The Response Surface Methodology as a tool to optimize the extraction and acid hydrolysis processes applied to babassu residues

Metodologia de Superfície de Resposta como ferramenta para otimizar os processos de extração e hidrólise ácida de resíduos de babaçu

Metodología de Superficie de Respuesta como una herramienta para optimizar los procesos de extracción e hidrólisis ácida de los residuos de babasú

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Abstract

The new approach used to find extractives, holocellulose and total lignin from typical Brazilian biomass residues was optimized through the Response Surface Methodology (RSM) in the present study. The effects of different reaction conditions, including the hydrolysis reaction and extraction time, as well as the alcohol substrate molar ratio were investigated. A quadratic polynomial regression model was used to analyze the experimental data. The coefficient of determination was higher than 0.85 and the model was considered to be adequate. The obtained data showed that the methodologies by the National Renewable Energy Laboratory must meet each biomass type. These data can be now applied to large-scale biomass fuel production using the optimized results.

Keywords: Central Composite Design. Rotatable Central Composite. Analysis of Variance. Lignocelulosic Biomass. Holocellulose. Total Lignin.

Resumo

Neste trabalho, a nova abordagem para obter extrativos, hemicelulose e lignina total a partir de típicos resíduos de biomassa brasileira é otimizada pela Metodologia de Superfície de Resposta (MSR). Os efeitos das variáveis reacionais, incluindo o tempo de reação e extração das hidrólises, assim como a razão molar do substrato álcool foram investigados. Foram usados modelos de regressão polinomiais quadráticos para analisar os dados experimentais. O coeficiente de determinação foi maior do que 0,85 e o modelo foi considerado adequado. Os dados obtidos demonstraram que as metodologias do Laboratório Nacional de Energia Renovável devem ser adequadas para cada tipo de biomassa. Além disso, com os resultados otimizados, estes dados podem ser empregados na produção de larga escala de combustíveis oriundos de biomassa.

Palavras-chave: Planejamento Composto Central. Composto Central Rotacional. Análise de Variância. Biomassa Lignocelulósica. Holocelulose. Lignina Total.

Resumen

En este trabajo, el nuevo enfoque para obtener extractivos, hemicelulosa y lignina total a partir de residuos típicos de la biomasa brasileña está optimizado por la MSR. Se investigaron los efectos de las variables de reacción, incluyendo el tiempo de reacción de hidrólisis, el tiempo de extracción y la relación molar del sustrato alcohol. Fueron utilizados modelos de regresión de polinomios cuadráticos a fin de analizar los datos experimentales. Lo coeficiente de determinación fue superior a 0,85 y lomodelo fue consideradoadecuado. Los datos obtenidos demostraron que las metodologías del Laboratorio Nacional de Energía Renovable deben ser adecuadas para cada tipo de biomasa. Además de eso, con los resultados optimizados, estos datos pueden ser utilizados en la producción a gran escala de combustibles procedentes de la biomasa.

Palabras clave: Planeamiento Compuesto Central. Compuesto Central Rotativo. Análisis de Varianza. Biomasa Lignocelulósica. Holocelulosa. Lignina Total.

1 Introduction

The world economic and population growth in the recent years has led to several global issues, such as greenhouse gas (GHG) emissions, fossil fuel reserve depletion, and global warming (SHARMA; CHANDRA; BEIG, 2015; WAN et al., 2015). Biomass-based fuels and chemicals are some of the promising alternative energy sources to replace fossil fuel and to decrease GHG emissions (MALICO et al., 2016).

A new approach has emerged and it consists of developing technologies for biorefinery. The concept of such technology is similar to that of the petroleum refinery, namely: biomass conversion into energy and chemical inputs. However, the biorefinery uses renewable resources, whereas the petroleum refinery uses non-renewable resources (FERNANDO et al., 2006; KAMM; KAMM, 2004;2006).

