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Combination of Ionic Liquid and Instant Catapult Steam Explosion Pretreatments for Enhanced Enzymatic Digestibility of Rice Straw

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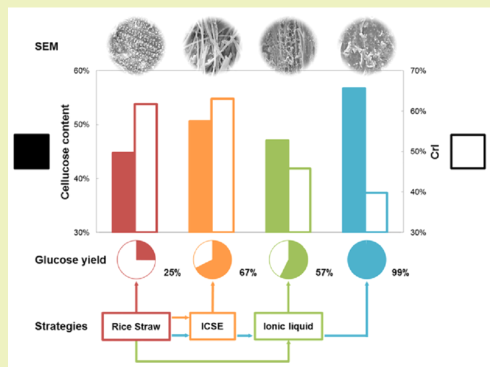
ABSTRACT: Lignocellulose rice straw was pretreated by three ionic liquids and instant catapult steam explosion (ICSE), and their effects on feedstock morphology, chemical composition, crystallinity index, thermostability, and glucose yield after enzymatic hydrolysis were investigated. Results showed that ionic liquid performed ideally in separation of lignocellulose components. Compared with the untreated feedstock, the addition of 1-ethyl-3-methylimidazolium acetate ([Emim]Ac) increased the glucose yield by 70.35% thanks to its marvelous solubility for cellulose and lignin. Moreover, the incorporation of ICSE further enhanced the degradation of lignocellulose. Compared to the sole utilization of ionic liquid, ICSE plus ionic liquid increased the glucose yield by 73.38% (1-butyl-3-methylimidazolium chloride, [Emim]Cl) and 74.01% (1-butyl-3-methylimidazolium chloride, [Bmim]Cl), respectively. ICSE tore up the feedstock into small and porous biomass with large specific surface area, which contributed to the superior performance of ionic liquid on rice straw dissolution. The structure changes of feedstock before and after pretreatment were observed by scanning electron microscopy, Fourier transformation infrared spectrometry, X-ray diffraction, and thermogravimetric analysis.



KEYWORDS: *Rice straw, Lignocellulose, Pretreatment, Ionic liquid, Instant catapult steam explosion, Structure*

INTRODUCTION

The world is facing more and more severe challenges in energy supply and environmental pollution that threaten the sustainable development of society.[1] What the world most needs are renewable, affordable, reliable, and available technologies to meet the increasing expectation of energy for human future. Biorefinery has been acknowledged as a commercial process to convert biomass into fuels such as ethanol and butanol, and high value-added chemicals,[2,3] though many challenges still exist for large scale production.

Lignocellulosic biomass, particularly abundant agricultural residues such as rice/wheat straw and corn stover, is one choice for the industrial production of biofuels, which has garnered worldwide attention.[1] Unfortunately, the recalcitrance of lignocellulosic biomass, resulted from complex composition and crystalline cellulose, directly deteriorates the efficiency of biomass utilization.[4] The separation of lignocellulosic components is an economically viable biorefinery via providing the polysaccharose and lignin to produce liquid fuels and high-value-added products.[5,6]

As a kind of new solvent, ionic liquid plays an attractive role in lignocellulose fractionation, with great potential for lignin extraction and carbohydrate dissolution.[7,8] The advantages of ionic liquid, such as environmental friendly, high polarity, nonvolatility, and designability, have led to extensive studies to develop processes for commercial applications.[9] Generally, the disadvantage of ionic liquid is that relatively high viscosity requires the small particles of feedstock and high temperature to achieve proper dissolution, which results in unstable properties of the ionic liquid, undesired side reactions, and biomass loss.[10] Moreover, the high cost of ionic liquid is the major barrier for industrial application.

