

Production of Furanic Compounds and Organic Acids from Brazilian Pequi (*Caryocar brasiliensis* Camb.) Residues Using Green Chemistry

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In the current search for renewable energy sources, residual biomass has gained ground in the concept of biorefinery. Furanic compounds such as 5-hydroxymethylfurfural (HMF), furfural (FF) and derivatives such as levulinic acid (LA), obtained from biomass, have emerged as important industrial chemical platforms. In this sense, this work aimed to use pequi bark, typical biomass and abundant in the Brazilian cerrado, in the production of HMF, FF and LA using the ionic liquid 1-*n*-butyl-3-methyl-imidazole bromide ([BMIM][Br]). The analysis of chemical composition of pequi bark showed that it has potential for use in the production of bioproducts, FF, HMF and LA, with yields of 65, 3 and 23.7%, respectively. High glucose conversion rates were found (> 90%). The analysis of variance (ANOVA) was applied to obtain the mathematical model with $\alpha = 0.05$, verifying the significance of the second order model established for HMF ($F = 0.00167$) and FF (0.004494). The model fit is satisfactory, obtaining the coefficient of determination (R^2) for the HMF and for the FF of 0.9599 and 0.08422, respectively. From the results obtained, it can be concluded that pequi bark has good precursor capacity for use in biorefinery processes.

Keywords: pequi, furanic compounds, residual biomass, Brazilian cerrado

Introduction

The chemical industry's current reliance on nonrenewable raw materials such as petroleum is a challenge for the sustainable economy in the present century. The impacts caused and the possibility of scarcity aroused the search for economically and environmentally viable energy sources. The use of residual biomass in the biorefinery is favored due to the low cost of operation, reuse of waste, high energy efficiency, renewable source, clean and requires no expansion of new arable land.¹

In the present scenario, furanic series compounds such as 5-hydroxymethylfurfural (HMF) and furfural (FF) as well as organic acids such as levulinic acid (LA) have gained prominence in biomass conversion processes, allowing a most sustainable chemical route in their production processes.^{2,3}

HMF is a valuable biomass-derived compound and the interest is due to its polyfunctional characteristic and consequent ability to form various chemical intermediates and products useful in industrial applications.³⁻⁶ HMF can be obtained from dehydration of fructose and also from fructose glucose isomerization as well as directly from cellulose.⁷ However, there are several concurrent reactions that may reduce the selectivity in HMF⁸ production which may be affected by the type of raw material, solvent and the catalyst.⁹

FF, on the other hand, is an input produced in biorefineries, which can be transformed into useful fuels and chemicals used in oil refining, plastics production, the pharmaceutical and agrochemical industry.¹⁰ Similarly, LA has been the subject of studies^{11,12} due to its diverse industrial applications such as solvents, resins, plasticizers, polymers, herbicides, biofuels, among others. LA has been identified as one of the twelve major chemical platforms by the US Department of Energy¹³ and can be obtained from cellulose-rich biomass resources.¹⁴

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In regard to the solvents used to obtain these inputs, aqueous systems stand out because they are economically and environmentally viable, but lead to the formation of large amount of humines and polymerization products, which compromises yield and selectivity.¹⁵ Organic solvents, on the other hand, minimize the formation of humins, but they have a high environmental impact, fossil origin and high cost.¹⁶ In this context, ionic liquids (ILs) have been widely used as a solvent and/or catalysts in a sustainable way for carbohydrate dehydration in furanic compounds¹⁷ and organic acids,¹⁸ as they increase conversion rates and selectivity, leading to energy savings compared to conventional solvents.^{17,19-21} Even though IL production is expensive, the fact that they can be reused decreases the effective cost of processing.^{22,23}

In this context, the fruit of the pequi tree (*Caryocar brasiliensis* Camb.), popularly known as pequi, is an endemic and multiuse fruit of the Brazilian Cerrado biome, available over 2 million km² across the country,²⁴ has many uses, being applied in various areas of the industry. Its fruit is abundant and has great potential for oil extraction to produce fuels and lubricants,^{25,26} while the peel, which represents about 84% of the weight of the ripe fruit, even though it has several chemical and medicinal substances, is thrown away.^{27,28} As a result, the residual biomass generated by pequi bark is very large, with no profitable return and there is no final destination for it.

Given the great need for the development of a diversified and sustainable national energy matrix, motivated not only by scarcity, but also by the major impacts generated by the petrochemical industry, the present work seeks the use of pequi bark for the production of furan compounds HMF and FF, and organic acids using IL. The big challenge is to achieve high selectivity, good yields and low production costs.

