor affects its dissolution capability, requiring a high temperature to achieve proper dissolution. Consequently, the high reaction temperature could lead to unstable properties of the ionic liquid, unwanted side reactions, and loss of treated biomass.^{9,24} For example, it was found that a significant loss of biomass yield was derived from the pretreatment with an ionic liquid at high temperatures of 150 and 180 °C.⁹ This could be due to the unwanted side reactions of conversion of the carbohydrate fraction into water-soluble products (monosaccharides, oligosaccharides, furfural, and hydroxymethylfurfural (HMF)) at high temperatures.⁹ The use of ionic liquid-organic solvent mixtures may alleviate these problems by offering lower viscosity of the pretreatment solvent. This comes with several advantages, such as, providing higher biomass loading and ease of handling and operation. From our previous work, the solubility properties of ionic liquids, the mixtures of ionic liquids, and organic solvents have been studied.

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It was found that the Hildebrand solubility parameters (δ_H) of the mixtures do not correspond to the mixing rule—their values tend to be closer to those of the ionic liquids than those of the organic solvent (dimethylacetamide (DMA)) for 40–60 vol % DMA added in the ionic liquids.²⁵ The knowledge gained from the previous study encourages the use of cosolvents of ionic liquids and organic solvents for the biomass pretreatment.

For this work, we point to the study of the use of cosolvents of ionic liquids and organic solvents for the biomass pretreatment process. The effects of organic solvent type, organic solvent fraction in ionic liquid, reaction temperature on product yield, and properties were investigated. The organic solvents, dimethylacetamide (DMA, $\delta_H = 22.7$), dimethylformamide (DMF, $\delta_H = 24.8$), dimethyl sulfoxide (DMSO, $\delta_H = 26.7$), and ethanolamine ($\delta_H = 31.3$), which have high boiling points and stability for using at high temperatures and have different Hildebrand solubility parameters (δ_H),²⁵ were selected to be applied in this work. They were mixed with effective ionic liquids, 1-ethyl-3-methylimidazolium acetate (EMIM-AC), or 1-butyl-3-methylimidazolium chloride (BMIM-Cl), to study the effect of organic solvent type on the biomass pretreatment. Furthermore, corncobs and rice straw, which are the major waste products from agriculture, were used as potential precursors in this work. The use of these two potential biomasses, which have high annual amounts (252 million tons for corncobs (about 0.3 tons of corncobs produced from every 1 ton of corn)^{26,27} and about 731 million tons for rice straw²⁸), are also considered to be beneficial for solving the problem of waste disposal and reducing air pollution caused by burning them.

EXPERIMENTAL SECTION

Materials and Characterization. The two potential biomasses, corncobs and rice straw, were milled and sieved to obtain particle sizes in the range of <150 μm for pretreatment experiments. The sieved biomasses were dried at 120 °C for 24 h in an oven to speed up the removal of excess moisture. The dried biomass samples were characterized for bulk density, crystallinity index, and chemical composition (NREL laboratory analytical procedure²⁹). The ionic liquids of 1-ethyl-3-methylimidazolium acetate (EMIM-AC, $\geq 96.5\%$), 1-butyl-3-methylimidazolium chloride (BMIM-Cl, $\geq 98.0\%$), and the mixtures of ionic liquids and organic solvents (dimethylacetamide (DMA), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), ethanolamine) acquired from Sigma–Aldrich were applied as solvents for the pretreatment process. Furthermore, all chemicals for biomass regeneration, enzymatic hydrolysis, preparing DNS assay, and chemical standards were purchased from Sigma–Aldrich (detailed in ref 9).

Biomass Pretreatment and Regeneration. The details of the biomass pretreatment and regeneration have been given in our previous work.⁹ A 100 mg portion of biomass was treated with 2 mL of ionic liquid or a mixture of ionic liquid and organic solvent at a reaction temperature for 24 h. The mixture of biomass and solvent was stirred with a magnetic stirrer and the reaction temperature was controlled using a silicone oil bath. The pretreated biomass was recovered from the pretreatment solvent by adding an antisolvent (water:acetone (1:1, v/v)) to precipitate its pulp and eliminate dissolved lignin and ionic liquid. The precipitated biomass was filtrated by filter paper (Whatman grade no. 1) and washed with deionized water to remove excess ionic liquid.⁹ The regenerated biomass was dried at 100 °C for 24 h before carrying out enzymatic hydrolysis reactions and characterizations. The biomass pretreatment were performed in triplicate to at least achieve a less than 5% variation in sugar conversion and amount of extracted lignin. Yield of regenerated biomass was defined as the following equation:

$$\text{yield of regenerated biomass (wt \%)} = \frac{\text{mass of regenerated biomass}}{\text{mass of raw biomass}} \times 100 \quad (1)$$

Enzymatic Hydrolysis and Quantification of Sugar Content.

The untreated or treated biomass was hydrolyzed at 50 °C for 24 h with cellulose from *Trichoderma viride* (crude powder of fungus, 4 U/mg solid) at a concentration of 34 U/L in 50 mM citrate buffer (pH 4.7). The mixture of hydrolysis solution in DNS assay (150 μL in 2850 μL) was boiled for 5 min and was then cooled in an ice–water bath. The absorbance of color-developed mixtures derived from reducing DNS by reducing sugars at 540 nm was measured by UV–vis spectrophotometer (Varian, Cary 4000) for quantifying sugar content. The concentrations of total reducing sugars were calculated from the standard curve of D-glucose. Sugar conversion was determined as follows:

$$\text{sugar conversion (wt \%)} = \frac{\text{mass of total reducing sugars}}{\text{mass of regenerated biomass}} \times 100 \quad (2)$$

Analysis of Extracted Lignin Content. The supernatant solution derived from the washed pretreated biomass with the first antisolvent was used for analyzing the extracted lignin content by UV–vis spectrophotometer (Varian, Cary 4000). The solution was diluted with 0.1 N NaOH before being subjected to measure its absorbance at 280 nm. The total dissolved lignin content was obtained from the standard curve of known concentrations of alkali lignin. The content of extracted lignin was calculated through the following equation:

$$\text{extracted lignin content (wt \%)} = \frac{\text{mass of extracted lignin}}{\text{mass of lignin in raw biomass}} \times 100 \quad (3)$$