To improve the effect of ionic liquid on lignocellulose fractionation, a cost-effective and efficient treatment to decrease size of feedstock and enlarge specific reaction area is necessary. Steam explosion is the most commonly employed physico-chemical process among various pretreatment technologies.[11] The instant catapult steam explosion (ICSE) process has unique features beyond the other steam explosions. Compared to the depressurization time of seconds, even minutes for conventional steam explosion, the ICSE device, equipped by a piston with the same diameter as the pressured vessel, could completely release pressure within 0.1 s, which consequently exerted much higher explosion power density on the biomass to decrystallize a structure effectively.[12,13] As a result, much shorter time and easier dissolution of biomass for ionic liquid pretreatment are realized.

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The aim of this study was to investigate the effect of ionic liquid and ICSE on the pretreatment of rice straw. Three types of ionic liquids were used after ICSE treatment. The morphological changes were verified by scanning electron microscopy (SEM) and a nitrogen adsorption method. Meanwhile, attenuation reflection-Fourier transformation infrared spectrometry (ATR-FTIR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA) were applied to examine structural characteristics. The chemical composition analysis and enzymatic hydrolysis of substrates were conducted to evaluate the applicability of ICSE and ionic liquid pretreatment methods.

■ MATERIALS AND METHODS

Materials. The rice straw (Hunan province in China, 2014) was dried naturally and tailored to a specified size range (10−50 mm) and rinsed by water, then dried at 60 °C for 48 h in an oven.

The ionic liquids were purchased from Lanzhou Institute of Chemical Physics (Chinese Academy of Sciences, Lanzhou, China). Their chemical structures and abbreviations are displayed in Figure 1.

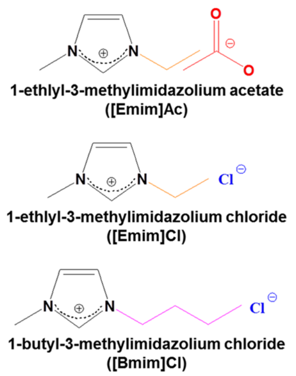

Figure 1. Ionic liquids used for pretreatment of rice straw.

Lignocellulose Pretreatment and Regeneration. A device for ICSE (QBS-80 SE, Hebi Gentle Bioenergy Co. Ltd., China) was used in this study. The rice straw was loaded into a 400 mL working chamber at 50 g/L. The pressure was maintained at 2.5 MPa for 90 s, and the piston driving device was triggered to release pressure within 0.1 s.[13] All ICSE-pretreated rice straw was collected and washed by deionized water and then dried.

The mixture of biomass and ionic liquid at a ratio of 1:10 (w/w) was stirred by a magnetic stirrer in a silicone oil bath, maintained at 140 °C for 4 h. The pretreated biomass was not completely dissolved, then recovered by adding an antisolvent (deionized water) to precipitate the carbohydrate-enriched residue and eliminate dissolved lignin and ionic liquid. The regenerated biomass was washed by deionized water and dried in freeze-dryer (Alpha 1-2LD plus, Christ, Germany) for 24 h prior to further analysis. All experiments were carried out in duplicate at least.

Compositional Analysis. The chemical composition of rice straw, including cellulose, hemicelluloses, lignin, and ash, were analyzed according to a NREL published protocol.[14,15] The protocol contains a two-step acid hydrolyzed process: First, the rice straw was hydrolyzed by 72% (w/w) H_2SO_4 at 30 °C for 1 h. Then, the reaction mixture was diluted by deionized water and further hydrolyzed with 4% H_2SO_4 in an autoclave at 121 °C for 1 h. Then, the reaction mixture was filtered, and the solid residue was washed and dried to determine the acid insoluble lignin, whereas the filtrate was collected to analyze the chemical composition of cellulose, hemicelluloses, and acid soluble lignin.

Enzymatic Hydrolysis. The enzymatic hydrolysis tests were performed by using cellulases (GENENCOR Accellerase 1500) with a loading of 30 FPU/g substrate. The reaction was conducted at 50 °C for 72 h in pH 4.8 acetate buffer.