Babassu (*Orbignya* sp.) residues are among the biomasses used in biorefinery. It is a native palm tree that grows in the Northern and

Northeastern states of Brazil. Its fruit is divided (TEIXEIRA, 2008) into epicarp (11–13%), mesocarp (20–23%), endocarp (57–63%), and kernels (7–9%). It is possible extracting oil from the kernels (SOLER; VITALI; MUTO, 2007; TEIXEIRA, 2008) and this oil is the main babassu product. It has been used by oleochemical, cosmetic, biofuel, and food industries (PAIVA, 2013; VINHAL; LIMA; BARBOSA, 2014). The other parts of the babassu fruit (epicarp, mesocarp and endocarp) have considerable potential for coal, tar, fuel, gas, starch, and alcohol production (CASTRO; CASTILHO; FREIRE, 2016; CINELLI et al., 2014; MANIGLIA; TAPIA-BLÁCIDO, 2016; TEIXEIRA, 2008., 2014).

The mesocarp and endocarp are mainly composed of (RAMBO et al., 2015a) carbohydrates (63.8% and 57.8%) lignin (28.6% and 29.2%) and extractives (1.55% and 5.0%), respectively.

The acid hydrolysis is the most promising technology used to convert these polymers into products of interest. It consists in catalyzing the chemical bond cleavage via nucleophilic substitution reaction in water medium. The polymeric carbohydrates are hydrolyzed into their monomeric forms during hydrolysis; these forms are soluble in liquid hydrolysis. The lignin is divided into acid insoluble and soluble materials. The acid insoluble material may also include ash and protein, which must be considered during the gravimetric analysis. On the other hand, the soluble lignin is hydrolyzed and must be considered in the ultraviolet-visible (UV/Vis) spectrophotometry (RAMBO et al., 2015b).

The National Renewable Energy Laboratory (SLUITER, 2008) recommends using the two-step acid hydrolysis to fractionate biomass components. The samples were kept at 30 °C for 1 h in the first step and autoclaved for 1 h at 120°C in the second step. The reflux for 16-24 hours in 95% ethanol using the Soxhlet apparatus was recommended for the extractives' analysis (SLUITER, 2005).

However, this extraction procedure is a general convention for lignocellulosic biomass, not for a specific feedstock. It may affect extraction and hydrolysis procedure performances. Therefore, we herein used the design of experiments (DoE) and RSM to optimize the best conditions (BOX; HUNTER; HUNTER, 1978; BARROS; SCARMINIO; BRUNS, 2002) and maximize yield in extraction and hydrolysis processes concerning Brazilian biomasses such as the babassu residues. Both methods are among the most relevant multivariate techniques used in analytical optimization (BEZERRA et al., 2008). They can be well applied when a response of interest is influenced by several variables, such as the one in this research.

Accordingly, the aim of this study was to investigate the use of babassu agro-industry residues (the mesocarp and endocarp) to produce chemical inputs optimized through the biorefinery concept. Thus, RSM and DoE were used to improve the performance of the experiments.

2 Experiment

2.1 Samples

Babassu samples (the mesocarp and endocarp) were collected in an industrial facility – TOBASA, located in Tocantins State, Brazil. The samples were dried, ground in Romer micromill (Romer Labs, São Paulo, Brazil), sieved (45 and 70 mesh) and stored for future chemical analyses.

2.2 Extraction

Approximately 1g of dried endocarp and mesocarp was extracted using Soxhlet ethanol apparatus. The reaction time (X_1) (5, 7, and 9 h) and ethanol concentration (X_2) (75, 85, and 95%) of babassu endocarps were set according to the factorial design to maximize extraction yield.

The following reaction times: 4, 5, 7, 9, and 10 h; and ethanol concentrations: 71, 75, 85, 95, and 98% were set according to DoE for babassu mesocarps.

The remaining solids were transferred to a Petri dish and left to air dry for 2 days after extraction; the extractive content was then determined.