Experimental

Samples

The bark of pequi (*Caryocar brasiliense*) used in this work was collected in the early months of 2018, in an indigenous village of the Xerente tribe located in the municipality of Tocantínia, Tocantins State, Brazil. Pequi barks were taken to the Laboratório de Química of Universidade Federal do Tocantins, where they were manually separated, oven dried at 60 °C for 24 h, ground in a Willye knife mill (star FT 50 model, Fortenox), and stored in tightly sealed glass bottles.

Extractives

This procedure was performed in a Soxhlet extractor with reaction times (8 h) associated with high ethanol concentrations (95%) according to Rambo *et al.*²⁹ The extraction cartridges received about 3 g of each sample of biomass. After that, they were covered with cotton wool and, then, taken to the extractor with 200 mL of ethanol. After the end of the reflux, the cartridges were placed on Petri dishes on the counter for 48 h to be dried. After 48 h, the moisture content of the extracted sample was determined again, so that the extractives content were calculated according to the weight loss after the extraction, deducting the moisture.

Acid hydrolysis

The acid hydrolysis was performed according to methodology developed by the National Renewable Energy Laboratory (NREL),³⁰ where the extracted sample (300 mg) was subjected to a two-stage acid hydrolysis process. In the first step, the sample in 72% sulfuric acid (3 mL) was transferred to a water bath (Fisatom, 550) maintained at 50 °C for 1 h and stirred every 10 min. In the second stage, 84 mL of water was added to the sample, and the sample was transferred to an autoclave (autoclave vertical, Phoenix) for 1 h at 120 °C. The pressure tubes were filtered through medium porosity crucibles (10 to 15 µm) using a vacuum compressor pump (LT 65, Limatec, coupled). The liquid fraction of the hydrolyzate was used for the production of bioproducts.

Lignin content

The acid insoluble lignin (AIL) and acid soluble lignin (ASL) content in the pre-treated biomass were quantified according to the NREL³⁰ laboratory analytical procedure. The insoluble acid residue (IAR) retained in the filter crucibles contained insoluble lignin, from which it was washed with distilled water until complete removal of the acid, and then heated to 105 ± 5 °C. The ASL content was measured by a UV-Vis spectrophotometer (HACH/Germany, DR5000) with the wavelength of 294 nm and the 4% H₂SO₄ solution was used as the blank. The total lignin (TL) is the sum of AIL + ASL.

Moisture

According to the ASTM D3173-87³¹ method, the moisture was determined after the sample (1 g) was heated to 105 ± 5 °C in an oven (SolidSteel SSD 110L) for 12 h.

Ash content

The ash content (AC) was determined according to the ASTM D3174-04³² and consists of analyzing the residue after combustion in muffle furnace at 600 °C for 4 h.

Cellulose, hemicellulose and lignin analysis

The acid detergent fiber (ADF) and cold neutral detergent (FDN), according to Trujillo *et al.*,³³ were used to determine hemicellulose content, while the lignin was determined by NREL methodologies³⁰ and cellulose by difference.

Synthesis of the ionic liquid 1-*n*-butyl-3-methyl-imidazole bromide

The ionic liquid 1-*n*-butyl-3-methyl-imidazole bromide ([BMIM][Br]) was synthesized by the reaction with bromobutane and 1-methylimidazole in three round neck bottom flasks fitted with a reflux condenser for 48 h at 70 °C with stirring according to the methodology of Dharaskar *et al.*³⁴

Experimental planning

The experimental planning and analysis was performed using the Protimiza Experimental Design program.³⁵ Based on previous experiments and the literature,^{1,9,36} the influence of temperature and reaction time was evaluated using a design composite central rotational (DCCR) with factorial design,²² including 4 assays in axial conditions and 3 center point repetitions, totaling 11 trials (Table 1). After the screening, a central composite design was developed to

determine the response surface and the optimal point for the FF and HMF selectivity.

Production of HMF and FF

The production of HMF and FF was performed according to DCCR and adaptations to the methodology contained in the literature,¹ where in a round bottom flask was added 2.5 mL of the hydrolyzate, 1 g of IL [BMIM][Br] in an oil bath at different reaction times and different temperatures (Table 1), kept under reflux. After completion of the reaction time, the sample was washed with ethyl acetate three times.

Production of LA

The production of LA was performed according to Bevilaqua *et al.*³⁷ for the best condition. Two grams (2 g) of pequi bark were added to 20 mL of 4.5% HCl in an oil bath during 70 min at 160 °C under reflux. After completion of the reaction time, the sample was filtered under vacuum, washed to neutral pH and stored for future analysis. In addition to the experimental procedure described above, the conversion of LA was tested using 750 mg of IL [BMIM][Br], followed by the addition of 25 mg of raw biomass and 75 mg of H₂O.