The carbohydrates in the supernatant were determined by HPLC (Waters 410, Waters, Taunton, MA) with the column (Biored Aminex HPX-87H, 300 mm × 7.8 mm, Hercules, CA) and Waters 410 refractive detector. A flow rate of 0.5 mL/min was applied with 10 mmol/L H_2SO_4 as the mobile phase. The glucose yield was calculated by the following equation:

$$\text{glucose yield} = (\text{glucose of hydrolysate} \times 0.9) / \text{cellulose of feedstock} \quad (1)$$

Analytical Methods. SEM (Quanta 450, FEI, USA) was used to observe the morphology of rice straw. The solid samples with the high vacuum gold jetting were fixed on the aluminum sample stubs. Images were acquired with a 20 kV acceleration voltage.

The ATR-FTIR spectrum of the samples was recorded by the FTIR spectrometer (EQUINOX55, BRUKER, Germany) between 500 and 3500 cm^{-1} at 2 cm^{-1} nominal resolution and 25 °C. The XRD diffractogram of the samples was obtained by the X-ray diffractometer (D/MAX-2400, RIGAKU, Japan). The lignocellulosic biomass was scanned in the range of 10−35° (2θ) with a step size of 0.02° and step time of 1 s at 40 kV and 100 mA under 25 °C. The crystallinity index (CrI) of materials is defined by

$$\text{CrI} = (I_{002} - I_{am})/I_{002} \times 100\% \quad (2)$$

where I_{002} is the maximum intensity of crystalline portion, and I_{am} is the intensity attributed to the amorphous portion.[16]

Thermal stability was detected by using TGA with a simultaneous thermal analyzer (TGA/Q500, TA Instruments, New Castle, DE). A 5 mg sample was heated from 30 to 500 °C at a speed of 10 °C/min, and nitrogen was the carrier gas.

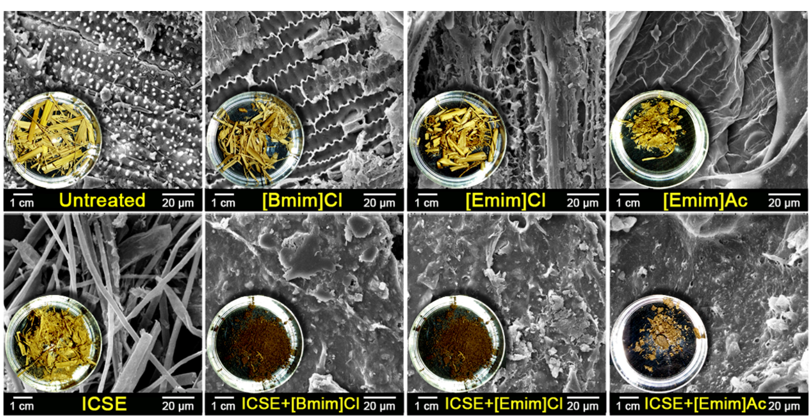

Figure 2. Photographs (plates in left bottom) and SEM micrographs of rice straw under various ICSE and ionic liquid pretreatments.

Physisorption apparatus (SSA-4200, Builder, China) was used to determine the specific surface area. Before the measurements, the samples were outgassed in the degas port of adsorption apparatus. The specific surface area of the samples was calculated as the standard Brunauer−Emmett−Teller (BET) method.[17]

RESULTS AND DISCUSSION

Morphology of Feedstock. The significant morphological changes could be observed through both naked eyes and microscope (Figure 2). Compared to the untreated rice straw with smooth surface and regular shape, the feedstock treated by ionic liquid featured rough appearance and twisted forms. [Bmim]Cl and [Emim]Cl dissolved the cellulose component and then regenerated it on the surface of feedstock. In addition to dissolution cellulose, [Emim]Ac further removed a large portion of lignin leading to the largest morphological change among three ionic liquids. ICSE, as a main force to decompose the big compact biomass into small fiber-like feedstock, definitely benefited the dissolution effect of ionic liquid treatment. The feedstock was transformed to tiny particles, and some of them melted together under ICSE+[Emim]Ac condition.