2.3 Holocellulose and lignin determination Hydrolysis

The dry babassu endocarp and mesocarp extracted samples (the content with the best extractives according to the DOE results) were subjected to two-stage acid hydrolysis using 72% sulfuric acid (3 mL) in water bath at 30°C, the samples were stirred every 10 minutes in the first step. The hydrolysis in the second step was conducted in acid concentration 4% (diluted in 84 mL water) in autoclave at 120°C. The reaction times in the first and second hydrolyses are listed in Table 1.

The acid soluble lignin (ASL) consisted of lignin solubilized under acidic hydrolysis conditions. The ASL was measured in diluted hydrolysate (4% acid solution of H_2SO_4) through UV spectroscopy in Kasuaki IL-592 spectrometer, absorbance 205 nm.

The filtration of the acid solid residue (AIR) after the acid hydrolysis was dried in oven overnight at 105°C, and then cremated at muffle (575°C) to determine the acid-insoluble ash (AIA). The Klason lignin (KL), which is considered the insoluble lignin, was determined through the difference between AIR and AIA, i.e., the residue minus the ash. Finally, the total lignin (TL) content was determined through the sum between the soluble and insoluble lignins found after the acid hydrolysis procedure was conducted.

The holocellulose can be determined by the amount of TL, extractives and ash of the dried biomasses after total hydrolysis and by calculating the content of polysaccharides different from 100%.

Table 1. **Factors and design levels of DoE**

Variables	Code	Level		
		-1	0	+1
1st Hydrolysis time (hours)	X_3	1	2	3
2nd Hydrolysis time (hours)	X_4	0.5	1	1.5

Source: Self-elaboration.

2.4 Experimental design and statistical analysis

The experiments were performed according to the response surface methodology (RSM) and rotational central composite design (CCD) methods, with three repetitions at central levels to find the estimated experimental error. The methodology consisted of a full factorial or fractional factorial design; or of an additional design, which is often a star design where in the experimental points are at a distance α from its center (BOX; WILSON, 1951).

Briefly, CCD consisted of $N= k^2 +2k +m$, wherein: k is the number of factors and m is the number of the center points replicated to find the experimental error (BEZERRA et al., 2008). The α values depend on the number of variables and they can be calculated through $\alpha = 2^{(k-p)/4}$. The α value was 1.41 in two variables, for instance. Seven (7) trials were herein carried out, without the α value, using CCD in the extraction and hydrolysis process.

Only the extractive content of the babassu mesocarp was available in the rotatable central composite design 2^2 (CCRD), it included 4 axial points and 3 central points, which have required 11 experiments. Based on such design, the α value was 1.41 and we could see the influence of independent variables on the assessment's effects, standard error and on the statistical significance (p-value).

The extraction time (X_1) and the ethanol molar ratio (X_2) were chosen as independent variables in the extractive models to cover data set earlier and their levels were adopted herein. The extractive yield (Y_1) was considered as a response variable.

The 1st (X_1) and 2nd hydrolyses (X_2) were chosen as independent variables, whereas the total lignin (Y_1) and holocellulose contents (Y_2) were considered response variables.

All experiments were performed in random (HELENO et al., 2016) order (overall randomization) to avoid biases.