Fourier transform infrared spectroscopy (FTIR) analysis

The infrared spectrometer (FT-IR CARY 630, Agilent Technologies) with range of 650 to 4000 cm⁻¹, using ATR diamond crystal (attenuated total reflectance), with 0.4 nm of increment and 32 scans of averaging was used to analyze all the samples ([BMIM][Br], hydrolyzed and the product after IL reaction).

Table 1. DCCR 2² planning matrix with 3 repeats at central point for HMF and FF production

Assay	time / h	Temperature / °C	HMF / ppm		Yield / %	FF / ppm		Yield / %
			Experimental	Predict		Experimental	Predict	
1	1	100	51.11	67.64	0.91	1067.41	836.87	68.58
2	3	100	99.80	120.50	1.78	1108.74	1149.85	71.24
3	1	140	74.53	152.98	1.33	683.03	879.71	43.89
4	3	140	7.85	90.48	0.14	339.59	807.99	21.82
5	0.5	120	140.57	99.28	2.51	722.67	798.07	46.43
6	3.5	120	138.90	92.05	2.48	1265.86	979.01	81.33
7	2	80	51.09	57.26	0.91	704.28	858.43	45.25
8	2	160	168.33	112.58	3.01	832.49	559.41	53.49
9	2	120	164.06	144.50	2.93	1255.46	1133.90	80.67
10	2	120	160.41	144.50	2.86	1080.61	1255.45	69.43
11	2	120	169.61	144.50	3.03	1211.00	1133.90	77.81

HMF: 5-hydroxymethylfurfural; FF: furfural.

High performance liquid chromatography (HPLC) analysis

To determine the carbohydrates, LA, HMF and FF of the hydrolyzate and after the reaction with ionic liquid, the samples were analyzed by HPLC using Shimadzu® chromatograph (LC-10 Avp series, Kyoto, Japan). Standards for LA, furfural and 5-HMF were purchased from Sigma-Aldrich (St. Louis, MO, USA). All samples were previously diluted and filtered in 0.22 µm polyvinylidene difluoride (PVDF) syringe.

Phenomenex Rezex ROA-organic acid H⁺ column (8%) was used to determine sugar content, using H₂SO₄ acid (5 mmol L⁻¹) as eluent, with a flow rate of 0.6 mL min⁻¹ and refractive index detector model RID-10A (Shimadzu). The injected sample volume was 20 µL.

The determination of LA present in the hydrolyzate was determined by liquid chromatography equipment (HPLC, Dionex Ultimate 3000), DAD 3000 diode array spectrophotometric detector, WPS-3000TSL injector module, Aminex HPX-87H column and refractive index detector RI-101 (Shodex). The mobile phase used was H₂SO₄ acid (5 mmol L⁻¹) with a flow rate of 0.6 mL min⁻¹, the sample injection volume was 20 µL and the column temperature maintained at 50 °C. The samples were previously diluted and filtered through a 0.22 µm porosity PVDF syringe filter. The concentrations of these compounds were calculated from the calibration curve obtained from the standard LA solution (Sigma-Aldrich, St. Louis, MO, USA, ≥ 98% purity).

LA yields were calculated according to Tiong *et al.*,³⁸ from equations 1-2:

$$\text{Theoretical yield of LA (\% by weight)} = \frac{\text{cellulose content} \times 0.71}{\text{biomass content}} \quad (1)$$

$$\text{LA yield (\%)} = \frac{(\text{AL concentration (ppm)} \times \text{liquid volume (2 mL)}) / 116}{\text{mg of glucose} / 162} \times 100 \quad (2)$$

HMF and furfural determination was performed using Phenomenex Luna column 5 µm C18(2) (250 × 4.6 mm) and pre-column Phenomenex C18 (4 × 3.0 mm) filled with material similar to the main column. The eluent flow was 1 mL min⁻¹ at 30 °C, with a total run time of 10 min. Isocratic elution was performed using an acetonitrile/water solution (1:8 with 1% acetic acid). The detector used was UV (SPD-10Avp) with a wavelength of 276 nm.

The yields of these compounds were calculated using the equations 3 and 4 proposed by Cai *et al.*:³⁹

$$\text{HMF yield (\%)} = \frac{(\text{HMF concentration (ppm)} \times \text{liquid volume (2.5 mL)}) / 126}{\text{mg of cellulose} / 162} \times 100 \quad (3)$$

$$\text{FF yield (\%)} = \frac{(\text{FF concentration (ppm)} \times \text{liquid volume (2.5 mL)}) / 96}{\text{mg of hemicellulose} / 132} \times 100 \quad (4)$$

Results and Discussion

Determination of chemical composition of biomass

The pequi bark analyzed was collected in a typical cerrado region during the rainy season. As pequi is found in many regions of Brazil, the chemical composition of pequi peel (*Caryocar brasiliense*) may vary according to soil composition, climatic characteristics and different qualities of the fruit. Table 2 shows the chemical composition of pequi bark.

