Conversion of rice husk biomass into reducing sugars: influence of pretreatment with water and [C16MIM][Br⁻] ionic liquid

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Abstract

Rice husk is an agricultural lignocellulosic-rich waste which can be used in the production of second-generation ethanol. A biomass pretreatment is necessary to release structural sugars because of the recalcitrance-related properties of lignin and silicon. The use of a long chain imidazolium ionic liquid (IL), 1-hexadecyl-3-methylimidazolium bromide ($[C_{16}MIM][Br^-]$), for rice husk pretreatment is reported for the first time. The influence of the $[C_{16}MIM][Br^-]$:water ratio and temperature on reducing sugars yield was investigated using an experimental design. Structural, chemical, and morphological modifications were observed by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TGA). Higher temperature (160°C) and lower water content (1:5, IL:water) improved sugar yield. The validation assay (180°C, 1:20 IL:water ratio, 10% (w/v) of biomass, 12 h) resulted in 38% yield of reducing sugars and 60% dissolution of biomass, whereas untreated biomass showed only 0.18% yield of reducing sugars. The characterization analysis confirmed the changes in rice husk structure and morphology after pretreatment with IL. Rice husk pretreatment with $[C_{16}MIM][Br^-]$ resulted in a higher concentration of reducing sugars compared to untreated biomass. Therefore, solid ionic liquids combined with water could be used as an alternative solvent for lignocellulosic biomass pretreatment.

1. Introduction

Biofuels are effective alternatives to substitute for fossil fuels, mainly in the transport sector which has been growing significantly. Nowadays, the most produced biofuels are the first-generation ones (Hira and de Oliveira, 2009; Sims et al., 2010). However, the use food crops as raw materials is considered to be a great issue because the price of these feedstocks increases (Chen et al., 2017; Hira and de Oliveira, 2009; Sims et al., 2010) and as a result, human and animal necessities could be affected (Chen et al., 2017; Mungodla and Liganiso, 2019). Second-generation fuels from lignocellulosic feedstocks and agricultural wastes (Joshi et al., 2017) such as sugarcane bagasse (Nasirpour and Mousavi, 2018), wheat straw (Li et al., 2009), rice straw (Nguyen et al., 2010), rice husk (Ang et al., 2012), forest residues (Aid et al., 2016), and municipal solid waste (Chen et al., 2017) have attracted attention because these materials are renewable and non-food sources. They are considered to be environmentally friendly and present versatility, availability, and low cost (Sorn et al., 2019).

Annually, more than 140 million tons of rice husks are produced in the world (Madduluri et al., 2020), corresponding to about 20% of the weight of rice grain (Díaz et al., 2014; Lynam et al., 2012; Saha and Cotta, 2008). Moreover, 1.69 million tons of rice husks were produced in Rio Grande do Sul, southern Brazil, in 2017 (CONAB, 2018; IRGA, 2018). Rice husk is an agro-industrial waste that could be used for power generation, and it also could be converted into biofuels due to the lignocellulosic composition (Lynam et al., 2012; Yang et al., 2012). Lignocellulosic biomass is composed of cellulose (30-50%), hemicellulose (15-35%), and lignin (10-30%) (Dadi et al., 2006; Pronyk and Mazza, 2016) in addition to a significant amount of silicon (Ndazi et al., 2007). Cellulose is the most abundant biopolymer on Earth, it

is composed of glucose monomers connected by β -1,4-glycosidic bonds (Chen et al., 2017; Dadi et al., 2006; Ibrahim et al., 2015; Meenatchi et al., 2017; Nemestóthy et al., 2017), and it has interesting characteristics such as biodegradability, biocompatibility, hydrophilicity, thermal and chemical stability, and renewability (Jiang et al., 2011; Wang et al., 2015). Hemicellulose is a complex polysaccharide, composed predominantly of xylose (pentoses sugars) and other sugars (hexoses). Lignin is a phenylpropanoic complex covalently attached to hemicellulose (Cunha-Pereira et al., 2015; Lopes et al., 2013; Vasheghani et al., 2016). Due to its ordered, rigid and complex structure, the rice husk composition hinders the access of microorganisms and enzymes. This structure presents high recalcitrance which limits its conversion into sugars. In addition, rice husk has abrasive characteristics related to silicon components that can damage equipment and pipes (Ndazi et al., 2007; Nemestóthy et al., 2017; Yang and Fang, 2014; Yang and Fang, 2015; Zhu et al., 2005). Therefore, a biomass pretreatment is necessary for chemical, structural and morphological changes to remove lignin (Díaz et al., 2014; Yang and Fang, 2014; Yang and Fang, 2015) and to increase the surface area and the availability of hemicellulose and cellulose for enzymatic saccharification (Ávila et al., 2018; Yoon et al., 2011; Zhu et al., 2005).