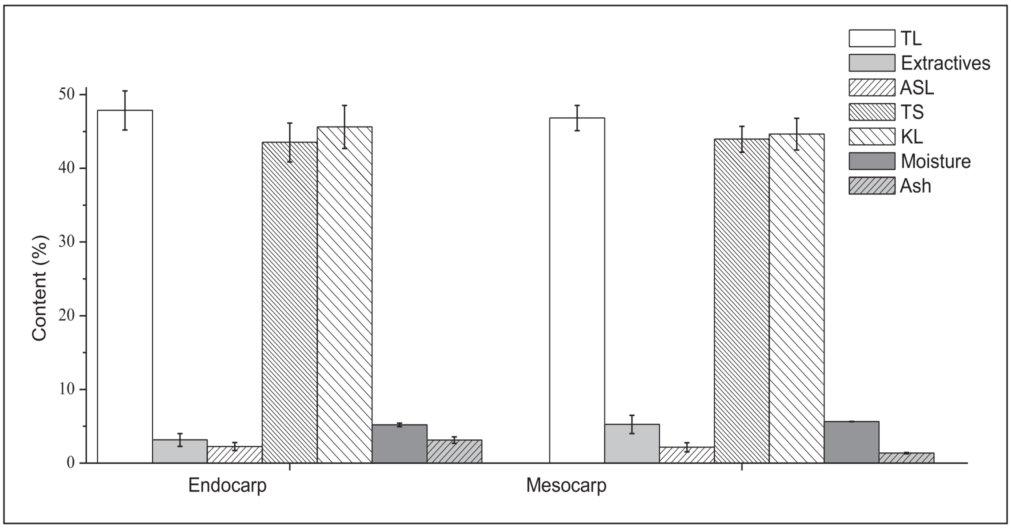
Results were analyzed in Protimiza software version 2014 (www.experimental-design.protimiza.com.br) to develop response surface models and to verify the effects of the independent variables on the response. Model fitness was assessed through coefficient of determination (R^2) and analysis of variance (ANOVA) (VIEIRA; HOFFMAN, 1989).

3 Results and Discussion

The statistical results of the chemicals (compounds) formed during babassu residue processing are summarized in Figure 1. The broadest range was shown by the extractives; they presented wide variation in the coefficient of variation (26.10 and 22.75 in the endocarp and mesocarp, respectively). These extractives were followed by TL (5.54) and holocellulose (6.10) in the endocarp. The mesocarp presented small variation range and low coefficients of variation (3.75 and 3.91 in TL and holocelluose, respectively).

The value at optimum conditions (1.5 h in the 2nd hydrolysis) provided holocellulose content higher than 45% in both babassu residues, thus indicating complete hydrolysis. Rambo et al., (2014) have assessed the acid insoluble residue through ^{13}C NMR (nuclear magnetic resonance) after the acid hydrolysis of some lignocellulosic biomasses. They found that approximately 14% to 16% of the polysaccharides remained in the biomass. However, the hydrolysis process performed through NREL (only 1 h in the 1st and 2nd hydrolyses) was not so efficient, since it was possible detecting carbohydrate signals in the residue after the hydrolysis. These data suggested optimized reaction conditions for each specific biomass.

Figure 1. **Mean and standard deviation of the chemical composition of babassu residues**



Source: Self-elaboration.
Legend: TL: Total lignin; ASL: Acid soluble lignin; TS: Total sugar; KL: Klason lignin.

Tables 2 and 3 show the results of endocarp and mesocarp extractives, respectively, based on the design of experiments. The central points (in both tables) presented small variation and indicated good process repeatability.

The CCD was used for endocarp extraction, whereas the DCCR was used in the mesocarp in combination with the addition of axial points (±1.4142).

Table 2. Factorial design of the contents of extractives of babassu endocarp

Variables	**-1**	**0**	**1**
(X_1)Time (h)	5	7	9
(X_2) Ethanol (%)	75	85	95
Experiments	**X_1**	**X_2**	**Y_1 (%)**
1	-1	-1	2.29
2	+1	-1	3.78
3	-1	+1	4.78
4	+1	+1	2.35
5	0	0	3.06
6	0	0	3.11
7	0	0	2.63

Source: Self-elaboration.

