Sustainable production of furfural and 5-hidroximetilfurfural from rice husks and soybean peel by using ionic liquid

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Abstract

In the current search for renewable energy sources, residual biomass has been highlighted as a potential source of chemical compounds that are currently obtained from petroleum. Among the derivatives obtained from this, 5-hydroxymethylfurfural and furfural are considered key parts in this process as they are key compounds in the fine chemical industry. This work aims at the use of the rice husks and soybean peel for the synthesis of 5-hydroxymethylfurfural and furfural using the ionic liquid [BMIM][Br]. The physical pre-treatment of biomasses was carried out followed by acid hydrolysis. For the synthesis of the furanic compounds, different temperatures and reaction times were used. The products obtained in each step were analyzed by infrared spectrophotometry and by high performance liquid chromatography. The best yields for rice husks was obtained with 4 hours of reaction at 120 °C (34%) and for soy peel with 3 hours of reaction at 120 °C (59%), for furfural production. For 5-hydroxymethylfurfural production the yields were 8.7% and 3.4% for rice and soy husks, respectively. It was found that glucose was the main group related to bio-products obtaining.

Keywords: furanic compounds; raw biomass; agricultural waste; green solvents.

Practical Application: This work aims at the use of rice husks and soybean peel, residual biomasses increasingly produced in Brazil, for the synthesis of 5-hydroxymethylfurfural and furfural using the ionic liquid [BMIM][Br]. The work emphasizes the use of residual biomasses, which are discarded in the majority of the time, in the use of chemical platforms of extreme importance in the world scenario. And it also highlights the use of ionic liquid, a green solvent, as a reaction solvent/catalyst for increasing the yield of the obtained products.

1 Introduction

The production of biochemicals and energy production from sustainable biomass have seen increasing interest due the positive effect on the environment, since it can decrease CO_2 emissions and atmospheric pollution (Chheda et al., 2007).

The current commercial production of 5-hydroxymethylfurfural (HMF) and furfural predominantly relies on the syrups extracted from energy crops (Rosatella et al., 2011; van Putten et al., 2013; Klãusli, 2014). Several renewable biomass resources which are alternative feedstock enables more sustainable manufacturing practice (Chen et al., 2017; Nguyen et al., 2016; Yu et al., 2017). From lignocellulosic biomass wastes, HMF can be obtained from cellulose, while furfural can be recovered from hemicelluloses (pentoses xylose and arabinose) (Rosatella et al., 2011; Zhang et al. 2017). Both products are promising and typical platform chemicals that can be produced from the direct acid-catalyzed dehydration of biomass sugars (van Putten et al., 2013; Chen et al., 2017; Wang et al., 2017; Kong et al., 2018).

Furfural (2-furaldehyde) is an important chemical solvent used in petroleum refining or as starting material for the preparation of other organic solvents such as furfural alcohol and tetrahydrofuran. The furfural derivatives also have a high demand for using in the plastic, herbicides, food, pharmaceutical and agricultural industries (Dias et al., 2006, 2007; Ribeiro et al., 2012). Furfural was included among the top 30 added-value chemicals from biomass (Werpy et al., 2004). HMF is also one of the top biomass derived biochemical that can be converted into many promising derivatives, for example, 2,5-dimethyltetrahydrofuran, ethoxymethylfurfural, 2,5-furandicarboxylic acid, furfuryl alcohol, dimethylfuran, and 2,5-diformylfuran (Mitra et al., 2015; Mukherjee et al., 2015a; Rout et al., 2015). These chemicals serve as the building blocks of diverse commodities, including pharmaceuticals, polymers, resins, solvents, fungicides, and biofuels (Rosatella et al., 2011; van Putten et al., 2013; Yu et al., 2017; Galaverna & Pastre, 2017; Kong et al., 2018).

To facilitate the conversion of hemicellulose and cellulose to HMF and furfural, respectively, ionic liquids (ILs) were used as solvent. They are useful, because they improved the conversion and selectivity, leading to improvements with respect to energy savings when they are compared to conventional solvents

(Stark, 2011). The decreased energy consumption results from the improved catalytic ability, and/or by the implementation of efficient processing technologies. Moreover, the ionic character of the ILs can play a positive role in enhancing the catalytic activity and the reaction selectivity (Olivier-Bourbigou et al., 2010), as well as in stabilizing the reactive catalytic species and/or the reaction intermediates (Zhang et al., 2011; Li & Yang, 2014).

Agricultural residues, such as rice hulls and soybean hulls, generated in large quantities in Brazil, are among the main sources used to obtain furfural and HMF, since they are rich in hemicellulose and cellulose (with approximately 20% and 36% respectively for rice husks, and 23% and 35% for soy peel) (Rambo et al., 2015).