Currently, ionic liquids (ILs) have attracted attention as potential solvents for biomass pretreatment (Lynam et al., 2012; Yang and Fang, 2015; Yoon et al., 2011). Ionic liquids are organic salts with relatively low melting points (below 100 °C) (Baek et al., 2017; Zhao et al., 2009; Zhu et al., 2006). They normally consist of an organic cation and an organic or inorganic anion (Chen et al., 2017; Liu et al., 2012; Vancov et al., 2012). ILs present relevant properties such as non-flammability, thermal and chemical stability, negligible volatility, and high solvent power. Also, they could be considered to be green and environmentally friendly solvents (Baek et al., 2017; Gogoi and Hazarika, 2017; Lopes et al., 2013; Zhu et al., 2006). The 1-hexadecyl-3-methylimidazolium bromide ($[C_{16}MIM][Br]$) ionic liquid presents a long carbon chain. It has high viscosity, and it is solid at room temperature. It has a relatively high melting point (66.91 °C) (Zhu et al., 2009), and it can be synthesized with high yield (over 90%). $[C_{16}MIM][Br]$ solubilized in water, over the critical micellar concentration, promotes the formation of an emulsion which increases both the interfacial area and mass-transfer efficiency. It is well known that an ionic liquid with a long alkyl chain reduces the surface tension more than one with a shorter alkyl chain, considering that both are at the same concentration in aqueous solution and have the same anion (Toh et al., 2006). Thus, $[C_{16}MIM][Br]$ could provide lower surface tension compared to other bromides with a C_2 or C_4 alkyl chain, which are commonly applied in the lignocellulosic materials.

Several ionic liquids have been described in cellulose dissolution. Some studies evaluated the pretreatment of palm with 1-butyl-3-methylimidazolium chloride ($[BMIM][Cl]$) (Tan et al., 2011), of soybean hull with 1-butyl-3-methylimidazolium acetate ($[BMIM][Ac]$) (Cunha-Pereira et al., 2015), of rice straw and microcrystalline cellulose with 1-ethyl-3-methylimidazolium acetate ($[EMIM][Ac]$) (Nguyen et al., 2010; Zhao et al., 2009) and of cedar and beech wood with 1-ethylpyridinium bromide ($[EtPy][Br]$) (Yokoo and Miyafuji, 2014). Rice husk pretreatment has been evaluated with different ionic liquids. Poornejad et al. (2014) and Lynam et al. (2012) described pretreatment using $[EMIM][Ac]$, and Lynam also showed complete removal of lignin. Ang et al. (2012) compared three ionic liquids: $[BMIM][Cl]$, $[EMIM][OAc]$, and 1-

ethyl-3-methylimidazolium diethyl phosphate ([EMIM][DEP]). However, there are no studies to date describing the use of [C₁₆MIM][Br⁻] ionic liquid as a solvent for rice husk pretreatment. Therefore, the aim of this work was to evaluate the influence of temperature and the concentration of water and [C₁₆MIM][Br⁻] ionic liquid on the pretreatment and conversion of rice husk into reducing sugars.

2. Material And Methods

2.1 Substrate

Rice husk was obtained from the rice industry of Santa Maria, Rio Grande do Sul, Brazil. The biomass was ground and sieved into particles smaller than 150 µm and stored at room temperature. The moisture of the rice husk was 7.9% (w/w), and the samples were preserved in a desiccator.