Table 2. Chemical analysis of the raw dry biomass

Component	Concentration ± SD / %
AIL	20.76 ± 0.4
ASL	5.48 ± 0.4
TL	25.71 ± 0.75
Humidity	7.00 ± 0.2
Ashes	2.82 ± 0.2
CF	25.27 ± 0.8
Cellulose	36.3 ± 0.08
Hemicellulose	5.35 ± 0.06
Extractives	34.47 ± 0.8

SD: standard deviation; AIL: acid insoluble lignin; ASL: acid soluble lignin; TL: total lignin; CF: fixed carbon.

The chemical characterization of bioproducts obtained from pequi bark has shown that this biomass can serve as raw material in the biorefinery field due to the high sugar content (cellulose and hemicellulose, about 41.65%). High lignin content (about 25%) indicates good results during pyrolysis processes. The low moisture content (about 7%) means a higher yield in bioproducts production, increasing the process efficiency. The low ash content (about 2.82%) is beneficial in pyrolysis processes and avoids side reactions during hydrolysis. The extractives content was high (about 35%) because it is a very oily biomass.²⁵

Rambo *et al.*²⁹ performed the chemical characterization of pequi stone, obtaining 7.20% moisture, 2.86% ash and 26.80% CF (fixed carbon), values very similar to those found in this work. da Paz *et al.*⁴⁰ determined 52.4% moisture and 0.7% ash in the fruit of pequi (*Caryocar brasiliense* Camb.) *in natura*. Ramos and de Souza⁴¹ performed the physical and chemical nutritional characterization of pequi fruits (*Caryocar coriaceum* Wittm.). In different regions of mid-north of Brazil, there is average pulp moisture content of 31.51% and ash around 3.05%. Some distinct results found between the works can be justified by taking into account the species analyzed, the part of the fruit used and the place where they were collected.

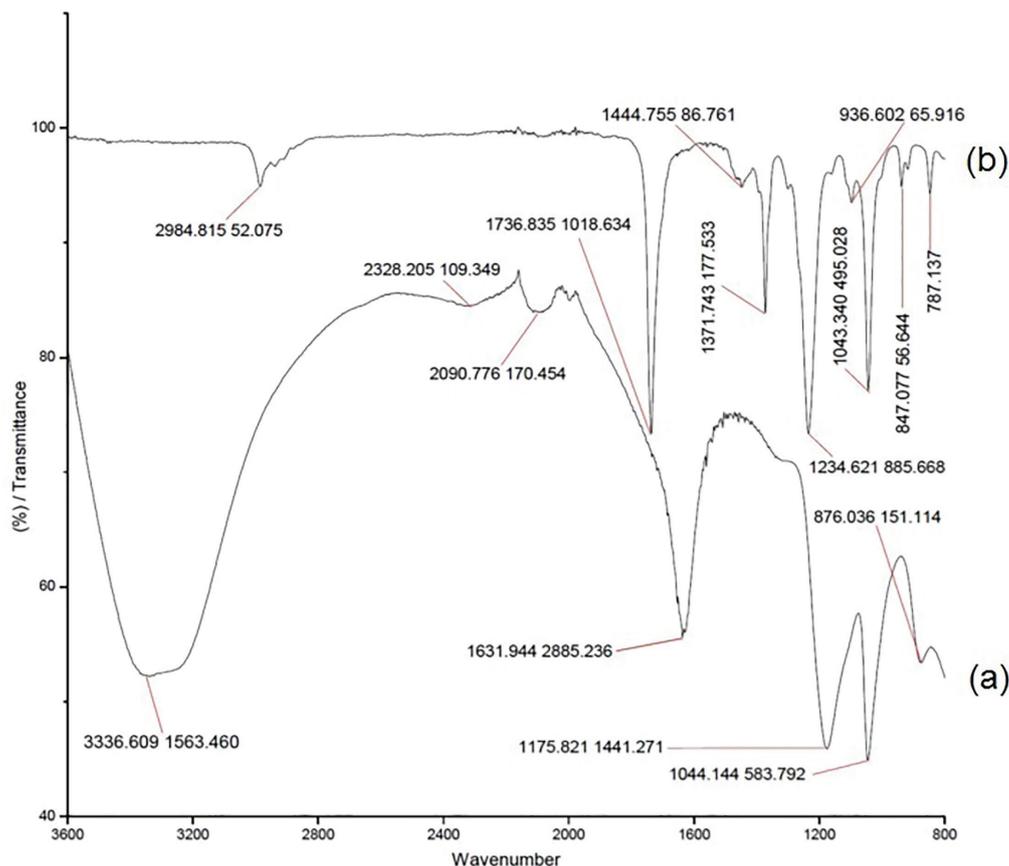


Figure 2. FTIR using ATR analysis of the hydrolyzed peel sample (a) and the product after reaction with the ionic liquid (b).