The objective of the present work was to develop a simple method for production of furfural and HMF from lignocellulosic biomass hydrolysis. The effects of ILs use conditions (e.g., temperature and reaction time) on experimental results were also explored.

2 Materials and method

2.1 Samples

One sample of each biomass (soy peel and rice husks) was obtained as waste from a local production farm, later they were cleaned and separated manually. As a physical pre-treatment step, the soy peel and rice husks were milled by using knives mill (22 mesh) (Start FT 50 - Fortinox).

2.2 Proximate analysis

The ash content was determined according to the ASTM D3174-04 (American Society for Testing) in furnace for 600 °C at 6 hours.

2.3 Soxhlet extraction

Approximately 1g of rice husks and soy peel were extracted using *Soxhlet* ethanol apparatus. The best conditions were used according to Rambo et al. (2016), where short reaction times (5h), associated with high solvent concentrations (95%), lead to higher yields.

2.4 Cellulose, hemicellulose and lignin analysis

The acid detergent fiber (FDA) and cold neutral detergent (FDN) according Trujillo et al. (2010), and NREL methodologies (National Renewable Energy Laboratory, 2019) were using to determine lignin, cellulose and hemicellulose content.

2.5 Acid hydrolysis

The acid hydrolysis was performed according to the adapted methodology developed by Browning (1967), 2g of each sample was weighed, and for that mass 10 mL of 72% sulfuric acid was added in a glass beaker. The mixture was brought to the water bath (Fisatom, 550, Brazil) at 50 °C for 7 minutes under constant stirring by using the glass stick. 40 mL of distilled water was added to stop the reaction, and the entire contents were placed in a 250 mL Erlenmeyer flask and autoclaved (Prismatec, CS) for 15 minutes at 121 °C. After cooling, the solid fraction was separated from the liquid fraction using centrifuge at 2000 RPM for 1 hour, then the liquid fraction was withdrawn with the aid of a glass pipette and solid fraction was washed and filtered on filter paper. The liquid fraction of the hydrolyzate was used for the synthesis of bioproducts.

2.6 Synthesis of the ionic liquid [BMIM][Br]

The ionic liquid 1-*n*-butyl-3-methyl-imidazole bromide, [BMIM][Br], was synthesized by the reaction with bromobutane and 1-methyimidizole in three round neck bottom flasks fitted with a reflux condenser for 48h at 70 ºC with stirring according to the methodology of Dharaskar et al. (2016).

2.7 Synthesis of 5-HMF and furfural

The synthesis of HMF and furfural was performed according to the methodology Yi et al. (2012), where in a round bottom flask was added 5 mL of the hydrolyzate, 2g of ionic liquid in an oil bath at 100, 120 and 140 °C for reaction times of 1, 2, 3 and 4 hours kept under reflux. After completion of the reaction time, the sample was washed with ethyl acetate three times.

2.8 FT-IR spectroscopy

The infrared spectrometer (FT-IR CARY 630, Agilent Technologies) with range of 650 to 4000 cm^{-1}, with 0.4 nm of increment and 32 scans of averaging was used for analyzed all the samples (feedstock raw, hydrolyzed and after LI reaction).

2.9 HPLC analysis

To determine the HMF and furfural of the hydrolyzate and the samples after the reaction with ionic liquid was carried out by using Phenomenex Luna C18 5μ (2) (250 x 4.6 mm) and pre-column Phenomenex C18 (4 x 3.0 mm) filled with material similar to the main column. The eluent flow was 1mL /min at 30 °C, with a total run time of 15 minutes. The isocratic elution with a solution of acetonitrile/water (1:8 with 1% acetic acid) the detector used was UV (SPD-10A) with wavelength at 276 nm. The yields of these compounds were calculated using the Equations 1 and 2:

$$\text{HMF yield (mol \%)} = \frac{(\text{HMF concentration} * \text{liquid volume}) / 126}{\text{Grams of cellulose} / 162} * 100 \quad (1)$$

$$\text{FF yield (mol \%)} = \frac{(\text{FF concentration} * \text{liquid volume}) / 96}{\text{Grams of hemicellulose} / 132} * 100 \quad (2)$$

2.10 Statistical analysis

Statistical analyses were carried out using Unscrambler (v 10.5, Camo Software, Oslo, Norway). All data collected were organized in plots and figures with Origin 8.0 (Northampton, MA, USA).

3 Results and discussion

The Figure 1 shows the chemical analysis of the soy peel and rice husks.

The lignin content is the major component in both biomasses. The low ash content is important for the bio-products formation. Extractives may have an influence on bio-refining technologies and storage dynamics of biomass, interfering in the acid hydrolysis procedure and give inaccurate results for the bio-products. However, the low values found for extractives (11.9 and 11.6%) for rice husks and soy peel, respectively, in this study does not indicate the need for removal (Browning, (1967).

