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SYNTHESIS OF 5-HYDROXYMETHYLFURFURAL USING IONIC LIQUID [BMIM][BR] FROM RESIDUAL SOYBEAN AND RICE BIOMASSES

Síntese de 5-hidróximetilfurfural utilizando líquido iônico [bmim][br] a partir das biomassas residuais de soja e arroz

Síntesis de 5-hidróximetilfurfural utilizando líquido iónico [bmim][br] a partir de las biomasas residuales de soja y arroz

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ABSTRACT

In contrast to the major environmental impacts of the petrochemical activity, renewable energy sources have been developing, and among this, biomass has stood out. Among the derivatives obtained from biomass, 5-hydroxymethylfurfural (HMF) is considered a key piece in this process. This work aims at the use of rice and soybean hulls for the synthesis of HMF using the ionic liquid [BMIM][Br], aiming the sustainability of this process. Initially the physical pretreatment of biomass followed by acid hydrolysis was carried out. For the synthesis of HMF, 5ml of the hydrolyzate, 2g of ionic liquid at 120ºC, were used in different reaction times. The results were analyzed by infrared spectrophotometry and by high performance liquid chromatography. The best results in both biomasses were after 2h of reaction reaching a concentration of up to 25 times greater when compared to the hydrolyzate, showing the high potential of ionic liquid [BMIM] [Br] in the synthesis of furanic compounds.

Keywords: Furanic compounds, raw biomass, ionic liquids.

RESUMO

Em contraposição aos grandes impactos ambientais da atividade petroquímica, as fontes de energia renovável vêm se desenvolvendo, e dentre estas a biomassa tem se destacado. Dentre os derivados obtidos a partir de biomassa o 5-hidroximetilfurfural (HMF) é considerado uma peça chave neste processo. Este trabalho visa a utilização da casca de arroz e soja para a síntese de HMF utilizando o líquido iônico [BMIM][Br], visando a sustentabilidade deste processo. Inicialmente foi realizado o pré-tratamento físico da biomassa seguido da hidrolise ácida. Para a síntese de HMF foram utilizados 5ml do hidrolisado, 2g de liquido iônico a 120ºC, em diferentes tempos reacionais. Os resultados foram analisados por espectrofotometria no infravermelho e por cromatografia líquida de alta eficiência. Os melhores resultados em ambas as biomassas foi após 2h de reação chegando a uma concentração de até 25 vezes maior quando comparado ao hidrolisado, mostrando o alto potencial do liquido iônico [BMIM][Br] na síntese de compostos furânicos.

***Palavras-chave:** compostos furânicos, biomassa residual, líquidos iônicos.*

RESUMEN

En contraposición a los grandes impactos ambientales de la actividad petroquímica, las fuentes de energía renovable se vienen desarrollando, y entre éstas la biomasa se ha destacado. Entre los derivados obtenidos a partir de la biomasa el 5-hidroximetilfurfural (HMF) se considera una pieza clave en este proceso. Este trabajo busca la utilización de la cáscara de arroz y la soja para la síntesis de HMF utilizando el líquido iónico [BMIM] [Br], visando la sostenibilidad de este proceso. Inicialmente se realizó el pretratamiento físico de la biomasa seguido de la hidrolisis ácida. Para la síntesis de HMF se utilizaron 5 ml del hidrolizado, 2 g de líquido iónico a 120ºC, en diferentes tiempos reactivos. Los resultados fueron analizados por espectrofotometría en el infrarrojo y por cromatografía líquida de alta eficiencia. Los mejores resultados en ambas biomasas fueron después de 2h de reacción llegando a una concentración de hasta 25 veces mayor cuando se compara al hidrolizado, mostrando el alto potencial del líquidos iónicos [BMIM] [Br] en la síntesis de compuestos furánicos.

***Descriptores**: compuestos furánicos, biomasa residual, líquidos iónicos.*

INTRODUCTION

Contemporary society depends on a wide variety of raw materials that can be used to produce a variety of products. Nowadays oil has been overwhelmed as the source of most of these products, generating a concern for alternatives to postpone its scarcity. In this context biomass is a low-cost, renewable resource that is available on a global scale, using it as raw material for many industrial areas could decentralize the global economy which is monopolized in oil, increase its sustainability and reduce the overall environmental impact (VAZ JUNIOR, 2017).