2.2 Ionic Liquid

[C₁₆MIM][Br⁻] ionic liquid was prepared by quaternization between hexadecyl bromide (1-bromohexadecane, Aldrich) and the corresponding imidazolium (methylimidazolium, Aldrich). The ionic liquid was obtained by mixing 0.139 mol of methylimidazolium with 0.139 mol of the alkyl bromide and adding a volume of ethyl acetate corresponding to 10% (w/v) of the total volume of reaction mixture. The reactions were conducted in a Teflon autoclave with a stainless steel jacket under static isothermal conditions, and a flowrate of nitrogen gas (20 mL/min) was injected for 3 min before closing the autoclave. The maximum quaternization yield (91%) occurred after 48 h at 50 °C. After cooling the autoclave, the reaction product was placed in a rotary evaporator for 1 h to remove the ethyl acetate. After the solvent elimination, the solid product was washed with ethyl acetate until a white crystal was obtained. The formation of the desired product was confirmed by elemental analysis (CHN) and ¹³C MAS-NMR in a spectrometer, Bruker DPX-400 (400.13 MHz), using dimethyl sulfoxide (DMSO) as solvent. The results are presented in the supplementary information in Figure S1 and Table S1.

2.3 Rice Husk Pretreatment With [C₁₆MIM][Br⁻] Ionic Liquid

Rice husk pretreatment was carried out in a Teflon autoclave with a stainless steel jacket heated in an oven. A sample of 0.1 g of rice husk was mixed with 1 g of ionic liquid dissolved in different volumes of deionized water. The reaction mixtures were placed in an oven for 12 h, for solvothermal treatment at different temperatures, according to an experimental design (Section 2.6). Then, 10 mL of deionized water was added to dilute the cellulose dissolved in the reaction, and the mixture was centrifuged at 4000 rpm in an Eppendorf centrifuge (model 5804R) during 15 min. The ionic liquid aqueous solution was separated from the undissolved biomass. Washing and centrifugation steps were carried out 4 times. Finally, the pretreated rice husk (biomass) was dried in an oven at 60 °C for 24 h (Ang et al., 2012) and characterized as described in section 2.5. Biomass dissolution was determined by weight difference before and after the pretreatment.

2.4 Enzymatic Hydrolysis

Enzymatic hydrolysis was based on the methodology described by Nguyen et al. (2010) with some modifications. The cellulase enzyme (Celluclast 1.5L ®) used was purchased from Novozymes (Denmark), and its activity was determined according to Ghose (1987). A sample of untreated/pretreated biomass (0.1 g) was mixed with 0.215 mL of Celluclast (initial activity of 8 UI – activity of endo and exocellulase) and 1 mL of deionized water. The mixture was incubated in orbital shaker at 120 rpm, 50 °C, for 72 h. Reducing sugars were quantified using the dinitrosalicylic acid (DNS) method (Miller, 1959), and the yield (%) was determined according to Equation (1):

$$\text{Reducing Sugars Yield (\%)} = \frac{\text{Weight of reducing sugars after hydrolysis}}{\text{Weight of pretreated biomass}} \times 100 \quad (1)$$

2.5 Rice Husk Characterization

Rice husk was characterized before and after the biomass pretreatment (validation condition, section 2.6). The composition of cellulose, hemicellulose, lignin, and ash was determined according to methodology of National Renewable Energy Laboratory (NREL) (Table 1).

Table 1: Chemical composition of rice husk biomass.

Composition	Untreated (wt.%)	Pretreated (wt.%)
Cellulose ^a	38.56 ± 2.34	21.05 ± 2.38
Hemicellulose ^a	13.71 ± 1.22	0.63 ± 0.55
Lignin ^a	21.08 ± 2.34	12.26 ± 0.15
Ash ^a	15.10 ± 0.12	9.44 ± 0.19
O ^b	42.81 ± 6.50	37.33 ± 7.03
C ^b	50.48 ± 7.42	45.80 ± 6.90
C ^b	18.16 ± 0.79	17.15 ± 0.83
Si ^b		

^a NREL methodology

^b EDS methodology

Morphological changes of rice husk were analyzed by a scanning electron microscope (SEM) (Sigma 300VP) with a Field Emission Gun (FEG) of Schotky (tungsten filament coated with zirconium oxide) equipped with a Gemini column. An X-Ray Energy Spectrometer (EDS) attached to an SEM was used for the determination of oxygen (O), carbon (C) and silicon (Si) content (Table 1).