at 120-140 °C for reaction times of 1-2 h. In a paper by Scapin *et al.*,³⁶ the best yields for FF production from rice husks were obtained with 4 h of reaction at 120 °C (34%) and for soy peel with 3 h of reaction at 120 °C (59%). In this same work, HMF was produced with yields of 8.7 and 3.4% for rice and soy husks, respectively.

Wang *et al.*⁴⁹ analyzed the influence of HCl dosage, temperature and reaction time (130 °C for 2 h) using cottonseed for the production of HMF with [BMIM][Cl]. When the amount of HCl added was 20% (relative to the cottonseed hull), the yield of HMF reached 51%. However, when the amount of HCl was increased, its yield decreased to 33%. FF yield had a similar trend but was significantly lower than HMF. In the present work we observed inverse behavior, FF was produced with yields that are higher than HMF, which can be explained by the differences in biomass composition (different hemicellulose and cellulose content) and the type of acid used (the nature of the acid used influences the hydrolysis efficiency).

High glucose conversion rates were found (> 90%), but the obtained LA yield was 23.7%. A part of the converted glucose probably formed other products such as formic acid, acetic acid, 5-HMF, and other unidentified compounds.⁵⁰ According to the literature, Kang and Yu⁵⁰ found yields of

12-16% for eucalyptus wood, while Bevilaqua *et al.*³⁷ and Kumar *et al.*,⁵¹ for rice husks, found yields in the range of 10-59 and 2-38%, respectively. It is noteworthy that the sample in question of this study presents a high composition of essential oils (found in extractives), which decreases the theoretical yield of LA when it is compared to rice husks and eucalyptus sawdust, for example.

Design and surface of response

The analysis of variance (ANOVA) applied to obtain the mathematical model with significance level $\alpha = 0.05$, verified the significance of the second order model established for HMF and FF, obtaining values of $F = 0.00167$ and 0.004494 , respectively (Table 3).

The ANOVA applied also demonstrated that for HMF production the temperature (x_2^2) and the interaction between time and temperature (x_1x_2) are significant and for furfural production only the temperature (x_2 and x_2^2) is significant. This can be concluded by analyzing the Pareto diagram for the HMF (Figure 3a) and FF (Figure 3b) yield data after the pequi bark reaction, from which it was observed that in this experiment the temperature variable is significant, having a strong influence on HMF as well as FF yields, since it

Table 3. Analysis of variance for HMF and FF yield from pequi bark

Variation source	Sum of squares		Degrees of freedom		Mean square		F_{Value}		F_{Table}	
	HMF	FF	HMF	FF	HMF	FF	HMF	FF	HMF	FF
Regression	36241.0	1083250.5	5	5	7248.2	216650.1	23.9	5.3	$F_{0.05} = 0.00167$	$F_{0.05} = 0.004494$
Residuals	1513.4	202963.8	5	5	302.7	40592.8				
Total	377540.3	1286214.3	10	10						

F_{Value} : test F value; F_{Table} : tabulated F value; HMF: 5-hydroxymethylfurfural; FF: furfural.

meets the criterion of having effects superior to p_{value} (descriptive level), which indicates the confidence level used in the design. It does not happen with the reaction time variable, which for both products of interest of this work was less influent in the obtained result. Evaluating also the relationship between time and temperature, it is possible to observe that for HMF it was presented with little relevance, which was different for furfural, where the relationship was relevant for the obtained results. It is also verified that the model fit is satisfactory, since the determination coefficient (R^2) for HMF and FF was 0.9599 and 0.08422, respectively.

Figure 4 shows the response surfaces generated for HMF (Figure 4a) and furfural (Figure 4b) yields, where it can be observed that for the system studied, temperature and time conditions show a maximum yield of HMF in the central region of the chart, after 2 h of reaction at 120 °C. As described in the literature,^{1,7,16} low temperatures do not favor HMF formation and high temperatures favor its degradation.