Measurement of Biomass Crystallinity. The X-ray diffractions of untreated and treated biomasses were measured for their crystallinity by a Bruker D8 Advance diffractometer. The X-ray diffraction patterns with Cu K α radiation ($k = 1.5406 \text{ \AA}$) were recorded over the angular range of 6–40°, with a step size of 0.02° and a step time of 1 s. The XRD data of biomasses was used to calculate crystallinity index (CrI) as the formula:³⁰

$$\text{CrI} = \frac{I_{002} - I_{\text{am}}}{I_{002}} \times 100 \quad (4)$$

where CrI is the crystalline index, I_{002} is the maximum intensity of the 002 lattice diffraction, near $2^\circ = 22.5^\circ$, and I_{am} is the intensity diffraction at suitable locations for the amorphous background at $2^\circ = 18.0^\circ$.

Characterizations of Structure and Morphology. The structure and morphology of biomasses before and after the pretreatment at different conditions were examined from SEM micrographs (scanning electron microscope (SEM): JEOL, JSM-6390LA) and photographs (digital single-lens reflex camera: Nikon D5000). For analysis of SEM micrographs, the samples were prepared by sputter-coating with platinum (Pt) to make the biomass samples conductive before being put into the SEM instrument. SEM images were taken at 500 \times magnification with the SEM instrument operated at 10 kV accelerating voltage.

RESULTS AND DISCUSSION

Biomass Characteristics. Basic physical properties and chemical compositions of the biomasses, corncobs, and rice straw are shown in Table 1. The corncobs and rice straw possess similar bulk densities. The value for corncob is slightly higher than that of rice straw (0.26 vs 0.21 g/cm³). Whereas, rice straw presents a higher crystallinity than that of corncob (the crystallinity indices of rice straw and corncob being 41.42% and 37.65%, respectively). Corncob has higher contents of polysaccharides than rice straw. It composes five carbohydrates of glucan, xylan, galactan, arabinan, and mannan, while rice straw consists of glucan, xylan, and arabinan. The main polysaccharide composition of corncob is glucan (40.41 wt %), followed by the composition of xylan (23.49 wt %). Rice straw provides the similar amounts of glucan and xylan (29.81 and 26.34,

Table 1. Biomass Characterizations

properties	corncob	rice straw
bulk density (g/cm ³)	0.26	0.21
crystallinity index (%)	37.65	41.42
chemical composition (wt %)		
glucan	40.41	29.81
xylan	23.49	26.34
galactan	5.83	
arabinan	3.48	1.91
mannan	4.24	
lignin (acid soluble lignin)	5.38	1.61
lignin (acid insoluble lignin)	15.82	23.35
ash	1.92	15.30
total	100.57	98.32

respectively). Rice straw may be considered to have poorer properties as a precursor for the bioconversion process than corncob as it not only renders a lower polysaccharide fraction and higher crystallinity but also has higher contents of ash (15.30 vs 1.92 wt %) and total lignin (24.96 vs 21.20 wt %).

Effect of DMA Fraction in Ionic Liquid on Pretreatment Products. DMA was selected for studying the effect of DMA fraction in ionic liquids as it is the most common solvent mixed with ionic liquids for biofuel production. As regarded from our previous work,⁹ it was found that the mixtures of DMA and ionic liquid showed a similar value of solubility parameters to that of pure ionic liquid, but not to that of DMA. For this work, the pretreatment of corncob with different fractions of DMA in EMIM-AC at 120 °C for 24 h was performed (Figure 1). The effect of DMA fraction on the important factors, which are sugar conversion, extracted lignin content, yield of regenerated biomass, and yield of reducing sugar, was investigated. Sugar conversion and extracted lignin content were examined to signify the improved properties of pretreated biomasses. The yield of regenerated biomass indicates the amount of the left biomass after the pretreatment. The pretreated biomasses, which are expected to possess improved properties to give a high conversion of sugar used as the source for chemical/fuel productions and have a low content of the left lignin which lowers the resistances of chemical and biological degradation, would provide more productivity for the bioconversion process. Moreover, the overall yield of sugar calculated from the yield of pretreated biomass and the sugar conversion should be also considered to optimize the pretreatment conditions. From this work, it presents that the pretreatments with EMIM-AC and the mixture of 40 vol % DMA in EMIM-AC give the similar values of sugar conversion, extracted lignin content, and yield of regenerated biomass (Figure 1a and b). However, there are slight decreases of sugar conversion and extracted lignin content and a slight increase of regenerated biomass yield (with increasing DMA fraction from 40 to 60 vol %). This is followed by the drastic decreases of sugar conversion and extracted lignin and the drastic increase of regenerated biomass yield at higher DMA fraction of 90 vol %. It may be explained that the ionic liquid has a significant influence on the biomass pretreatment even though 40–60 vol % DMA is added in EMIM-AC, corresponding with the Hildebrand solubility parameters (δ_H) derived from previous work.²⁵ The values of the solubility parameter for 40–60 vol % DMA added in EMIM-AC are closer to that of the ionic liquid (δ_H (40–60 vol % DMA in EMIM-AC) = 25.07–25.49 and δ_H (EMIM-AC) = 25.16²⁵). However, a mixture of 90 vol % DMA added in EMIM-AC renders extremely