Biomass crystallinity and structural changes were examined by X-Ray Diffraction (XRD) (Rigaku Miniflex ® 600 Cu K α radiation, λ = 1.5406 Å, 40 mA, 40 kV). The samples were scanned over a 2 θ range between 10 and 80° at 0.02° per step with scan speed of 0.5 s. The biomass crystallinity index (CrI) was determined according to Equation (2) (Ang et al., 2012):

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

where I_{002} is the maximum intensity for the crystalline portion of the rice husk sample at about 2 θ = 22.6°, and I_{am} is the intensity attributed to the amorphous portion of rice husk sample at 2 θ = ~18.7°.

Fourier Transform Infrared Spectroscopy (FTIR) was employed to analyze the chemical changes in biomass using a spectrometer (Shimadzu, IR Prestige 21 with the method of direct transmittance KBr pellets). The spectra were obtained with an average of 45 scans in the range between 4000 and 400 cm⁻¹ with 2 cm⁻¹ resolution.

Biomass decomposition was analyzed before and after the pretreatment (Assays 1 and 5 of the CCRD, section 2.6) by Thermogravimetric Analysis (TGA), Derivative Thermogravimetry (DTG), and Differential Thermal Analysis (DTA) using a Shimadzu Model DTG-60H instrument. Samples were heated from ambient temperature up to 1000 °C, at a rate of 10 °C/min, in an oxidizing atmosphere (synthetic air supplied at 40 mL/min). Alumina was used as the reference material in thermal analysis.

2.6 Experimental Design

A Central Composite Rotatable Design (CCRD) (Rodrigues and lemma, 2014) was performed to evaluate the influence of ionic liquid:water ratio (1:5 – 1:30 (w/v)) and temperature (80 – 160 °C) on the rice husk pretreatment (Table 2). Previous assays (data not shown) were performed to define the pretreatment time and temperature range. Since longer reaction periods showed no influence on the biomass pretreatment, the sample mixture was pretreated for 12 h. The ratio of ionic liquid dissolved in deionized water was based on the work of Fu and Mazza (2011). The biomass loading in the pretreatment was fixed at 10% (w/v). According to the CCRD results, a validation assay was performed. Three assays were carried out at a higher temperature (180 °C) and at an IL:water ratio of 1:20 (central point). Experimental data were analyzed using Statistica ® 7.0 (Stat Soft Ink., Tulsa, OK, USA) considering a significance level of 90% ($p < 0.10$).

3. Results And Discussion

3.1 Effect of Rice Husk Pretreatment Using [C₁₆MIM][Br] Ionic Liquid (IL)

Table 2 shows the reducing sugars yield according to the experimental design. The highest reducing sugars yield (28.95%) was obtained for the IL:water ratio of 1:20 at highest temperature (160°C) evaluated (Assay 8). The lowest reducing sugars yield (7.99%) was observed for the highest water

content (1:30, IL:water ratio) at 120 °C (Assay 6). The effectiveness of the biomass pretreatment could be proven because all assays released a greater amount of reducing sugars after the pretreatment compared to enzymatic hydrolysis of untreated biomass (0.18%), showing yields at least 44 times greater.

Table 2: Coded (in parenthesis) and real variables values in the central composite rotatable design (CCRD) for the rice husk pretreatment with [C₁₆MIM][Br⁻] ionic liquid.