The model equation was obtained with the variables time (x_1) and temperature (x_2). The equations for the coded variables are described below, where Y_1 represents the yield in HMF and Y_2 the yield in FF.

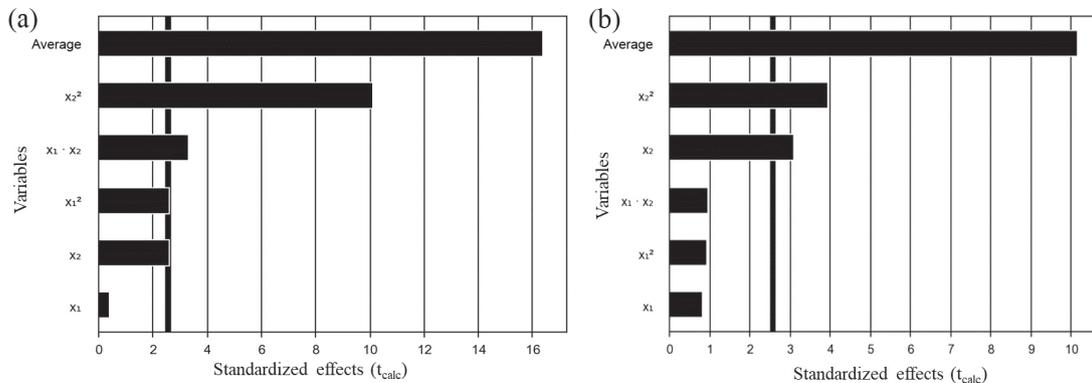


Figure 3. Pareto diagram of (a) HMF and (b) FF DCCR standard effects, where x_1 is time and x_2 is temperature.

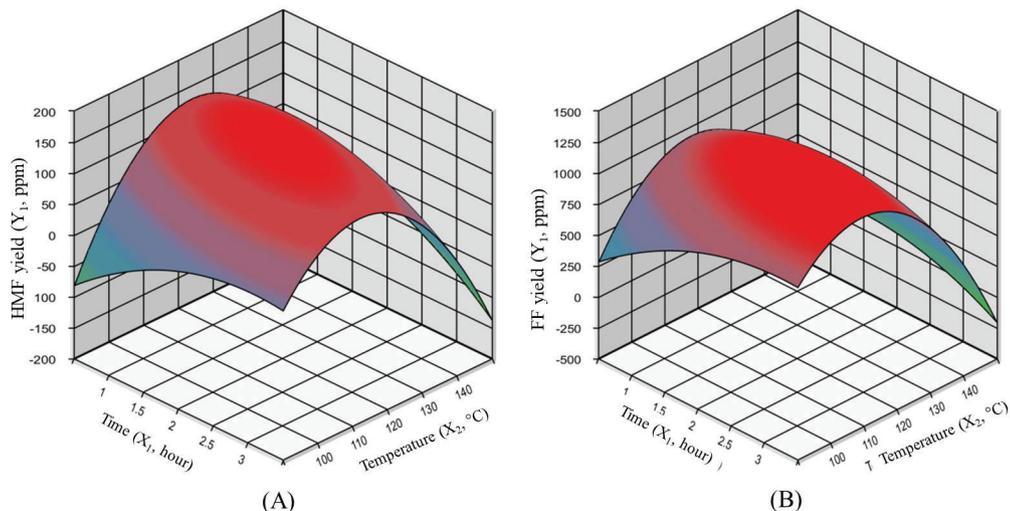


Figure 4. Response surface for (a) HMF and (b) FF.

$$Y_1 = 164.70 - 2.55x_1 - 19.16x_1^2 - 15.90x_2 - 73.85x_2^2 - 28.84x_1x_2 \quad (5)$$

$$Y_2 = 1182.36 + 58.26x_1 - 79.27x_1^2 - 221.05x_2 - 332.95x_2^2 - 96.19x_1x_2 \quad (6)$$

Conclusions

The use of residual biomass in biorefinery processes is extremely important for a society that seeks to add value to products that are economically and environmentally sound. In view of this, the reuse of pequi bark eliminates an environmental liability, helps to reduce the cost involved with the production of high value-added chemicals and it is a biomass widely distributed throughout the Brazilian cerrado. Chemical characterization has shown that pequi bark can serve as a precursor for high added value compounds. The production process of furanic compounds using DCCR, combined with the use of IL [BMIM][Br] was efficient for FF production (65%), but resulted in low HMF (3%). The yield of LA was 23.7% with a selectivity of 8.7%.