SEM observation confirmed the analysis through appearance of feedstock. The surface of the untreated rice straw was tight and regular, revealing that crystalline fibril was well covered by other components. After ICSE pretreatment, the surface was transformed into small and long fibers due to the extremely large mechanical force applied by steam explosion. [Bmim]Cl-treated rice straw was still similar to untreated rice straw, showing the worst effect on structure change, which were thicker and more regular than those treated by [Emim]Cl and [Emim]Ac. ICSE+ionic liquids treatment converted feedstocks into a melting status that were totally different from the untreated feedstock. The increase of external surface area would consequently increase cellulose accessibility to enzymes.[18]

As another evidence for morphology change, BET offered information about internal specific surface area of feedstock (Table 1). ICSE treatment increased this value of rice straw by 86.79%, which improved the dissolution of rice straw by ionic liquids.[19] In addition, ionic liquid also increased the specific surface area of feedstocks by removing the components, which finally promoted the enzymatic hydrolysis.

Table 1. Data for Structure Change and Glucose Yield

conditions	specific surface area (m^2/g)	CrI (%)	glucose yield (%)
untreated	1.59	61.75	25.08 ± 1.78
ICSE	2.97	63.05	67.65 ± 1.16
[Bmim]Cl	10.64	52.01	45.53 ± 1.88
ICSE+[Bmim]Cl	19.38	42.19	79.23 ± 2.01
[Emim]Cl	11.44	45.81	57.30 ± 1.25
ICSE+[Emim]Cl	44.98	39.83	99.34 ± 0.19
[Emim]Ac	30.86	17.07	84.58 ± 3.37
ICSE+[Emim]Ac	50.70	18.81	95.04 ± 2.33

Chemical Composition. The compositional analysis of untreated and treated rice straw were summarized in Table 2. As far as the same cation concerned, the ionic liquid with Cl^- had little impact on biomass composition, changing cellulose, hemicellulose and lignin by 5.23%, 0.96%, and 6.92%, respectively. Ionic liquid with Ac^- performed better in increasing the cellulose content by 35.62% due to its significant removal of hemicellulose (from 18.81% to 12.90%) and lignin (from 25.61% to 16.16%).

While dealing with rice straw by ICSE before ionic liquids treatment, greater enhancement of cellulose content was found, which increased 19.51% ([Bmim]Cl), 24.29% ([Emim]Cl), 12.32% ([Emim]Ac), respectively. The ICSE process could disrupt the cross-linked structure of rice straw, leading to porous and loose materials, and promoted ionic liquid infiltrate the materials. Moreover, ICSE itself is an ideal pretreatment method to achieve more hemicellulose removal.[13] Although two-step pretreatment lowered the solid yield, the increase of cellulose brought better impact for the following operation of enzymatic hydrolysis.

Spectrum Analysis for Feedstock. FTIR and XRD spectra were performed to monitor the changes of chemical function group and cellulose crystallization degree in rice straw (Figure 3).

The bands at 3330 and 2927 cm^{-1} representing the O−H and C−H stretching confirmed the appearance of the lignocellulosic matrix in both untreated and treated materials.[20] The band at 1035 cm^{-1} corresponding to the C−O stretching vibration showed the strongest absorption for all regenerated materials, which confirmed the natural traits of lignocellulose still remained in treated materials.[21−23]

All treated materials showed higher intensity at bands 797 and 897 cm^{-1}, indicating that their cellulose contents were more amorphous than that of untreated rice straw. These bands are sensitive to the amount of amorphous cellulose, and broadening them reflects higher porosity of the cellulose.[24] The band at around 1732 cm^{-1}, relating to the C═O stretching of the hemicellulose acetyl, reflects the hemicellulose content. After ICSE treatment, this band exhibited declined absorbance, meaning that some hemicellulose was degraded.