Table 3. Factorial design of the content of extractives of babassu mesocarp

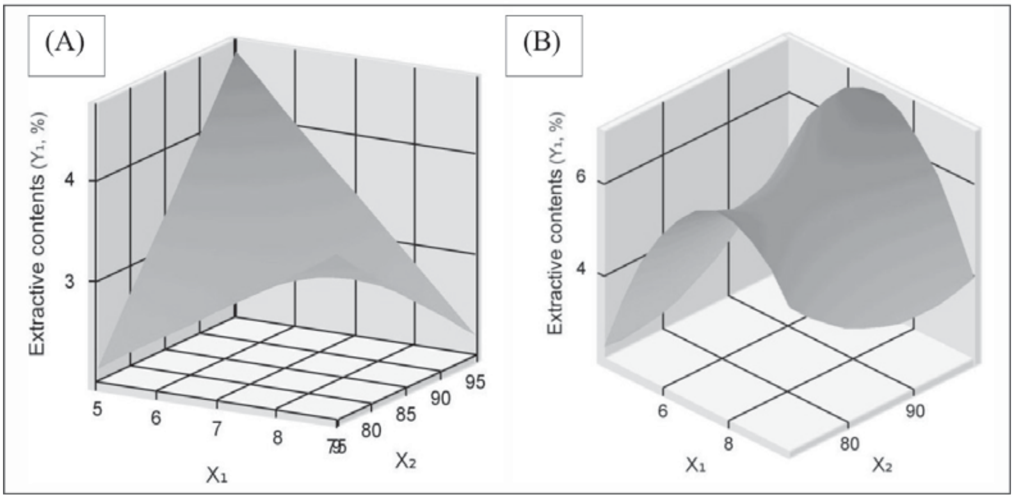
Variables	**-1.41**	**-1**	**0**	1	**1.41**
(X_1) Time (h)	4	5	7	9	10
(X_2) Ethanol (%)	71	75	85	95	98
Experiments		**X_1**	**X_2**	**Y_1 (%)**	
1		-1	-1	4.37	
2		+1	-1	5.64	
3		-1	+1	5.72	
4		+1	+1	5.12	
5		-1.41	0	2.35	
6		+1.41	0	3.92	
7		0	-1.41	6.27	
8		0	+1.41	6.67	
9		0	0	5.90	
10		0	0	5.93	
11		0	0	5.91	

Source: Self-elaboration.

The quadratic model was validated for the variable 'extractives' and used to generate the surface response to optimize the process. Figures 2(A) and 2(B) presented one minimum and one saddle point as critical points, respectively. The saddle point was an inflexion point between a relative maximum and a relative minimum (BEZERRA et al., 2008), wherein the maximum or minimum optimal values could not be assessed through the saddle point. Again, it was possible finding the optimum region by visually inspecting the surfaces.

Figure 2(A) shows that short reaction times associated with high solvent concentrations lead to higher yields. Likewise, long reaction times associated with low ethanol concentrations also favor extraction. Figure 2(B) shows great yields when the extraction time was set at 7 hours, for any ethanol concentration value. There was yield decrease when extreme extraction times were adopted (4 h and 10 h).

Figure 2. Endocarp (A) and (B) mesocarp surface response



Source: Self-elaboration.

The difference between values was small (error below 0.20%) in the predicted (4.62%±0.33) and experimental (4.78%) response values under optimum endocarp conditions (9 h and 75% ethanol). The error in the predicted (6.92%±0.41) and experimental (6.67%) response values under optimum mesocarp conditions (9 h and 85% ethanol) was 0.25%.

Tables 4 and 5 show the TL and holocellulose results of endocarp and mesocarp, respectively based on the CCD. The central points (in both tables) presented small variation (standard deviation less than 0.52%) and it indicated good process repeatability.

Table 4. Factorial design of TL (Y_1) yield and holocellulose content (Y_2) of babassu endocarp free of extractives

Variables	-1	0	1	
(X_1) 1st Hydrolysis time (h)	1	2	3	
(X_2) 2nd Hydrolysis time (h)	0.5	1	1.5	
Experiments	**X_1**	**X_2**	**Y_1 (%)**	**Y_2 (%)**
1	-1	-1	45.96	45.40
2	+1	-1	53.26	38.10
3	-1	+1	48.94	42.42
4	+1	+1	45.32	46.04
5	0	0	47.48	43.88
6	0	0	46.61	44.75
7	0	0	47.41	43.95

Source: Self-elaboration.