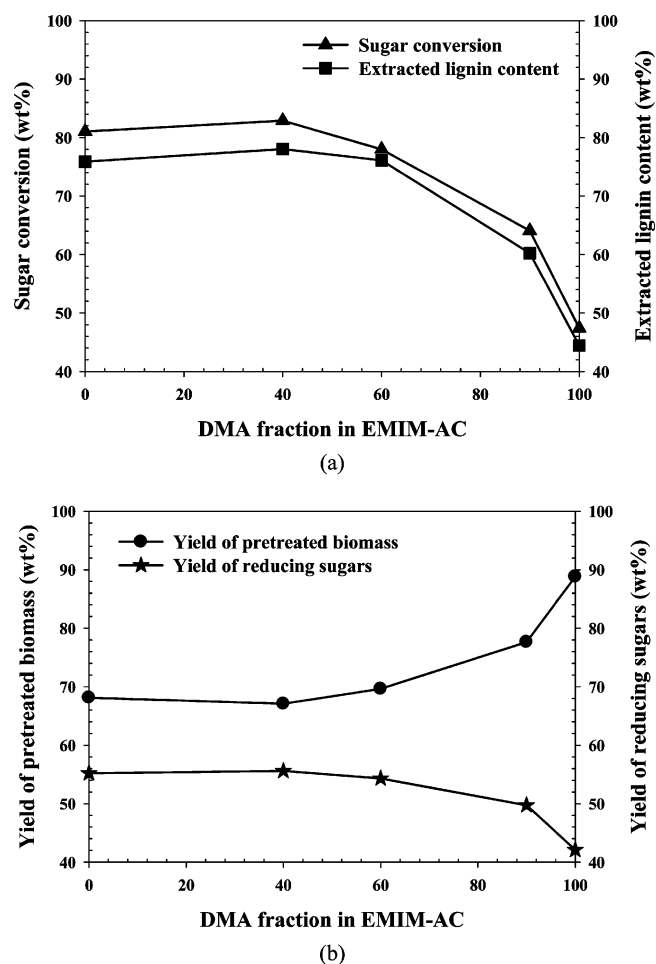


Figure 1. Effect of DMA fraction in EMIM-AC on corn cob pretreatment (a) sugar conversion and extracted lignin content and (b) yield of regenerated biomass and yield of sugar conversion.

low efficiencies on the biomass pretreatment. This may be attributed that this mixture shows a lower capability of pretreatment due to a stronger influence of DMA. It was also marked from previous work that the Hildebrand solubility parameter of this mixture was significantly lower (δ_H (90 vol % DMA in EMIM-AC) = 24.90²⁵) than that of the pure ionic liquid, but close to that of DMA (δ_H (DMA) = 22.70).²⁵ Furthermore, it may be noted that even though there are profound decreases of sugar conversion (16.38 wt % decreased) when the amount of DMA was increased from 60 to 90 vol %. However, the yield of reducing sugar reduces only 5.22 wt % due to a drastically increased yield of regenerated biomass at 90 vol % DMA added (Figure 1b). From this study, the optimized amount of added DMA for the biomass pretreatment can be obtained. The cost of pretreatment solvent could be reduced by adding a suitable proportion of organic solvent to give reasonable properties of pretreated biomass.

Effect of Reaction Temperature on Pretreatment Products. Figure 2a and b illustrates the effects of the pretreatment temperature on the sugar yield and conversion, extracted lignin content, and yield of regenerated biomass. The corncob pretreatments, with the mixture of 40 vol % DMA in EMIM-AC at different temperatures varying in the ranges of 25–150 °C were examined. The yield of regenerated corncob decreases when the pretreatment temperature increases from 25 to 150 °C. Whereas, the increases of sugar conversion, extracted

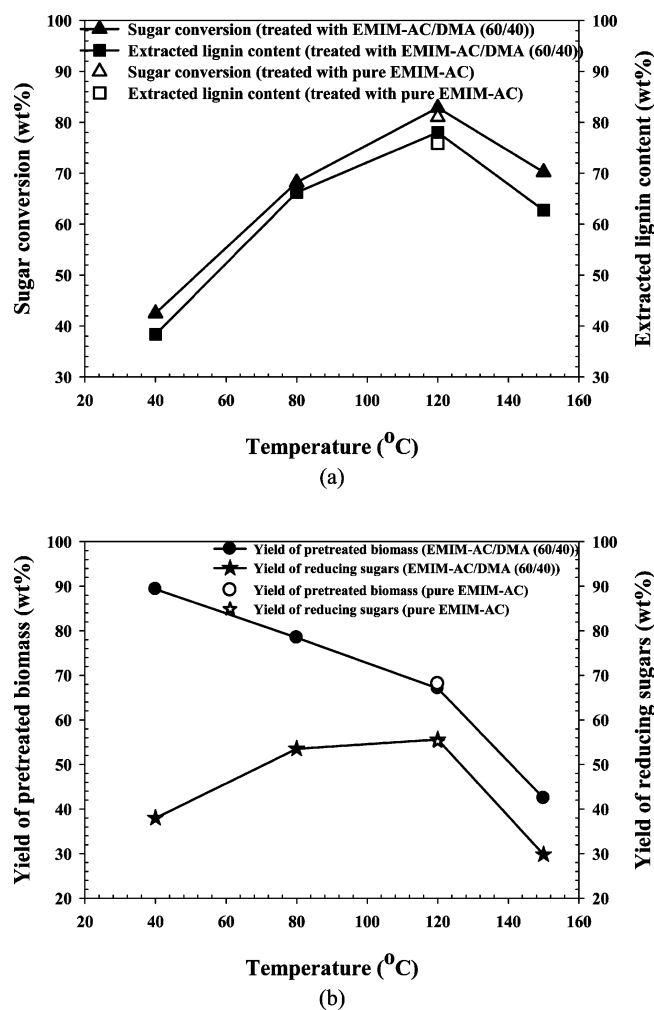


Figure 2. Effect of pretreatment temperature on corncob pretreatment with EMIM-AC/DMA (60/40 vol %) (a) sugar conversion and extracted lignin content and (b) yield of regenerated biomass and yield of sugar conversion.