Lignin characteristic peaks at 1211 cm^{-1} (syringyl ring and C—O stretching vibration), 1320 cm^{-1} (C−O vibration in the syringyl ring), 1419 cm^{-1} (C—H deformation), 1459 cm^{-1} (asymmetric bending in CH_3), and 1610 cm^{-1} (C═C stretching vibration) were less intense in the spectra of the ICSE+ionic-liquids-treated materials in comparison with the

Table 2. Compositional Analysis of Feedstock

conditions	cellulose (%)	hemicellulose (%)	lignin (%)	ash or other (%)	solid yield (%)
untreated	44.75 ± 1.09	18.81 ± 0.60	25.61 ± 2.25	10.83 ± 0.22	100
[Bmim]Cl	47.62 ± 1.53	19.22 ± 0.62	22.94 ± 0.81	10.22 ± 0.34	89.73 ± 2.79
[Emim]Cl	47.09 ± 0.64	18.99 ± 0.87	22.44 ± 1.82	14.48 ± 0.24	88.50 ± 2.70
[Emim]Ac	60.69 ± 0.97	12.90 ± 1.01	16.16 ± 0.51	10.25 ± 0.40	83.83 ± 4.82
ICSE	50.62 ± 0.84	13.39 ± 0.72	24.24 ± 0.43	11.75 ± 0.11	84.58 ± 1.40
ICSE+[Bmim]Cl	56.97 ± 0.42	7.47 ± 0.72	23.77 ± 0.48	11.79 ± 1.11	76.09 ± 3.02
ICSE+[Emim]Cl	58.53 ± 0.35	8.90 ± 0.57	21.41 ± 0.41	11.16 ± 0.14	74.66 ± 2.05
ICSE+[Emim]Ac	68.17 ± 0.77	4.43 ± 0.91	16.98 ± 0.30	10.42 ± 0.30	70.61 ± 3.28

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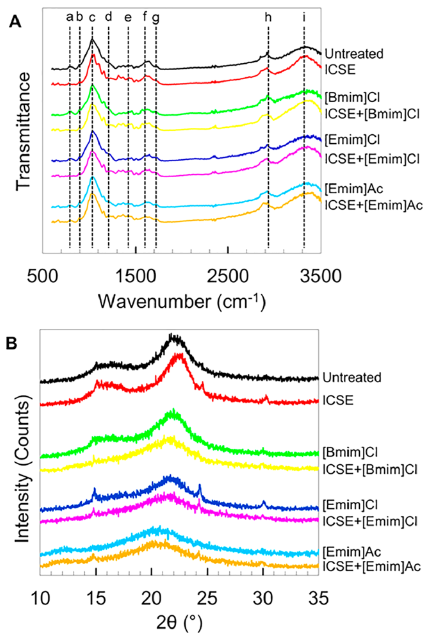

Figure 3. Spectrum analysis of rice straw under different pretreatment conditions. (A) ATR-FTIR spectra with bands (cm^{-1}): a, 797; b, 897; c, 1035; d, 1211; e, 1419; f, 1610; g, 1732; h, 2927; i, 3330. (B) X-ray diffraction spectra.

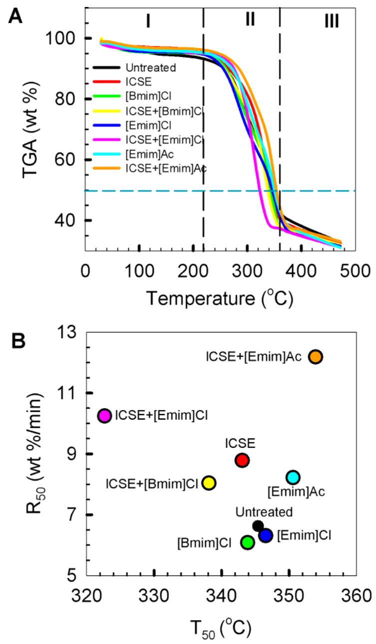

Figure 4. Profiles of TGA (A) and plots of T_{50} and R_{50} (B) for rice straw under different pretreatment conditions in a pyrolysis environment.

untreated rice straw. In other words, the lignin content in the lignocellulose was preferentially transferred into the ionic liquids.