Biomass has some factors that favor its use in biorefinery processes, they are: low operating cost; ease of storage and transportation; reuse of waste; high energy efficiency; it is a renewable and clean source of energy and emits less polluting gases (Nguyen et al., 2016, Yu et al., 2017).

Brazil is among the largest grain producers in the world and, consequently, in agricultural waste, according to Embrapa soy production in the 2015/2016 crop was 95.6 million tons and rice 11.8 million tons (CASSALES, 2010).

In this context the furan compounds obtained from biomass have been highlighted as a chemical platform in conversion processes. According to Azevedo (2015), 5-hydroxymethylfurfural (HMF) has been considered a key factor in the construction of this promising biomass-based economy. Furfural has currently an annual production of around 200,000 tons, being characterized as the industrial chemical of the most important furanic series in the market (ALVARÃES, et al., 2015)

A wide range of efficient catalysts have been reported to promote fructose dehydration in HMF, but such a transformation can also occur in the absence of catalysts, using specific solvents such as ionic liquids (LIs). LIs are salts with a melting point below 100 ° C, which in the last decades have been widely used as reaction media or catalysts for the dehydration of carbohydrates in HMF (LI; YANG, 2014).

From the HMF, it is possible to synthesize several chemical compounds with high added value, it is worth mentioning some such as: 2,5-furanedicarboxylic acid, used in the production of polymers, and their esters have been identified as possible fuels; the natural δ-aminolevulinic acid herbicide is the active ingredient of the pharmaceutical Ranitidine, the 2,5-diformylfuran (DFF), 2,5-dihydroxymethylfuran and 5-hydroxy-4-keto-2-pentenoic compounds are used to produce various polymers and plastics, as well as a promising compound for the production of bio-PET (DONATE, 2014).

The main current problem of HMF production is the low yields and the generation of by-products, opening a great opportunity for studies that aim to potentiate the results with the best methods. At this point we can highlight the use of ILs as an alternative to potentiate production with low pollution conversion factor (Stark, 2011; YI et al., 2010). With growing concern with economic development and environmental protection, syntheses from renewable materials and Ionic Liquids can offer a competitive alternative, with new possibilities for producing valuable chemical inputs.

Therefore, the present work aims at the use of new routes in the production of HMF from biomass, using ionic liquids, comparing yields of different biomasses, aiming to increase yield and reduce the emission of pollutants, seeking the sustainability of this process.

MATERIALS AND METHODS

Determination of Chemical Composition of Biomasses

The analyzes of the chemical composition of the biomass were performed through physical and chemical pre-treatments, followed by quantitative and qualitative evaluations using equations, calibration curves, High Performance Liquid Chromatography (HPLC) and Infrared Radiation (IV).

The physical pre-treatment used was grinding in a knife mill. The chemical pretreatment chosen was adapted from the methodology of Dunning and Dallas (1949).

The biomass was oven dried at 60° C for 24 hours, and then milled in a knife mill. 2 g of the same and 10 ml of 72% sulfuric acid were added in a glass beaker, and the mixture was brought to the water bath at 50° C for 7 minutes under constant stirring with the aid of the glass stick. 40 mL of distilled water was added to stop the reaction, and the entire contents were placed in Erlenmeyer 250 mL and autoclaved for 15 minutes at 121° C. After cooling the material, the solid fraction was separated from the liquid fraction using the centrifuge at 2000 rpm for one hour, then the liquid fraction was withdrawn with a pipette, and the solid fraction was washed and filtered on previously weighed filter paper. The liquid fraction of the hydrolyzate was used to evaluate carbohydrates, mainly the 5-hydroxymethylfurfural and furfural content, and for reaction with ionic liquid. The solid fraction was used to analyze the content of insoluble lignin and ash.