Assay	IL:Water Ratio (w/v)	Temperature (°C)	Reducing Sugars Yield (%)	Biomass dissolution (%)
1	1:9.36 (-1)	91.63 (-1)	8.29	10.09
2	1:27.09 (+1)	91.63 (-1)	9.61	11.72
3	1:9.36 (-1)	148.37 (+1)	25.06	45.91
4	1:27.09 (+1)	148.37 (+1)	22.24	41.23
5	1:5 (-1.41)	120 (0)	15.51	33.76
6	1:30 (+1.41)	120 (0)	7.99	19.55
7	1:20 (0)	80 (-1.41)	8.37	11.85
8	1:20 (0)	160 (+1.41)	28.95	48.50
9	1:20 (0)	120 (0)	13.59	22.87
10	1:20 (0)	120 (0)	15.48	23.26
11	1:20 (0)	120 (0)	16.02	25.03
Untreated	-	-	0.18	-

The Pareto chart (Figure 1) shows the influence of variables on reducing sugars yield according to the results in Table 2. The linear (L) and quadratic (Q) effects of temperature on reducing sugars yield were positive ($p < 0.10$), and the linear effect was greater. This positive linear effect of temperature indicates that increasing the temperature increases the yield. In addition, the linear effect of the IL:water ratio was negative ($p < 0.10$), suggesting that a lower ratio should be used for a higher yield of reducing sugars.

The second-order equation (Equation 3) describes the influence of the IL:water ratio and temperature on reducing sugars yield after the pretreatment and enzymatic hydrolysis, and it was estimated from the coded matrix (Table 2).

$$RS\ Yield = 15.025 - 1.516 * C - 1.37 * C^2 + 7.325 * T + 2.103 * T^2 - 1.035 * C * T \quad (3)$$

RS Yield is the reducing sugars yield after enzymatic hydrolysis (%); C and T are the coded values for the IL:water ratio (w/v) and temperature (°C), respectively.

The prediction and significance of the empirical model were evaluated by analysis of variance (ANOVA) at a 90% confidence level (Table 3). The model was validated since the determination coefficient (R^2) was 97% and the calculated F value ($F_{\text{calc}} = 30.98$) was higher than the tabulated F value ($F_{\text{tab}} = 3.45$), indicating a satisfactory correlation between the independent variables and the response and showing that the model was predictive. Reproducibility of the assays could be demonstrated by central points (Assays 9-11).

Table 3: Analysis of variance (ANOVA).

	Sum of Squares	Degree of Freedom	Mean Square	F
Regression	499.458	5	99.892	30.982
Residual	16.121	5	3.224	
Total	515.579	10		

$$R^2 = 0.97$$

$$F_{5;5;0.1} = 3.45$$

The response surface (Figure 2) generated with the validation model (Equation 3) shows the reducing sugars yield as a function of temperature and the IL:water ratio. As observed in Figure 2, higher temperature improved the reducing sugars yield, while the IL:water ratio had no significant influence within the evaluated range. A validation assay was performed, and $38.04 \pm 2.1\%$ yield of reducing sugars was obtained. This result was higher than Assay 8, the best condition of the CCRD. Moreover, this experimental value is in agreement with the value predicted by the coded model at the validation condition (39.93%). A control assay to evaluate the contribution of IL in the rice husk pretreatment was also carried out at 180 °C, 10% (w/v) biomass loading, using only water (20 mL, central point) for 12 h. In this condition, 23.76% yield of reducing sugars was observed, and this value was lower than that obtained in the presence of IL, which indicates that the IL acted during the pretreatment step by modifying the rice husk structure and improving the reducing sugars yield.

Temperature had a greater influence on reducing sugars yield. Sriariyanun et al. (2015) also observed the positive influence of high temperature pretreatment of rice straw on reducing sugars yield. The authors obtained 68.26% yield of recovered sugars with 50% of 1-allyl-3-methylimidazolium chloride ([AMIM][Cl]) at 150 °C.

Different ionic liquids have been evaluated for rice lignocellulosic material pretreatment. Ang et al. (2012) compared three ionic liquids for rice husk pretreatment (1.5% (w/v) rice husk:ionic liquid ratio) at 100 °C during 10 h, obtaining 42.1%, 39.9%, and 28.6% yield of reducing sugars for [EMIM][Ac], [EMIM][DEP] and [BMIM][Cl], respectively. Lynam et al. (2012) found complete removal of lignin from 1 g of rice hulls using 10 g of [EMIM][Ac], at 110 °C for 8 h.