lignin content, and yield of reducing sugar are obtained with increasing temperature. The maximum values (82.89, 78.03, and 55.61, respectively) were achieved at a temperature of 120 °C. However, about 15–25% of sugar conversion, extracted lignin content, and yield of reducing sugar decrease at a higher temperature of 150 °C. It is possible that the decrease of yield of regenerated biomass at the higher temperature may be caused by the loss of lignin component due to the lignin extraction by ionic liquid and/or decomposition of holocellulose.⁷ However, the observations of the vigorous decrease of regenerated biomass but lower efficiency of lignin extraction at the pretreatment temperature of 150 °C may result from the major decomposition of the carbohydrate fraction to produce biochemical products, for example, monosaccharides, oligosaccharides, furfural, and HMF.⁷ In addition, it is noted that the mixtures of EMIM-AC and DMA not only provide similar results of sugar yield and conversion, extracted lignin content, and yield of regenerated biomass with those of pure EMIM-AC,⁹ but they also offer no loss and decomposition of the mixture solvents, even treated at the high pretreatment temperature of 150 °C. Therefore, it is possible to perform the biomass pretreatment at high temperatures as an alternative condition, but it should be operated with a

shorter pretreatment time to avoid the decompositions of biomass and mixture solvent.

Effect of Organic Solvent Type on Pretreatment Products. The corncob pretreatments with the mixtures of EMIM-AC and different organic solvents (60/40 vol %) at 120 °C for 24 h were investigated to study the effect of organic solvent types on the pretreatment process (Figure 3). The

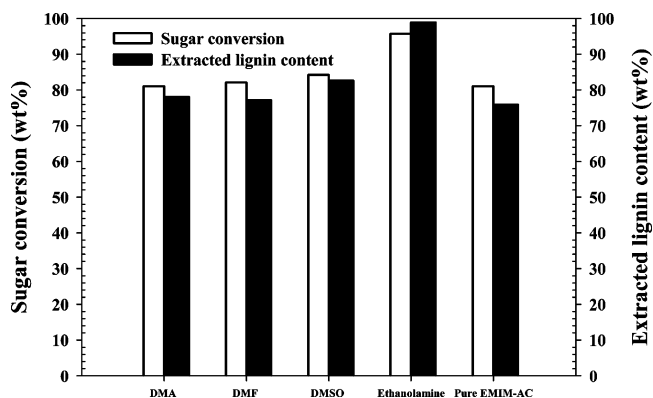


Figure 3. Effect of organic solvent type of EMIM-AC/organic solvent mixture (60/40 vol %) on corncob pretreatment.

pretreatments with mixtures of EMIM-AC/DMA, EMIM-AC/DMF, and EMIM-AC/DMSO provide relatively similar values of sugar conversion and extracted lignin content, being about 82.05–84.24 and 77.16–82.58 wt %, respectively. However, severely higher capabilities of sugar conversion and lignin extraction are obtained from pretreatments with mixtures of EMIM-AC/ethanolamine. The values of sugar conversion and extracted lignin content can reach 95.72 and 98.92 wt %, respectively. Furthermore, it should be noted that under the same conditions, the pretreatments using the mixture solvents of EMIM-AC and different organic solvents exert close or higher values of sugar conversion and extracted lignin content than the values derived from using EMIM-AC, indicating that the mixtures of EMIM-AC and organic solvent have been shown as a promising solvent for biomass pretreatment. This may be presumed that the addition of organic solvent in ionic liquid would change the solubility parameter of the mixture solvent to provide more effectiveness for biomass dissolution and lignin extraction. Especially, in the case of using ethanolamine as added organic solvent, ethanolamine, which has the largest change of Hildebrand solubility parameter (δ_H (ethanolamine) = 31.3 vs δ_H (EMIM-AC) = 25.16²⁵) among the other organic solvents, could contribute the greater change in the enhancement of biomass pretreatment.

Besides, ethanolamine, which presents the best organic solvent mixed with ionic liquid, was used to compare its pretreatment capabilities with those of pure EMIM-AC and also with those of the mixture of EMIM-AC/ethanolamine (60/40 vol %) for corncob and rice straw (Figure 4a and b). The properties of the two biomasses can be improved by pretreatments with the three solvents. They contribute to a 3–5 fold increase in sugar conversion compared with that of untreated biomasses (25.84 and 17.41 wt % for untreated corncobs and untreated rice straw, respectively). The mixture of EMIM-AC/ethanolamine (60/40 vol %) renders the highest sugar conversion and lignin extraction for the pretreatments of corncobs and rice straw. EMIM-AC shows a higher sugar conversion than that of ethanolamine, while ethanolamine (60/40 vol %) gives a profoundly higher lignin