The XRD intensity profile collected for untreated rice straw exhibited the well resolved spectrum of cellulose I, also known as the crystalline cellulose, with the two characteristic reflections (I_{am}) and (I_{002}) at 2θ values of 13−18° and near 22.6°, by which CrI can be calculated according to eq 2, and the results are shown in Table 1. The low CrI means a high amount of amorphous cellulose present in the materials.[25] The CrI of ICSE-treated rice straw was similar to the CrI of the untreated one, showing ICSE has no significant influence on the CrI of lignocellulose. All the ionic-liquid-treated materials had lower CrI than the untreated feedstock. Among them, material regenerated from [Emim]Ac treatment featured the lowest value. The results confirmed the materials regenerated from ionic liquid pretreatments exhibited higher porosity.

After ICSE+ionic liquid pretreatment, the intensity of peak near 22.2° decreased and the position shifted to the left. The peak between 14° and 16° essentially disappeared, leading to significant decrease of CrI. Among them, ICSE+[Emim]Ac treated materials gave the lowest CrI, similar to [Emim]Ac-treated materials, and the CrI of the materials with ICSE +[Emim]Cl and ICSE+[Bmim]Cl pretreatments were deceased by 13.05% and 18.88% compared to sole ionic liquid pretreatment. These results demonstrated that ionic liquids could disrupt the crystal structure of cellulose in lignocellulose and act more efficiently with the assistance of ICSE. The cellulose existed in the untreated rice straw as the form of crystalline cellulose I, but cellulose II with low crystallinity was recovered after ionic liquid and ICSE treatment. The cellulose II would benefit the following enzymatic hydrolysis.

Thermal Stability of Feedstock. As illustrated in Figure 4, the TGA profiles represented the instantaneous weight loss percentage of the tested lignocellulosic biomass, which can be roughly divided into three regions for rice straw. The first stage (<220 °C) featured the gentle weight decline (less than 10%) resulted from the dehydrating procedure and the release of volatile components. The second stage, as the temperature between 220 and 360 °C, was the main process for thermal decomposition of hemicellulose, cellulose, and lignin, where the weight of the lignocellulose had a steep drop to below 40%. The third stage showed the slow weight loss as the temperature higher than 360 °C, where only the heavy components of rice straw were left.

Although a notable difference was observed (Figure 4A), it was still inconvenient to analyze the profiles of same biomass under various pretreatments. To obtain a comprehensive correlation between weight loss and conditions, two indicators, T_{50} and R_{50}, representing the temperature at the level of 50% weight loss and corresponding speed of weight loss at T_{50},[26] are illustrated in Figure 4B. Generally speaking, the value of T_{50} relates to the component contents because of the increasing thermostability following the order of hemicellulose, cellulose, and lignin. The larger T_{50} value means relative higher lignin content in the feedstock. The large value of R_{50} mainly relates to the large specific surface area, stemming from more porous structure accelerating the thermal decomposition.

Overall, the values of T_{50} ranged from 323 to 354 °C and the values of R_{50} were between 6.10 and 12.18%/min, indicating the considerable change of TGA caused by different pretreatments. The plots on the right side and on the top of Figure 4B are for high lignin content and large reaction area, respectively, which is consistent with the results demonstrated in previous sections. In detail, the plots of rice straw treated by [Bmim]Cl and [Emim]Cl located near the untreated feedstock, revealing composition and structure of those materials changed a little. However, the [Emim]Ac gives great impact on rice straw, because the R_{50} and T_{50} values of treated materials significantly increased. Through ICSE treatment, the thermal stability decreased as the structure of materials become loose and lift up. Moreover, two plots for materials treated by ICSE+[Emim] Ac and ICSE+[Emim]Cl had the longest distances from

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untreated feedstock, indicating the best treatment performance on feedstock.