Intermediate conditionalities were required for products optimization (Figure 2). For rice husks the best yield was obtained with 4 hours of reaction at 120 °C and for soy peel with 3 hours of reaction at 120 °C, with respectively 34% and 59% of furfural production. High temperatures decrease the FF yield (12.7 and 3.5%) for rice husks and soy peel, respectively.

For HMF production the best yields (8.7 and 3.4%) respectively for rice and soy husks, were obtained with only 1 hour of reaction at 140 °C for both biomasses. Long reaction times (>3h) decreased the yield of HMF less than 1.0%. The low yield can be attributed to parallel reactions that occur in the acid hydrolysis or the most probable that has occurred is the levulinic acid and formic acid production (Bevilaqua et al., 2013; Mukherjee et al., 2015b).

Another reason for the higher yield of furfural, when it is compared to HMF, is that robust crystalline cellulose is far less reactive than amorphous hemicellulose; thus, furfural formation occurs much sooner than 5-HMF production in conventional catalytic systems. Therefore, the development of a single catalytic system for the production of both furfural and 5-HMF from raw biomass is still challenging (Mazzotta et al., 2014).

Others studies such as (Zhang & Zhao, 2010) obtained under the optimal conditions furfural yield 25%, which is close to the estimated value, 34% for this rice husks specie. Peleteiro et al. (2016), in a review speaking from furfural production using ionic liquids, the selective production of furfural from native lignocellulosic material using ILs obtained values ranging from 0.1-36%. Normally high values of furfural (> 15%) are associated with separate reactions to obtain HMF and furfural. A single
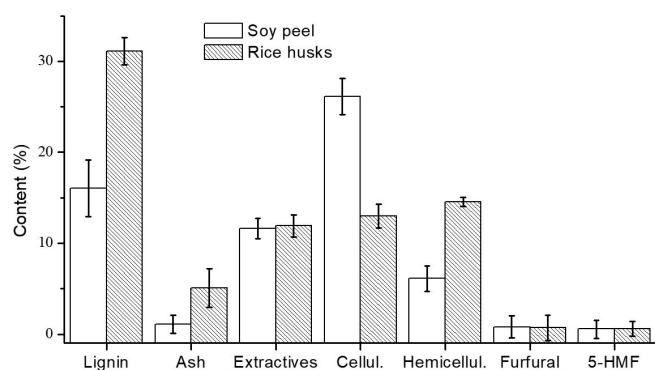
reaction to obtain the two bio-products leads to limited yields. According to Girisuta et al. (2013), 50% of the pentoses are converted to furfural.

The FTIR spectra of samples after the acid hydrolysis and after the liquid ionic treatment are shown in Figure 3. It is possible to check that changes occurred in the chemical structures of both biomasses after the ILs application. The peak at 3340 cm^{-1} is assigned to O-H bonding in cellulose, appearing only in the hydrolyzed biomass. The partial removal of cellulose is associated with the reduction of intensity of this peak in the biomass treated with liquid ionic. Bands at 1600-1500 cm^{-1} in the hydrolyzed are characteristic from aromatic skeletal vibrations in lignins. The intensity of the peak at 1600 cm^{-1} for the biomasses treated with IL disappears, thus revealing the removal of lignin after the treatment using IL. Peaks pertaining to hemicellulose and cellulose (1157 cm^{-1}, 1160 cm^{-1}, 1040-1060 cm^{-1}) show increased absorbance after the pretreatment (Figure 3B). The band at 1730 cm^{-1} after the IL reaction is assigned to C=O groups in acetyl and uronic ester groups of hemicellulose (unconjugated C=O stretch in xylans), which demonstrates that the reaction with IL made this band more prominent, favoring the release of xylose and, consequently, the formation of furfural. The bands at 1250 cm^{-1} and 1374 cm^{-1} are reported as being of stretch C-O of ether bonds from alkyl ester of the acetyl group and C-H deformation, both originating of hemicelluloses (Kumar et al., 2009; Naik et al., 2010; Banerjee et al., 2014).