For the determination of the insoluble lignin content the residue present in the filter paper was washed with distilled water aiming the removal of the acidity. The paper was then oven dried at 60° C and weighed hourly until constant mass was reached.

The following equation was used based on the work of Rocha (2000) to calculate the percentage of lignin:

$$lignin = \frac{M_K - M_C}{M_A} \times 100$$

M_K = Mass of insoluble lignin.

M_C = Mass of ashes.

M_A = Dry mass of sample.

Determination of Ash Content

To determine the ash content, the lignin retained in the filter paper was carefully placed in a crucible previously calcined and weighed in analytical balance. Then the crucible with the lignin was brought to the muffle at 600° C for four hours. After cooling the ash sample was weighed and the following equation was used for the calculations according to Rocha (2000):

$$ashes = \frac{M_C}{M_A} \times 100$$

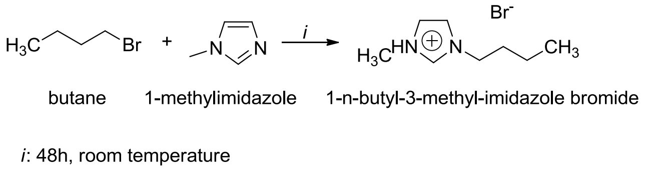
M_C = Mass of ashes.

M_A = Dry mass of sample.

Synthesis of Ionic Liquid

The synthesis of 1-*n*-butyl-3-methyl-imidazole bromide ([BMIM][Br]) (Figure 1) was performed according to the methodology of Souza (2014), with the mixture of *n*-butane and 1-methylimidazole added in the molar ratio of 1.1: 1 in a flat bottom flask under stirring for 48h at room temperature.

Figure 1: Synthesis of [BIMIM][Br] (adapted from SOUZA, 2014).



Synthesis of HMF

The synthesis of HMF followed the methodology of YI et al. (2011). 5ml of hydrolyzed sample, 2g of LI [BMIM][Br] were used in an oil bath at 120ºC under constant stirring, varying the reaction time. After the reaction the product was washed three times with ethyl acetate.

Analysis of HPLC

An analysis of HPLC was performed to determine carbohydrate, HMF and Furfural from soybean and hydrolyzed rice samples, and also from the samples after reacting with LI.

In the determination of the sugar contents, a Shimadzu chromatograph was used, using Phenomenex Rezex ROA-Organic acid H^+ column (81%), using H_2SO_4 acid (5mM) as eluent, with a flow of 0.6 mL min^{-1} and detector refractive index model SPD-10A VP brand Shimadzu. The volume of the sample injected was 20μL. The samples were previously diluted and filtered on C18 Sep-Pack filter (Millipore). The concentrations of these compounds were calculated from calibration curves obtained from standard solutions.

The determination of HMF and furfural was performed using Phenomenex Luna C18 5μ (2) (250 x 4.6 mm) column 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. Isocratic elution with acetonitrile / water solution (1: 8 with 1% acetic acid) and the detector used was UV (SPD-10A) with wavelength at 276 nm. The concentrations of these compounds were calculated from calibration curves obtained from standard solutions.

Analysis of IV

In order to verify the presence of HMF, furfural and carbohydrates present in the hydrolysates of the soybean and rice hulls, the samples were taken to the Laboratory of Research in Environmental Chemistry and Fuel (LAPEQ), to be submitted to analysis using FT Infrared spectrophotometer-IR CARY 630, Agilent Technologies brand with a scan range of 600 to 3500 cm^{-1}.

RESULTS AND DISCUSSION

Chemical composition of biomasses

All analyzes were performed in triplicate. Table 1 shows the chemical composition of the soybean and rice hulls, respectively, after acid hydrolysis. This composition may vary depending on the processing and growing conditions of this crop.

Table 1: Chemical composition of biomass.

Components	Concentration (%)	
	Soybean	Rice
Insoluble Lignin	6,03	31,12
Ashes	1,10	5,07
Glucose	2,77	1,78
Fructose	7,06	4,19
HMF	0,05	0,01
Furfural	0,25	0,04

Analysis of HPLC

Chromatograms obtained from HPLC analysis were used to calculate the amounts of glucose, fructose, HMF and furfural in the samples before and after the IL reaction. Figures 2 and 3 present the chromatograms of the rice and soybean samples before the reaction (hydrolyzate) and after the reaction with the IL.