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Author Contributions

Elisandra Scapin and Magale K. D. Rambo were responsible for the conceptualization, data curation, formal analysis, project administration, visualization, writing original draft, review and editing; Guenther C. C. Viana for the conceptualization, data curation, visualization and writing original draft; Mariana S. Borges for the data formal analysis, software, and writing original draft; Michele C. D. Rambo for the formal analysis, software, funding acquisition and writing review and editing; Cláudio Carneiro for the data curation, software, validation, writing original draft, review and editing.

References

1. Yi, Y.; Lee, J.; Chung, C.; *Environ. Chem. Lett.* **2015**, *13*, 173.
2. Nguyen, C. V.; Lewis, D.; Chen, W.-H.; Huang, H.-W.; ALOthman, Z. A.; Yamauchi, Y.; Wu, K. C.-W.; *Catal. Today* **2016**, *278*, 344.
3. Yu, I. K. M.; Tsang, D. C. W.; Yip, A. C. K.; Chen S. S.; Ok, Y. S.; Poon, C. S.; *Bioresour. Technol.* **2017**, *237*, 222.
4. Teong, S. P.; Yi, G.; Zhang, Y.; *Green Chem.* **2014**, *16*, 2015.
5. Galaverna, R.; Pastre, J. C.; *Rev. Virtual Quim.* **2017**, *9*, 248.
6. Rout, P. K.; Nannaware, A. D.; Prakash, O.; Rajasekharan, L.; *Chem. Eng. Sci.* **2015**, *142*, 318.
7. Rosatella, A. A.; Simeonov, S. P.; Frade, R. F. M.; Afonso, C. A. M.; *Green Chem.* **2011**, *13*, 754.
8. Kuster, B. F. M.; *Starch* **1990**, *42*, 314.
9. de Carvalho, E. G. L.; Rodrigues, F. A.; Monteiro, R. S.; Ribas, R. M.; da Silva, M. J.; *Biomass Convers. Biorefin.* **2018**, *8*, 635.
10. Luo, Y.; Li, Z.; Li, X.; Liu, X.; Fan, J.; Clark, J. H.; Hu, C.; *Catal. Today* **2019**, *319*, 14.
11. Di, X.; Zhang, Y.; Fu, J.; Yu, Q.; Wang, Z.; Yuan, Z.; *Process Biochem.* **2019**, *81*, 33.
12. Liang, C.; Hu, Y.; Wang, Y.; Wu, L.; Zhang, W.; *Process Biochem.* **2018**, *73*, 124.
13. Chen, S. S.; Maneerung, T.; Tasang, D. C. W.; Ok, Y. S.; Wang, C.-H.; *Chem. Eng. J.* **2017**, *328*, 246.
14. Serrano-Ruiz, J. C.; Dumesic, J. A.; *Energy Environ. Sci.* **2011**, *4*, 83.
15. Sanborn, A. J.; *US pat. 7579489B2* **2009**.
16. Putten, R.-J. V.; Waal, J. C. V. D.; de Jong, E.; Rasrendra, C. B.; Heeres, H. J.; de Vries, J. G.; *Chem. Rev.* **2013**, *113*, 1499.
17. Li, H.; Yang, S.; *Int. J. Chem. Eng.* **2014**, *7*, 978.
18. Kang, S.; Fu, J.; Zhang, G.; *Renewable Sustainable Energy Rev.* **2018**, *94*, 340.
19. Stark, A.; *Energy Environ. Sci.* **2011**, *4*, 19.
20. Olivier-Bourbigou, H.; Magna, L.; Morvan, D.; *Appl. Catal., A* **2010**, *373*, 1.
21. Zhang, L.; Xi, G.; Zhang, J.; Yu, H.; Wang, X.; *Bioresour. Technol.* **2017**, *224*, 656.
22. Tiong, Y. W.; Yap, C. L.; Gan, S.; Yap, W. S. P.; *IOP Conf. Ser.: Earth Environ. Sci.* **2018**, *164*, 012007.
23. Asim, A. M.; Uroos, M.; Naz, S.; Sultan, M.; Griffin, G.; Muhammad, N.; Khan, A. S.; *J. Mol. Liq.* **2019**, *287*, 110943.
24. Amorim, D. J.; Rezende, H. C.; Oliveira, É. L.; Almeida, I. L. S.; Coelho, N. M. M.; Matos, T. N.; Araújo, C. S. T.; *J. Braz. Chem. Soc.* **2016**, *27*, 616.
25. Cardoso, C. M. M.; Zavarize, D. G.; Vieira, G. E. G.; *Ind. Crops Prod.* **2019**, *139*, 111485.
26. Oliveira, M. E. B.; Guerra, N. B.; Barros, L. M.; Alves, R. E.; *Aspectos Agronômicos e de Qualidade do Pequi*; Embrapa Agroindústria Tropical: Fortaleza, 2008.
27. Ribeiro, M. C.; Boas, E. V. B. V.; Riul, T. R.; Pantoja, L.; Marinho, H. A.; Santos, A. S.; *Cienc. Tecnol. Aliment.* **2012**, *32*, 386.
28. Bezerra, N. K. M. S.; Barros, T. L.; Coelho, N. P. M. F.; *Rev. Bras. Plant. Med.* **2015**, *17*, 875.
29. Rambo, M. K. D.; Alexandre, G. P.; Rambo, M. C. D.; Alves, A. R.; Garcia, W. T.; Barúque, E.; *Food Sci. Technol.* **2015**, *35*, 605.

30. Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D.; *NREL/TP-510-42618: Determination of Structural Carbohydrates and Lignin in Biomass*; National Renewable Energy Laboratory (NREL): Golden, USA, 2008.
31. ASTM D3173-87: *Standard Method for Determination of Moisture Content in Biomass*; American Society for Testing and Materials (ASTM), West Conshohocken, PA, 2003.
32. ASTM D3174-04: *Standard Method for Ash in the Analysis Sample of Coal and Coke*; American Society for Testing and Materials (ASTM), West Conshohocken, PA, 2004.
33. Trujillo, A. I.; Marichal, M. J.; Carriquiry, M.; *Anim. Feed Sci. Technol.* **2010**, *161*, 49.
34. Dharaskar, S. A.; Varma, M. N.; Shende, D. Z.; Yoo, C. Y.; Kailas, L.; Wasewar, K. L.; *Arabian J. Chem.* **2016**, *9*, 578.
35. Rodrigues, M. I.; Costa, P.; *Protimiza Experimental Design Software*; Protimiza, Campinas, Brazil, 2014.
36. Scapin, E.; Rambo, M. K. D.; Viana, G. C. C.; Marasca, N.; Lacerda, G. E.; Rambo, M. C. D.; Fernandes, R. M. N.; *Food Sci. Technol.* **2019**, DOI: 10.1590/fst.04419.
37. Bevilaqua, D. B.; Rambo, M. K. D.; Rizzetti, T. M.; Cardoso, A. L.; Martins, A. F.; *J. Cleaner Prod.* **2013**, *47*, 96.
38. Tiong, Y. W.; Yap, C. L.; Gan, S.; Yap, W. S. P.; *Ind. Crops Prod.* **2019**, *128*, 221.
39. Cai, C.; Qiyang, L.; Tan, J.; Wang, T.; Zhang, Q.; Longlong, M.; *BioResources* **2017**, *12*, 1201.
40. da Paz, J. G.; Pacheco, P.; da Silva, C. O.; Pascoal, G. B.; *Rev. Cient. Linkania Master* **2014**, *1*, 73.
41. Ramos, K. M. R.; de Souza, V. A. B.; *Rev. Bras. Frutic.* **2011**, *33*, 500.
42. Dharaskar, S. A.; Varma, M. N.; Shende, D. Z.; Yoo, C. K.; Wasewar, K. L.; *Sci. World J.* **2013**, DOI 10.1155/2013/395274.
43. Rajkumar, T.; Rao, G. R.; *J. Chem. Sci.* **2008**, *120*, 587.
44. Tao, F.; Song, H.; Chou, L.; *Carbohydr. Res.* **2011**, *346*, 58.
45. Yu, I. K. M.; Tsang, D. C. W.; *Bioresour. Technol.* **2017**, *238*, 716.
46. Yang, Y.; Hu, C. W.; Abu-Omar, M. M.; *Green Chem.* **2012**, *14*, 509.
47. Wang, P.; Yu, H.; Zhan, S.; Wang, S.; *Bioresour. Technol.* **2011**, *102*, 4179.
48. Rambo, M. K. D.; Rambo, M. C. D.; Melo, P. M.; de Oliveira, N. M. L.; Nemet, Y. K. S.; Scapin, E.; Viana, G. C. C.; Bertuol, D. A.; *J. Braz. Chem. Soc.* **2020**, *31*, 273.
49. Wang, S.; Du, Y.; Zhang, P.; Cheng, X.; Qu, Y.; *Korean J. Chem. Eng.* **2014**, *31*, 2286.
50. Kang, S.; Yu, J.; *Biomass Bioenergy* **2016**, *95*, 214.
51. Kumar, S.; Ahluwalia, V.; Kundu, P.; Sangwan, R. S.; Kansal, S. K.; Runge, T. M.; Elumalai, S.; *Bioresour. Technol.* **2018**, *251*, 143.

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