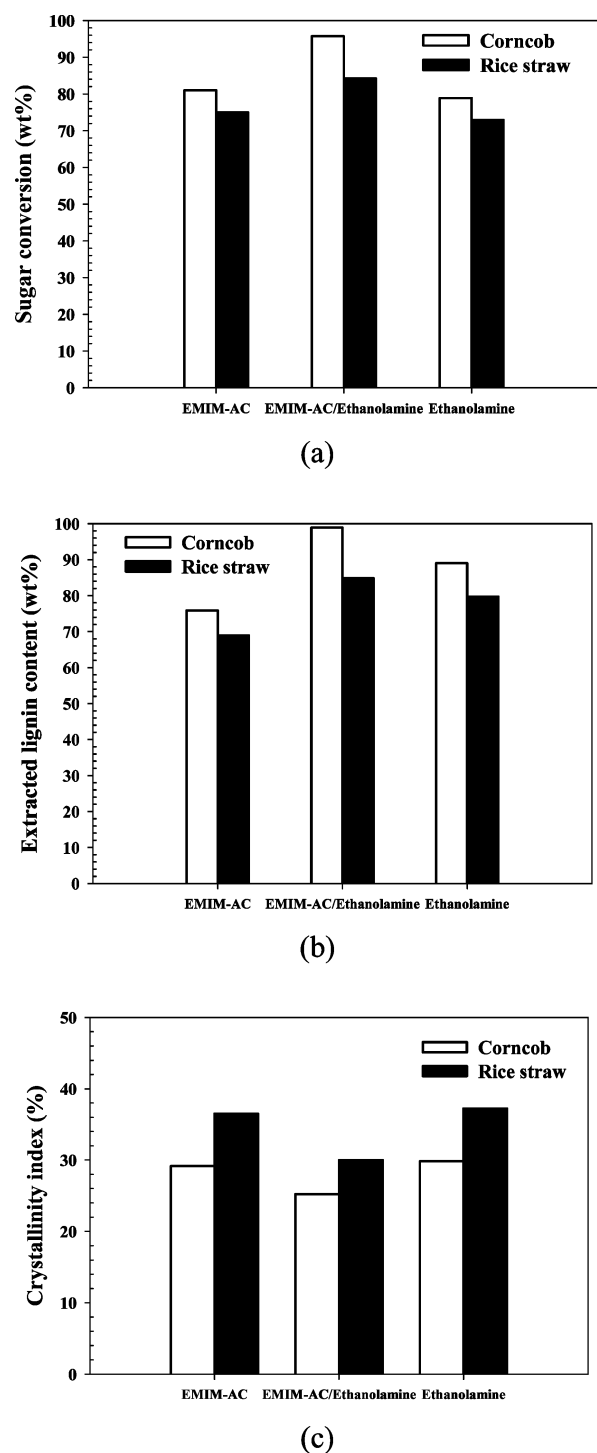


Figure 4. Effect of solvent type of EMIM-AC, EMIM-AC/ethanolamine (60/40 vol %), and ethanolamine on (a) sugar conversion, (b) extracted lignin content, and (c) crystallinity index derived from pretreatments of corn cob and rice straw.

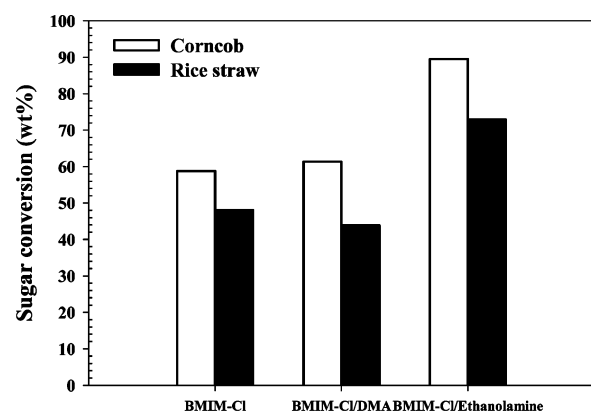
extraction for the pretreatments of both biomasses. It is interesting to note that the combination of the effective solvents of EMIM-AC and ethanolamine enhances the pretreatment capabilities of the mixture solvent of EMIM-AC/ethanolamine for the process. Upon comparison of the two biomass pretreatments, it was found that corn cob pretreatments with the three solvents provide higher values of sugar conversion and lignin extraction than those of rice straw pretreatment. This is

due to (1) the stronger recalcitrances of rice straw, which contains higher ash content and crystallinity which impedes the ionic liquid accessibility to selectively extract lignin and disrupts holocellulose structure, (2) the lower amount of polysaccharide fraction, and (3) the higher lignin content, resulting in the lower sugar conversion and the higher lignin content on the regenerated biomass.

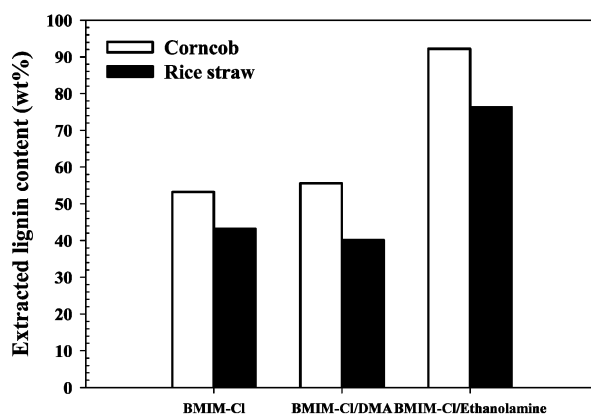
In addition, BMIM-Cl was also used as a solvent or in the mixture of solvents for biomass pretreatment in this study. Figure 5a and b indicates that even though BMIM-Cl has been addressed as an excellent solvent for cellulose dissolution,^{17,22,23} the corn cob and rice straw pretreatments with the ionic liquid exert a much lower sugar conversion (58.81 and 48.00 wt % for corn cob and rice straw, respectively) and extracted lignin content (53.23 and 43.20 wt % for corn cob and rice straw, respectively) than those derived from the pretreatments with EMIM-AC, ethanolamine, and the mixture of EMIM-AC/ethanolamine (60/40 vol %) (Figures 4 and 5). Nevertheless, slight increases of sugar conversion and lignin extraction were obtained using the mixture of BMIM-Cl/DMA (60/40 vol %) for corn cob pretreatment, whereas this solvent provides a poorer pretreatment of rice straw than those of pure BMIM-Cl. However, the use of BMIM-Cl/ethanolamine (60/40 vol %) mixture provides extreme enhancements of biomass pretreatments, giving about 25–39 wt % increase in sugar conversion and lignin extraction compared to those of BMIM-Cl. This may be presumed that ethanolamine in the mixture solvent assists the performances of BMIM-Cl to achieve the dissolution inside cellulose because of an increase in extraction of blocking lignin by ethanolamine, which is known to react with 1-, 3-, and 4-substituted benzene ring groups in lignin complex and CO groups in COOH groups in hemicelluloses.³¹

As mentioned above, the mixture solvents of ionic liquid and organic solvent are a promising solvent for biomass pretreatment. In addition, it should be also noted that they show an ease of handling and practical usages. The lower viscosity of mixture solvent renders a more simple washing out of mixture solvent from regenerated biomass. The solvent amount is still maintained even it is operated at a high temperature of 150 °C. Moreover, it is found that the mixture of EMIM-AC/ethanolamine (60/40 vol %) provides a higher loading (223.6 g cellulose/mL) of cellulose than that of EMIM-AC (176.6 g cellulose/mL) when the cellulose dissolutions at 120 °C were investigated.