Fu and Mazza (2011) compared various pretreatment methods for triticale straw, and they found a higher fermentable sugar yield (81%) for a mixture of [EMIM][Ac] and water (50% w/w) than for pure ionic liquid (67.4%). Hou, Li, Zong (2013) achieved satisfactory glucose (> 80%) and xylose (> 44%) yields after rice straw pretreatment using 50% ILs-water mixtures. However, both studies used different IL:water ratios than those used in this work. The long carbon chain of [C₁₆MIM][Br] presents a high viscosity and solid state at room temperature. When dissolved in aqueous media, it lowers the surface tension (Toh et al., 2006). Therefore, [C₁₆MIM][Br] interacts with the biomass in a different way compared with other ionic liquids in aqueous media, which present distinct alkyl chain compositions and properties. This is attributed to the influence of water on the system (Ferrari et al., 2019).

Higher biomass dissolution ($\approx$ 45%; Table 2) could be related to the high temperature pretreatment (148.37 and 160 °C; Assays 3, 4 and 8), whereas low temperature pretreatment (80 and 91.63°C) provided approximately 11% of biomass dissolution (Assays 1, 2 and 7). Validation assays performed at 180 °C, presented $60 \pm 3.45\%$ of biomass dissolution, confirming the effect of temperature. Hou et al. (2012) also observed higher dissolution at higher temperatures, which was associated with the removal of polysaccharides from rice straw.

Higher reducing sugar yields were also associated with greater biomass dissolution (Table 2). Ionic liquids could change the lignocellulosic matrix (section 3.2) at the same time that they hydrolyze some cellulose and hemicellulose to single sugars. Lignocellulose dissolution in ionic liquids increases with increasing temperature. This can be attributed to the hydrogen bond destabilization in the lignocellulosic matrix (Gogoi and Hazarika, 2019). Comparing the chemical composition of the validation assay with that of untreated biomass (Table 1), there is a clear reduction in the composition of cellulose and hemicellulose with the pretreatment, which suggests that the ionic liquid influences the biomass dissolution. Thus, knowing that long chain ionic liquids have strong Van der Waals forces (Losada-Pérez et al., 2016) and high viscosity, it could be suggested that [C₁₆MIM][Br] ionic liquid helps the interaction with cellulose (Brandt et al., 2013) and increases biomass dissolution. Moreover, Table 2 shows that the untreated sample led to no biomass dissolution, and it had the lowest reducing sugars yield.

3.2 Structural and Morphological Analysis

3.2.1 Biomass Characterization

The results indicated that the pretreatment influenced the composition of biomass (Table 1). The cellulose, hemicellulose, and lignin content were reduced because the interaction between ionic liquid and the lignocellulosic biomass, as previously discussed. Moreover, the removal of silicon could be associated with the influence of temperature and the interaction of ionic liquid and biomass (Lynam et al., 2012; Yang and Fang, 2015).

3.2.2 Scanning Electron Microscopy (SEM)

The morphological changes are shown in Figure 3. Untreated rice husk (Figure 3a) showed a packed and inaccessible morphology and non-porous material. The lignocellulosic matrix makes the access of enzymes difficult (Ebrahimi et al., 2017; Poornejad et al., 2013). Figure 3b shows the morphological modification after the pretreatment, where the packed structure was changed to a wave-shaped, more accessible, and disordered morphology which could improve enzymatic hydrolysis. These considerable changes in the morphology of pretreated material could be related to the reduction of cellulose, hemicellulose, and silicon content (Table 1).

3.2.3 X-Ray Diffraction (XRD)

The crystalline structure of rice husk was analyzed by X-Ray Diffraction (XRD). The enhancement of enzymatic hydrolysis is usually associated with lower crystallinity index values, which means a more accessible structure for enzymes (Gogoi and Hazarika, 2017; Yoon et al., 2011). Figure 4 shows an increase in the crystallinity degree after the ionic liquid pretreatment (CrI = 59.5%). This was confirmed by comparing the intense and sharp diffraction peak profile located at $2\theta = 22^\circ$. This highest crystallinity was a result of removing amorphous biomass such as hemicellulose.