It is seen that the treatment with IL favored hemicellulose, making its derivatives more prominent, which is clearly seen in a higher yield of furfural than 5-HMF (Figure 2).
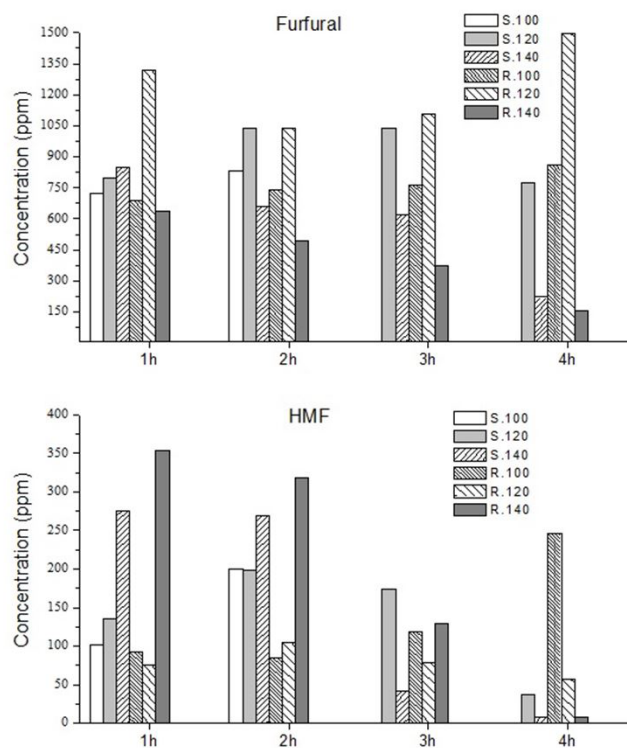

Figure 2. Effect of time and temperature in furfural and HMF concentration. (where S.: soy peel, R.: rice husks).
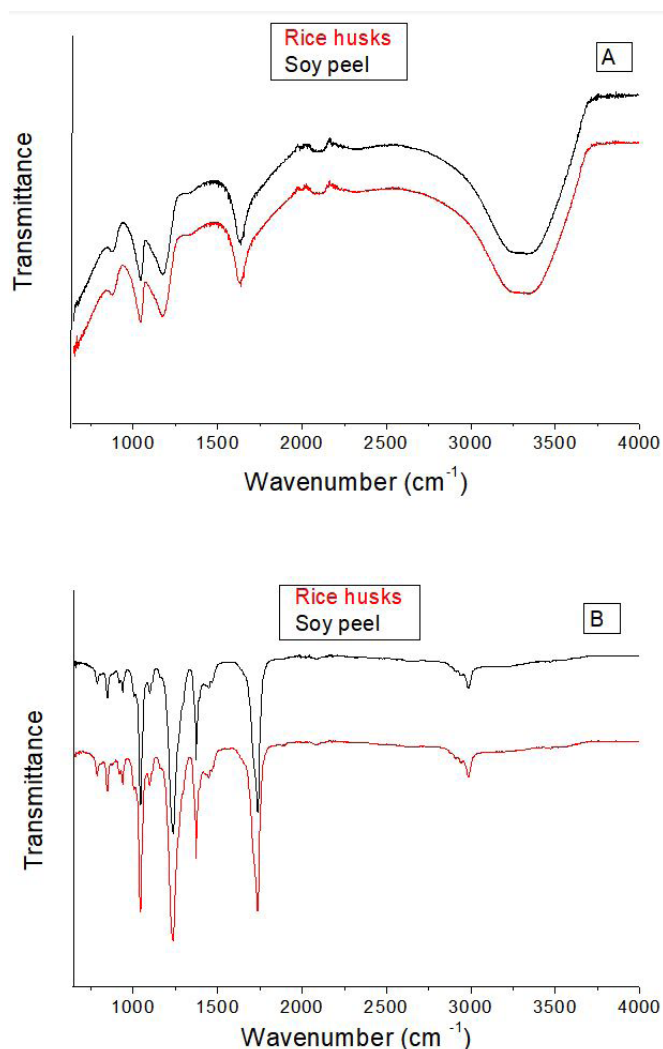

Figure 1. Descriptive statistics of the raw biomasses.

Figure 3. The FTIR spectra of (A) raw hydrolyzed and (B) hydrolyzed with liquid ionic.

4 Conclusion

Residual biomasses of soybean hulls and rice husks, coming from crops increasingly produced in Brazil, appear as promising raw materials for the synthesis of furanic compounds of high commercial value such as 5-HMF and furfural. One of the reasons for the low yields of 5-HMF and furfural is probably due to the high content of extractives present in the two biomasses during the acid hydrolysis. The use of the ionic liquid as a solvent is advantageous because it is a green, non-polluting solvent and can be reused at the end of each reaction. In addition, a large increase in HMF and furfural concentration was observed after the reaction using the ionic liquid [BMIM][Br], thus demonstrating its efficiency in the conversion of sugars into furanic compounds. Comparing the best yields between the biomasses, it was concluded that for HMF production, as well as for furfural production, the rice husk showed higher concentrations. However, there is still a need for further studies aimed at optimizing the hydrolysis process and the synthesis reaction for the production of 5-HMF and furfural in high yields.

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