Figure 2: Chromatograms of the rice husk before (hydrolyzed) and after the reaction with IL.

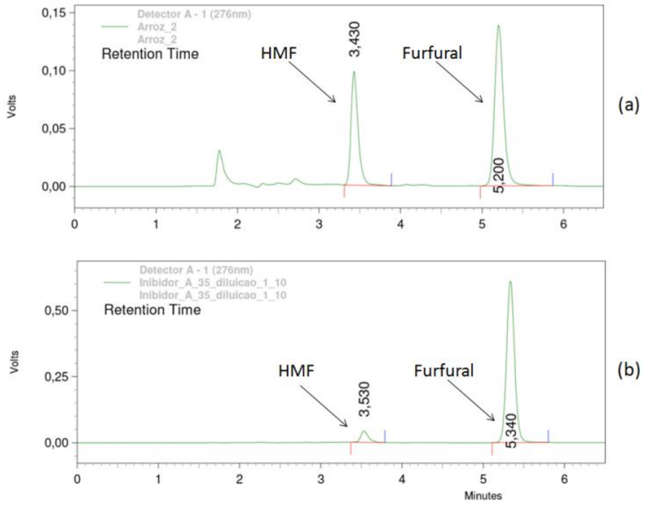
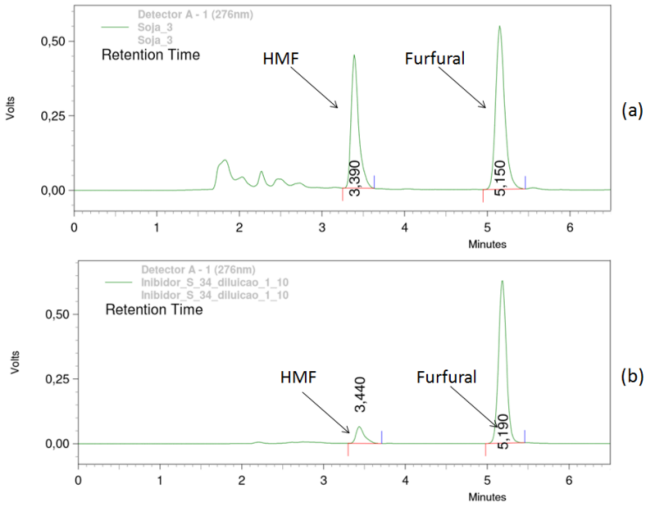


Figure 3: Chromatograms of the soybean peel before (hydrolyzed) and after the reaction with LI.



Analysis of Infrared radiation

Infrared analysis of the soybean and rice hydrolysed samples and the samples after reaction with the IL were performed. In Figures 4 and 5, part (a) shows the spectra of the hydrolyzed samples and part (b) the samples after reaction with IL.

Figure 4: Spectrum IV of the rice husk before and after the reaction with IL.