Previous studies showed a similar crystallinity pattern that was also associated with the high temperature pretreatment and hydrolytic cleavage of glycosidic bonds (Ang et al., 2012; Ang et al., 2013; Gao et al., 2018; Gogoi and Hazarika, 2019; Johar et al., 2012; Kim et al., 2016; Yang and Fang, 2015). Also, a small shoulder peak located at $\sim 21^\circ$ and a shift from peak at 21.8° to 22.5° can be seen, which ensure lattice expansion (Cheng et al., 2012) related to the changes in the structure of the cellulose matrix after the pretreatment process. Moreover, the change in the crystallinity was confirmed by the presence of two additional peaks located at 26.5° and 34.5° which represent the quarter length of one cellobiose unit (Ouyang et al., 2015).

3.2.4 Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups of untreated and pretreated rice husk were assessed by FTIR, and the spectra are presented in Figure 5. Both profiles were similar and associated with native rice husk. The FTIR spectrum showed bands located at 790, 898, 1085, 1423, 1511, 1637 and 2919 cm^{-1} (Ang et al., 2012; Yang and Fang, 2015). The C-O stretching bands at 1085 cm^{-1} correspond to cellulose/hemicellulose and lignin (Ang et al., 2012; Trinh et al., 2015). In addition, these bands are associated with the presence of the lignin-carbohydrate bonds in the biomass. After the pretreatment, the infrared-absorption intensity decreased as a result of the cellulose/hemicellulose dissolution caused during heating (Yang and Fang, 2015; Guo et al., 2008). Both untreated and pretreated biomass presented the C-O stretching bands located at 898 cm^{-1} and the C-H stretching located at 2919 cm^{-1} which appears in cellulose rich material (Yang and Fang, 2015). No significant changes were observed, suggesting cellulose retention, which is characteristic of rice husk. However, some bands were reduced after the ionic liquid pretreatment, such as the silicon bonds represented by bands located at 790 cm^{-1} , C-O stretching bands at 1085 cm^{-1} , C=O of acetoxy groups in hemicellulose located at 1734 cm^{-1} (Boukir et al., 2019; Equihua-Sánchez, Barahona-

Pérez, 2019), and the lignin aromatic skeletal stretching located at 1423 and 1511 cm^{-1} (Boonsombuti et al., 2020; Yang and Fang, 2015). These results suggested the removal of silicon, hemicellulose, and lignin. This could be related to the structure destruction, which is in agreement with the XRD discussion. In addition, a reduction of absorption band located at 1637 cm^{-1} was observed, which could be associated with the adsorbed water in the biomass (Ang et al., 2012).

3.2.5 Thermogravimetric Analysis (TGA)

TGA analysis was used to quantify hemicellulose, cellulose and lignin in the rice husk biomass. Lignocellulosic materials have a mixture of approximately 53 wt.% of hemicellulose and cellulose and 19 wt.% of lignin (Singh et al., 2013). These values are in agreement with the results found in the biomass characterization (Table 1). Thermogravimetric analysis in O_2 atmosphere was performed to evaluate the biomass decomposition. Figure 6 shows the TGA, Differential Thermal Analysis (DTA), and Derivative Thermogravimetry (DTG) profiles of untreated rice husk in oxidant atmosphere.

Figure 6 shows four weight loss stages. The first stage refers to the moisture content (9.20 wt.%) at the temperature range of 30-137 $^{\circ}\text{C}$, and an endothermic peak can be seen in the DTA curve in the same range with a maximum at 70 $^{\circ}\text{C}$. The second stage (0.80 wt.%) is relatively constant at the temperature range of 137-181 $^{\circ}\text{C}$ and refers to the chemisorbed water (Maschio et al., 1992). The third ($\approx$ 53 wt.%) and the fourth ($\approx$ 19 wt.%) stages, starting at 181 $^{\circ}\text{C}$ and ending at 578 $^{\circ}\text{C}$, involve hemicellulose, cellulose, and lignin decomposition. The maximum weight loss was in the range of 360-515 $^{\circ}\text{C}$. DTA curves showed two exothermic peaks with a maximum at 345 $^{\circ}\text{C}$ and 460 $^{\circ}\text{C}$, referring to the cellulose/hemicellulose and lignin decomposition, respectively (Singh et al., 2013). The results are in agreement with previous studies (Carrier et al., 2011; Pijarn et al., 2010; Yang et al., 2006) and are summarized in Table 4.