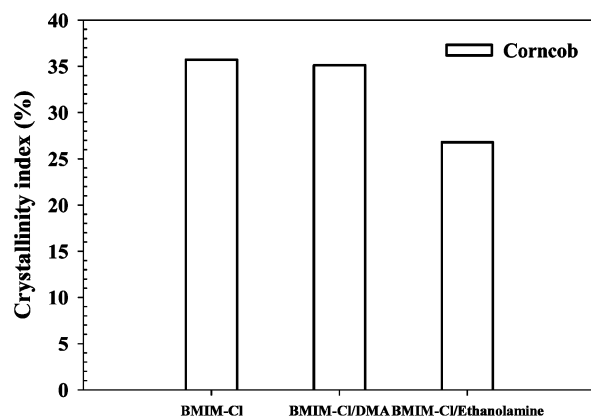
Product Characteristics. Biomass Crystallinity. The crystallinity of the biomass is a significant drawback for applying it to the bioconversion process. The high crystallinity causes high resistances in chemical and biological degradation. For this work, the crystallinity index of biomass was determined from the X-ray diffraction patterns. Figure 6 shows the X-ray diffraction spectra of untreated and treated corncobs and rice straw. The untreated corncobs and rice straw have the similar characteristics of X-ray diffraction spectra, showing a main peak of crystalline cellulose at 22° with a broad shoulder of amorphous cellulose and lignin and hemicellulose at 15°. After the pretreatment, a peak with a lower intensity remained, leading to lower crystallinity indices (Figure 6). Corn cob pretreated with EMIM-AC/DMA (60/40 vol %) presents a decrease of X-ray diffraction intensity compared with that of the untreated corn cob. However, the significant decreases of intensity are derived from using EMIM-AC/ethanolamine (60/40 vol %) for corn cob and rice straw pretreatments. Moreover, it was observed that the crystallinity index is inversely proportional to the sugar conversion (Figures 4



(a)



(b)

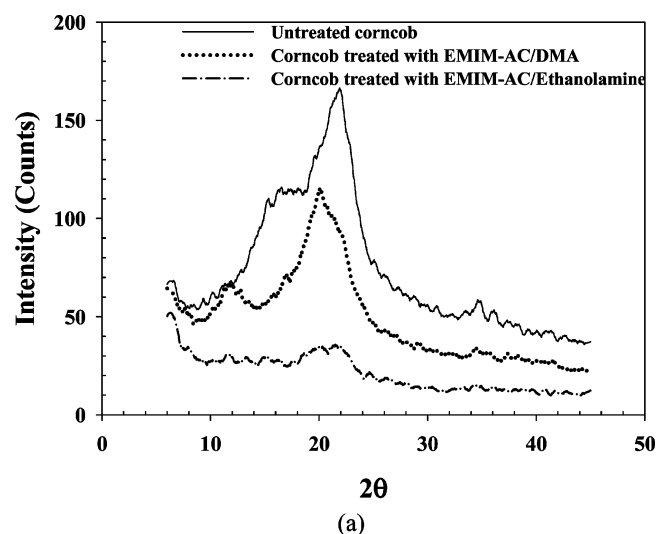


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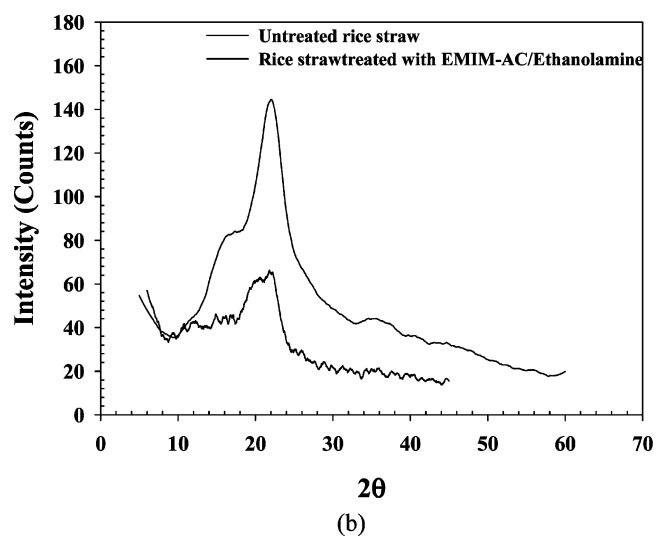
Figure 5. Effect of solvent type of BMIM-Cl and BMIM-Cl/organic solvent mixtures (60/40 vol %) on (a) sugar conversion, (b) extracted lignin content, and (c) crystallinity index derived from pretreatments of corncob and rice straw.

and 5). The order of decrease of crystallinity index related with the increase of sugar conversion is acquired from the corncob pretreatment with the following solvents: BMIM-Cl < BMIM-Cl/DMA < ethanolamine < EMIM-AC < BMIM-Cl/ethanolamine < EMIM-AC/ethanolamine.

Biomass Structure and Morphology. The structure and morphology of untreated biomasses and biomasses pretreated



(a)



(b)

Figure 6. X-ray diffraction spectra of untreated biomasses and biomass treated with EMIM-AC/organic solvent mixtures (60/40 vol %) (a) corncob and (b) rice straw.

with various solvents at 120 °C for 24 h were examined with SEM micrographs and photographs. Figures 7 and 8 illustrate the SEM images of corncob and rice straw, respectively. In addition, the SEM micrographs of untreated rice straw and rice straw pretreated with EMIM-AC at the same conditions have been displayed in our previous work.⁹ The changes in structure and morphology of biomasses before and after pretreatment with ionic liquids and the mixtures of ionic liquid and organic solvent were noted. At the same magnification, the rough flakes of untreated corncob and rice straw were observed. The pretreated corncob presents a flat sheet with rough surface and high porosity. The pretreated rice straw possesses more fine particles with rougher surface when they are pretreated with EMIM-AC. The two biomasses pretreated with the mixture solvent of EMIM-AC/DMA (60/40 vol %) provide flat and rough surfaces. More flat surfaces were attained when the mixture of EMIM-AC/ethanolamine (60/40 vol %) was applied. Furthermore, the changed structures can be noticeably observed from their photographs (Figures 9 and 10). The corncob and rice straw pretreatments with the mixtures of EMIM-AC/DMA (60/40 vol %) and EMIM-AC/ethanolamine (60/40 vol %) provide greatly