Enzymatic Hydrolysis. So far, the composition changes and structure transformation of rice straw under different pretreatment conditions have been discussed, but the actual behavior in the production of biobased chemicals and biofuels required more straightforward evidence: how much sugar can be reached after enzymatic hydrolysis on pretreated feedstock? The results are summarized in Table 1 and Figure 5.

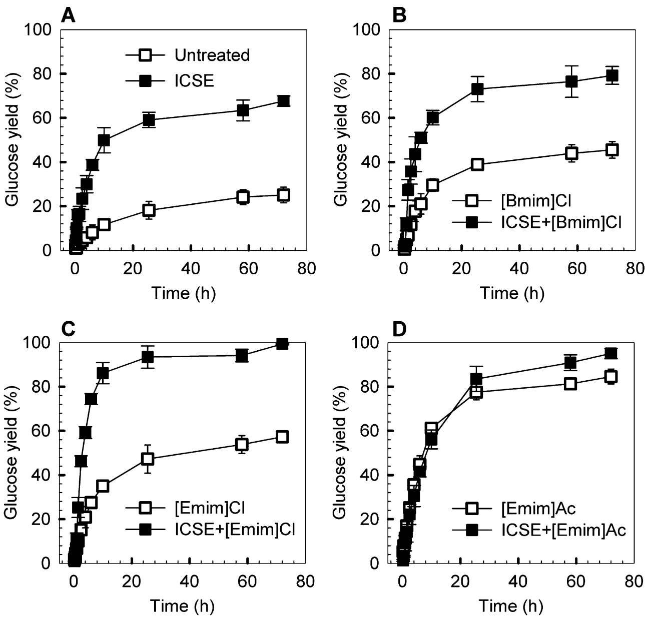

Figure 5. Enzymatic hydrolysis of rice straw under different conditions.

It was no doubt that the hydrolysis of untreated rice straw provided the lowest sugar yield due to the lowest specific surface area and the highest CrI, which prohibited the accessibility of enzyme. Among three ionic liquids, [Emim]Ac treatment, increasing the glucose yield by 237.24%, was the most powerful chemical to alter the morphology and components of rice straw thanks to its outstanding ability of delignification. ICSE, with a 169.74% increased glucose yield, is another preferable pretreatment method in this work.

The completed contact between ionic liquid and feedstock played a pivotal role in such a physical dissolution process. With the help of ICSE, ionic liquids exhibited higher efficiency for lignocellulose treatment, resulting from decrease of particle size and the increase specific surface area. Therefore, the improvement of glucose yield for feedstock treated by ICSE +ionic liquids was realized, and the results are shown in Figure 5B,C,D. The enhancement ratios for [Bmim]Cl, [Emim]Cl, and [Emim]Ac were 74.02%, 73.37%, and 12.37%, respectively. What was most notable was that ICSE+[Emim]Cl and ICSE +[Emim]Ac almost reached the theoretical top of glucose yield, an exciting outcome for the next bioconversion by microbes.

CONCLUSION

In this study, an innovative steam explosion method (ICSE) was used to enhance the performance of ionic liquids including [Bmim]Cl, [Emim]Cl, and [Emim]Ac on rice straw. After ICSE+ionic liquid pretreatment, the obvious morphological changes were observed due to increased specific surface area in feedstock by ICSE. Moreover, the removal of lignin and hemicellulose benefited more cellulose exposed at the surface of rice straw. The spectrum of FTIR and XRD revealed the change of chemical function group and cellulose crystallinity, and TGA confirmed the composition and porosity change. All detected changes were consistent with the significant difference in sugar yield during enzymatic hydrolysis, which indicated that ISCE enhanced the pretreatment performance of ionic liquid. The highest value reached was 99.34% by using a combined pretreatment with ICSE and [Emim]Cl. Although ionic liquids are still too expensive to apply for bulk and low-value-added products, ICSE offers a promising option to improve the economic feasibility of ionic liquids in lignocellulose pretreatment.

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Notes

The authors declare no competing financial interest.

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