Table 4: TGA/DTA of rice husk before the ionic liquid pretreatment.

Stage	TGA	DTA			Decomposition
	Temperature ($^{\circ}\text{C}$)	Weight loss (wt.%)	Maximum peak temperature ($^{\circ}\text{C}$)	Peak character	
1	30 – 137	9.20	70	Endothermic	Moisture
2	137 – 181	0.80	-	-	Chemisorbed water
3	181 – 408	53.44	345	Exothermic	Cellulose, hemicellulose
4	408 – 578	18.87	460	Exothermic	Lignin

After the biomass pretreatment (Assays 1 and 5 of the CCRD, Figures 7a and 7b, respectively), four weight loss stages were observed. However, the first and second stages were almost constant. These results were expected due to the drying process (moisture content and chemisorbed water $\approx$ 3%) at the

temperature range of 30-150 °C. A low endothermic peak can be seen in DTA curve in this range with a maximum at 70 °C. The third stage ($\approx$ 53 wt.%) involves hemicellulose and cellulose decomposition, and it started at a lower temperature (150 °C) compared to the untreated rice husk (Figure 6). The DTG profile showed that both temperature and IL treatment changed and separated cellulose, hemicellulose, and lignin into fractions with different structural compositions (Figures 7a and 7b). Similar results were previously reported with different ionic liquids (Zhang et al., 2014). For both assays (1 and 5), one peak corresponding to the hemicellulose fraction was clearly observed at 250-300 °C, and another one, characteristic of cellulose, was observed in the range of 300-400 °C. This result is in agreement with the XRD analysis (section 3.2.3), considering that an intensification in the crystallinity index was observed (Moniruzzaman and Ono, 2013; Zhang et al., 2014). Moreover, a greater weight loss in hemicellulose was observed compared to the untreated biomass, suggesting an ease in the thermal breakdown of the ionic liquid pretreated biomass (Singh et al., 2015). DTA curves showed two exothermic peaks in the range of 240-390 °C, lower temperature compared to the untreated rice husk. No exothermic peak in the DTA profile was detected at the temperature range of lignin decomposition.

4. Conclusions

This study evaluated the effect of $[C_{16}MIM][Br]$ ionic liquid on rice husk pretreatment at different temperatures and IL:water ratios. Temperature showed a great influence on the pretreatment within the studied range. This was confirmed by validation assays (180 °C, IL:water ratio 1:20) with $38.04 \pm 2.1\%$ yield of reducing sugars and $60 \pm 3.45\%$ biomass dissolution. Despite the biomass loss, the pretreated rice husk showed changes in its structure and morphology that improved enzymatic hydrolysis. $[C_{16}MIM][Br]$ ionic liquid modified the rice husk structure and improved the reducing sugars yield, making it promising for the lignocellulosic biomass pretreatment.

Declarations

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Conflict of interest

The authors declare no competing financial interest, or conflict of interest or scientific interest.

Availability of data and material

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Code availability

Not applicable.

Informed Consent

The authors declare consent to participate. The authors declare consent for publication.

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Figures

Figure 1

Pareto chart for reducing sugars yield as a function of the independent variables. L: Linear effect. Q: Quadratic effect

Figure 2

Response surface for reducing sugars yield as a function of temperature and ionic liquid:water ratio

Figure 3

SEM images for (a) untreated and (b) pretreated rice husk (validation condition)

Figure 4

XRD for untreated and pretreated rice husk (validation condition)

Figure 5

FTIR spectra for untreated and pretreated rice husk (validation condition). The wave number (cm⁻¹) of FTIR: (a) 790; (b) 898; (c) 1085; (d) 1423; (e) 1511; (f) 1637; (g) 2919

Figure 6

FTIR spectra for untreated and pretreated rice husk (validation condition). The wave number (cm⁻¹) of FTIR: (a) 790; (b) 898; (c) 1085; (d) 1423; (e) 1511; (f) 1637; (g) 2919

Figure 7

TGA/DTA/DTG for rice husk after the ionic liquid pretreatment: (a) Assay 1 and (b) Assay 5 of the CCRD

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