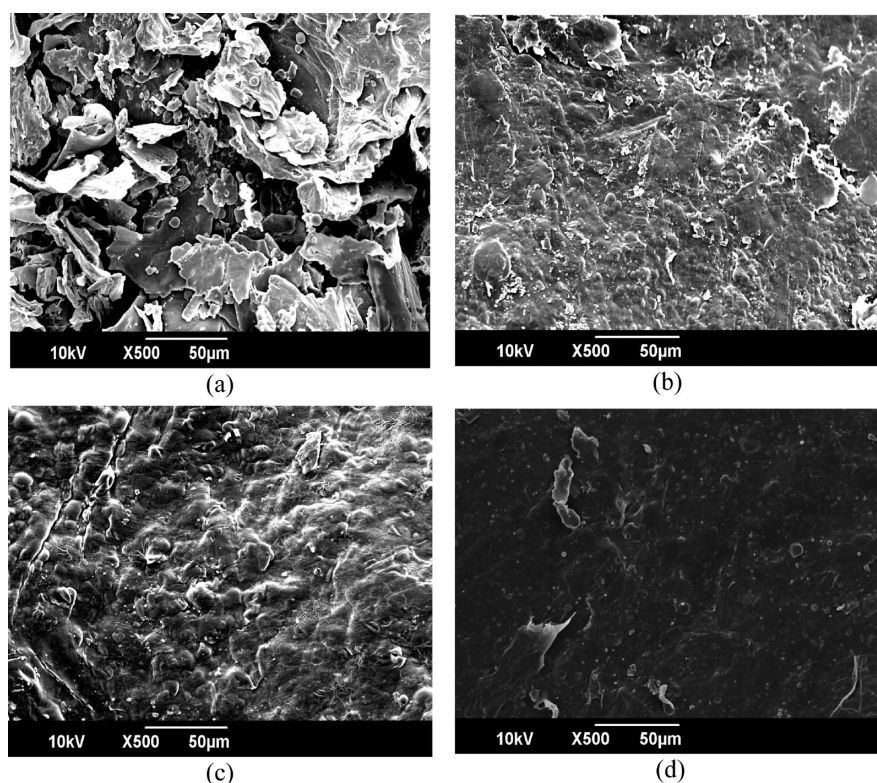


Figure 7. SEM micrographs of (a) untreated corn cob, (b) corn cob treated with EMIM-AC, (c) corn cob treated with EMIM-AC/DMA (60/40 vol %), and (d) corn cob treated with EMIM-AC/ethanolamine (60/40 vol %).

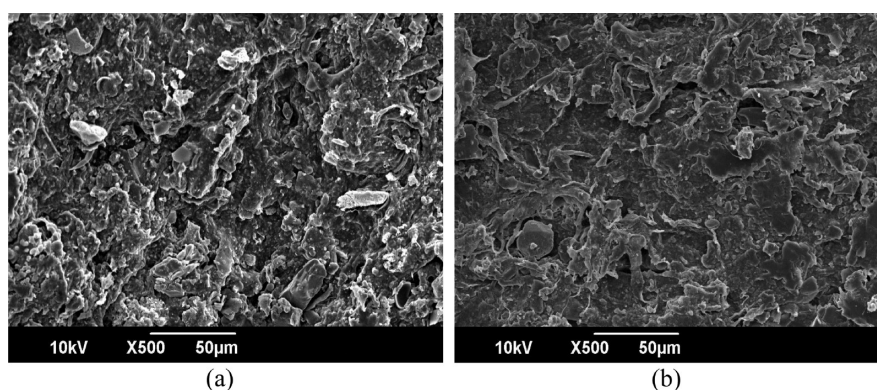


Figure 8. SEM micrographs of (a) rice straw treated with EMIM-AC/DMA (60/40 vol %) and (b) rice straw treated with EMIM-AC/ethanolamine (60/40 vol %).

thin and flat sheets. Nevertheless, corn cob pretreated with BMIM-Cl, which gives the lowest sugar conversion, shows thicker flakes compared with those derived from pretreatment with the mixture solvents (Figure 9). The color of the pretreated biomasses is pale when the biomasses are pretreated with ethanolamine and EMIM-AC/ethanolamine (60/40 vol %), possibly because ethanolamine acts as a solvent to dissolve and extract some pigment or extractives of the biomasses. Therefore, it may be concluded that the changes of biomass color or structure and morphology from rough flakes to a flat sheets with rougher surfaces signifies that the biomass properties are improved by the pretreatment with ionic liquid or the mixtures of ionic liquids and organic solvents. The thin and flat surfaces could lead to more accessibilities of chemical and microbes and/or enhancement of enzymatic saccharification.^{9,12,33}

CONCLUSION

This study provides the basic knowledge of the effects of organic solvents in ionic liquids on biomass pretreatment. It is found that the mixtures of 40–60 vol % DMA in EMIM-AC give closer values of sugar yield and conversion, extracted lignin content, and yield of regenerated biomass compared with those of EMIM-AC, while the lower efficiencies of biomass pretreatment are attained at 90 vol % DMA. The cosolvent of EMIM-AC/DMA (60/40 vol %) renders the maximum sugar yield and conversion and extracted lignin content at pretreatment temperature of 120 °C, and it shows no loss or decomposition even treated at the high temperature of 150 °C. The mixture solvents of EMIM-AC/DMA, EMIM-AC/DMF, and EMIM-AC/DMSO (60/40 vol %) offer relatively close or slightly higher values of sugar conversion and extracted lignin content compared to those of EMIM-AC. Nevertheless, the extremely higher values of sugar conversion