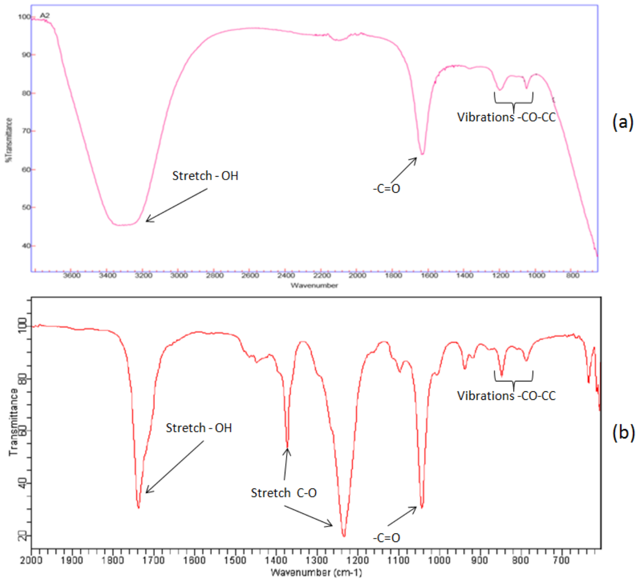
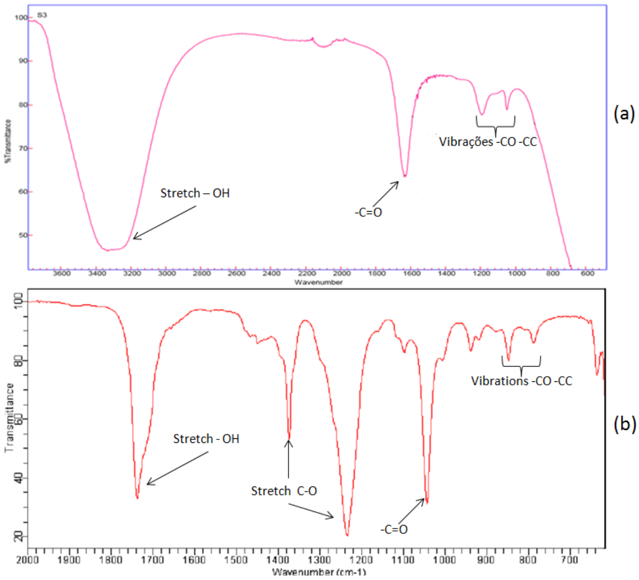


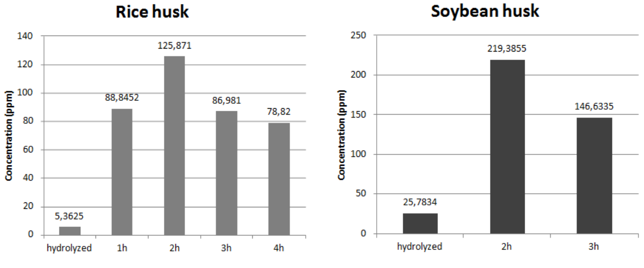
Figure 5: Spectrum IV of the soybean peel before and after the reaction with LI.



Synthesis of HMF

The HMF synthesis was carried out using 5 ml of hydrolyzed sample (soybean hull and rice hull), 2 g of IL [BMIM][Br] in an oil bath at 120ºC under constant stirring at four different reaction times (1,2 , 3 and 4 hours). As we can observe the best results were obtained after 2 hours of reaction, where the HMF concentration increased about 25 times when compared to the hydrolyzate. In reaction times of 3 and 4 hours, we observed an increase in the HMF concentration when compared to the hydrolyzate, but there was a decrease when compared to the reaction time of 2 hours (Figure 2 (a)).

Figure 6: Graphs of HMF concentration at different reaction times for the rice (a) and soybean (b) peels.

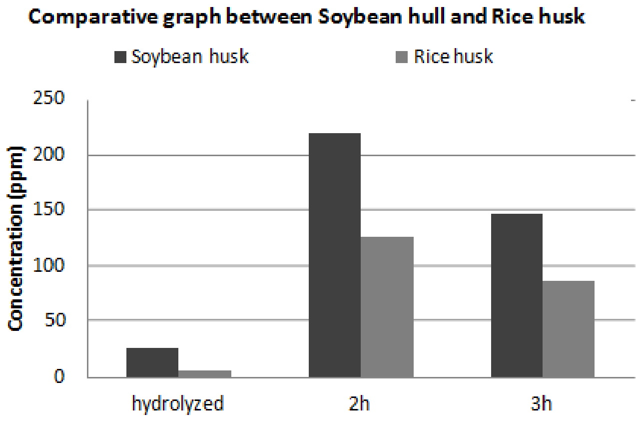


(a) (b)

For soybean, the time taken for the synthesis was 2 and 3 hours of reaction and once again the best yield was obtained with 2 hours of reaction, reaching a quantity 8 times higher than that of the hydrolyzate (Figure 2 (b)).

In analyzing Figure 2, it can be seen that since the hydrolyzate the soybean peel sample has a higher concentration of HMF in its composition, and this remained at all reaction times, however statistically the rice hulls obtained a greater increase in their concentration, while the soybean peel at its best yield increased 8-fold, the rice reached about 25-fold but HMF after the reaction.

Figure 7: Comparative graph between HMF yields in different biomasses.

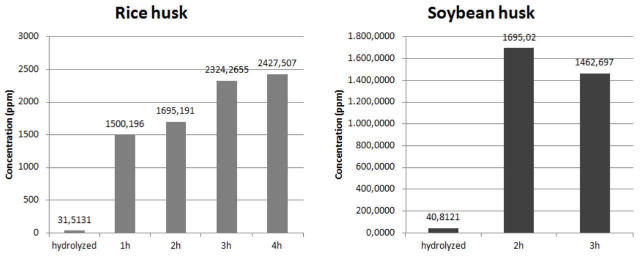


Synthesis of Furfural

In the synthesis of Furfural it is possible to observe a different behavior in the yield in relation to the time in each biomass. For the rice husk (Figure 3 (a)) the yields only increased over time having their best result with the reaction time of 4h, having an increase in Furfural concentration of more than 70 times.

For the soybean hulls (Figure 3 (b)), the behavior of the increased concentration of furfural was similar to that of HMF, as it presented a better yield in 2h of reaction, with a reduction in the concentration in the following hours. At 2h, which was the best result, he heard an increase in Furfural concentration by 40 times compared to the hydrolyzate.

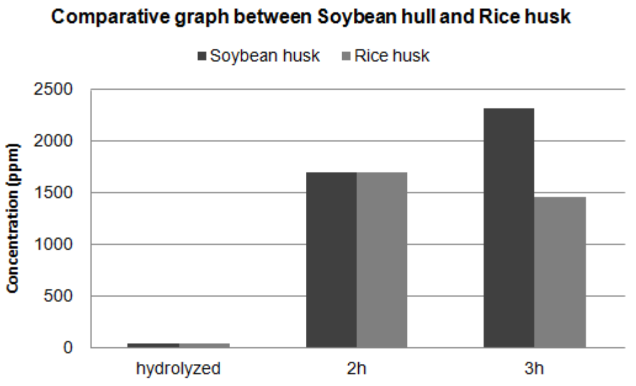
Figure 8: Graphs of Furfural concentration in different reaction times.



(a) (b)

When comparing the increase of the Furfural concentration between the two biomasses in the different reaction times (Figure 4), it was possible to observe that before the reaction the soybean hull presented a concentration a little larger than the rice hull, but after 2h of reaction concentrations were practically the same. It is also possible to verify that after 3h of reaction the rice husk sample continued to increase its concentration, and in the soybean hull sample there was a decrease, presenting a lower yield when compared to the reaction time of 2h.

Figure 9: Comparative graph between the yields of furfural in different biomasses.



CONCLUSION

It can be concluded that the results obtained for ash, lignin, glucose and fructose content are within the estimated value for the corresponding biomasses according to the literature.

The analysis of the infrared spectra allowed us to observe the compounds present in the sample, because from the peaks presented we can see that the desired sugars (Glucose and Fructose) were available and even before the reaction it was possible to observe the presence of HMF and Furfural.

From the HPLC analyzes of the hydrolyzed samples a large amount of glucose and fructose was observed and only traces of HMF and Furfural. The high glucose content and mainly fructose is a positive result as these are the precursors for HMF synthesis. After the reaction with [BIMIM] [Br], a great increase in the concentration of HMF and furfural was observed, thus proving the efficiency of the Ionic Liquor [BIMIM][Br] in the conversion of sugars to furanic compounds.

Regarding the reaction times, it was observed that the time of 2 hours led to the higher yield of HMF.

Finally, we can conclude that the soybean hulls have a higher efficiency for HMF production than the rice husk, presenting a yield of approximately 60% higher when comparing the best yields of the two biomasses. In contrast to the production of furfural, the rice husk obtained better yields, when comparing the best yields between the biomass the rice husk obtained a yield 30% higher than that of the soybean hulls.

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