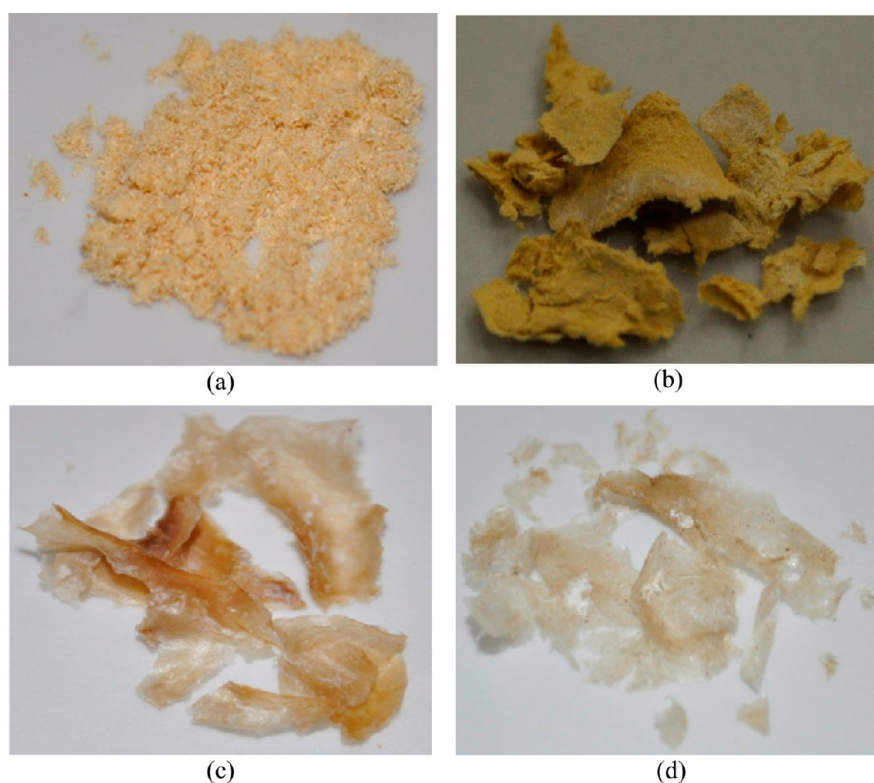


Figure 9. Photographs of (a) untreated corn cob, (b) corn cob treated with BMIM-Cl, (c) corn cob treated with EMIM-AC/DMA (60/40 vol %), and (d) corn cob treated with EMIM-AC/ethanolamine (60/40 vol %).

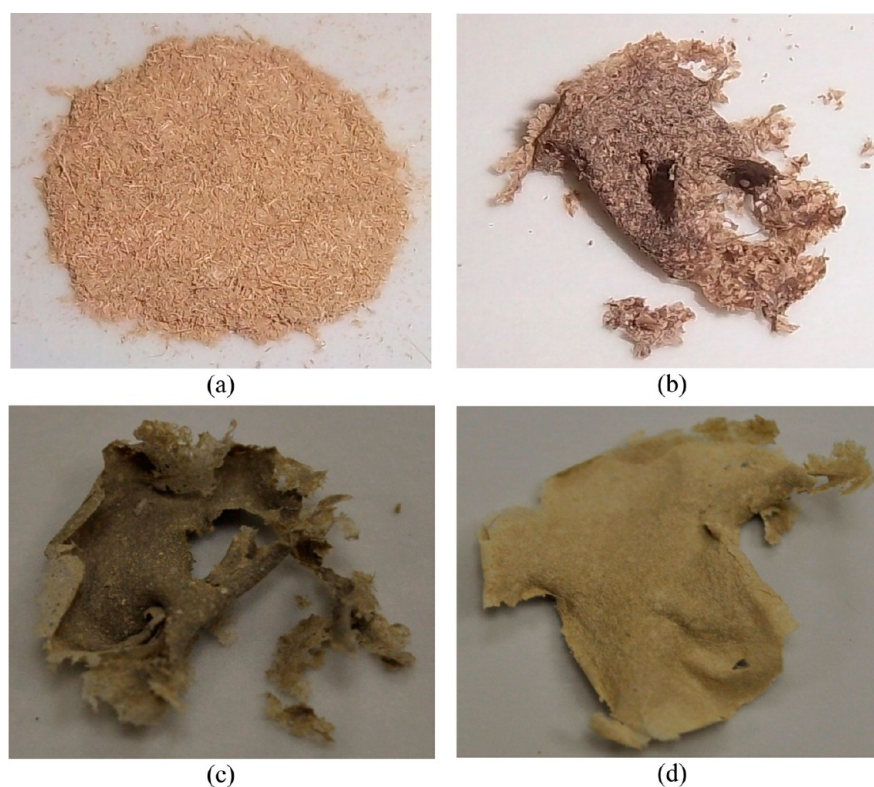


Figure 10. Photographs of (a) untreated rice straw, (b) rice straw treated with EMIM-AC/DMA (60/40 vol %), (c) rice straw treated with EMIM-AC/ethanolamine (60/40 vol %), and (d) rice straw treated with ethanolamine.

and extracted lignin content are acquired from using EMIM-AC/ethanolamine (60/40 vol %), achieving more than 95 wt %. It was also found that the sugar conversion and extracted lignin content

can reach ≥ 90 wt % with the application of BMIM-Cl/ethanolamine (60/40 vol %) mixture, giving about 25–39 wt % increase compared to those of BMIM-Cl. The use of

cosolvents of ionic liquids and organic solvents for the pretreatment process shows a number of advantages including possessing lower viscosity to render more simple washing out of the mixture solvent from regenerated biomass and higher loading of cellulose than that of ionic liquid. Furthermore, it is possible that the mixture solvents can be recycled or reused since the studied organic solvents have the high thermal stability, having higher boiling point than 150 °C. Thus, they can be operated at the high temperatures and can be simply separated from antisolvents such as water, ethanol, or water–acetone by evaporation to reuse for next batches.

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Notes

The authors declare no competing financial interest.

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