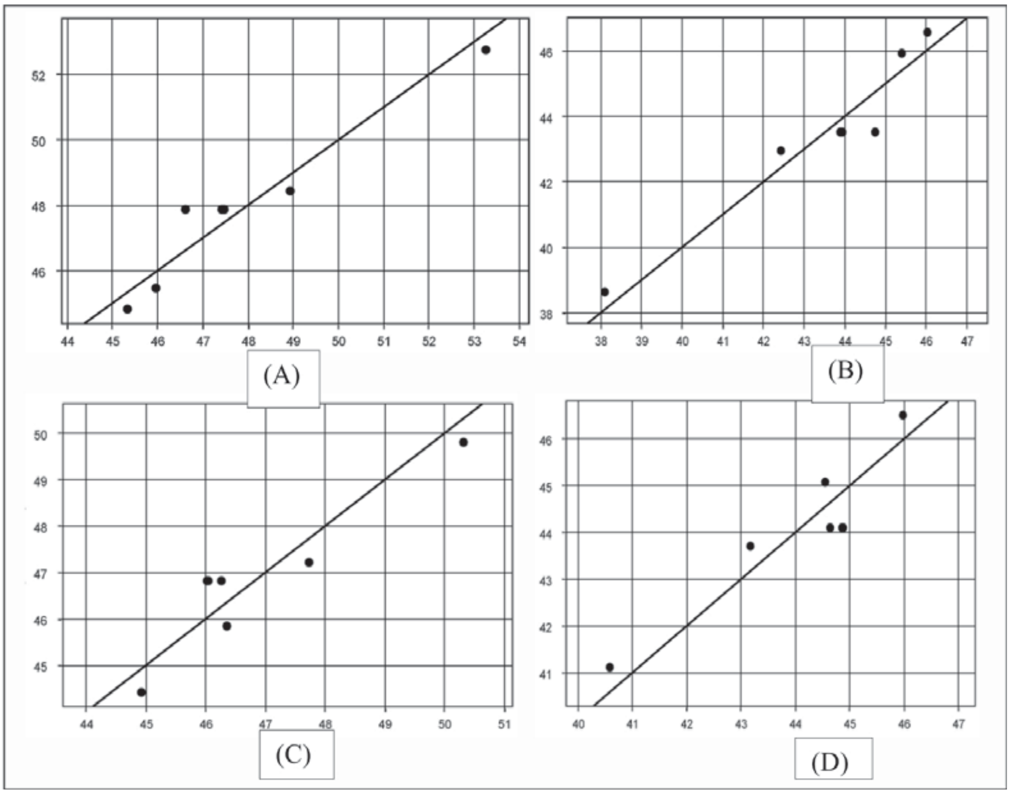
Table 5. Factorial design of the TL and holocellulose contents of babassu mesocarp free of extractive

Variables	**-1**	**0**	**1**	
(X_1) 1st Hydrolysis time (h)	1	2	3	
(X_2) 2 nd Hydrolysis time (h)	0.5	1	1.5	
Experiments	**X_1**	**X_2**	**Y_1 (%)**	**Y_2(%)**
1	-1	-1	46.36	44.54
2	+1	-1	50.32	40.58
3	-1	+1	44.93	45.97
4	+1	+1	47.73	43.17
5	0	0	46.03	44.87
6	0	0	46.26	44.64
7	0	0	46.04	43.86

Source: Self-elaboration.

The visual inspection of the residual graphs led to valuable information about model suitability. Figure 3 shows the plot of predicted values against the corresponding experimental results.

Figure 3. Plot of Endocarp biomass in TL (A) and in the holocellulose parameters (B). Plot of mesocarp biomass in TL(C) and in the holocellulose(D) where axis X are the predicted value and in the axis Y are the experimental values

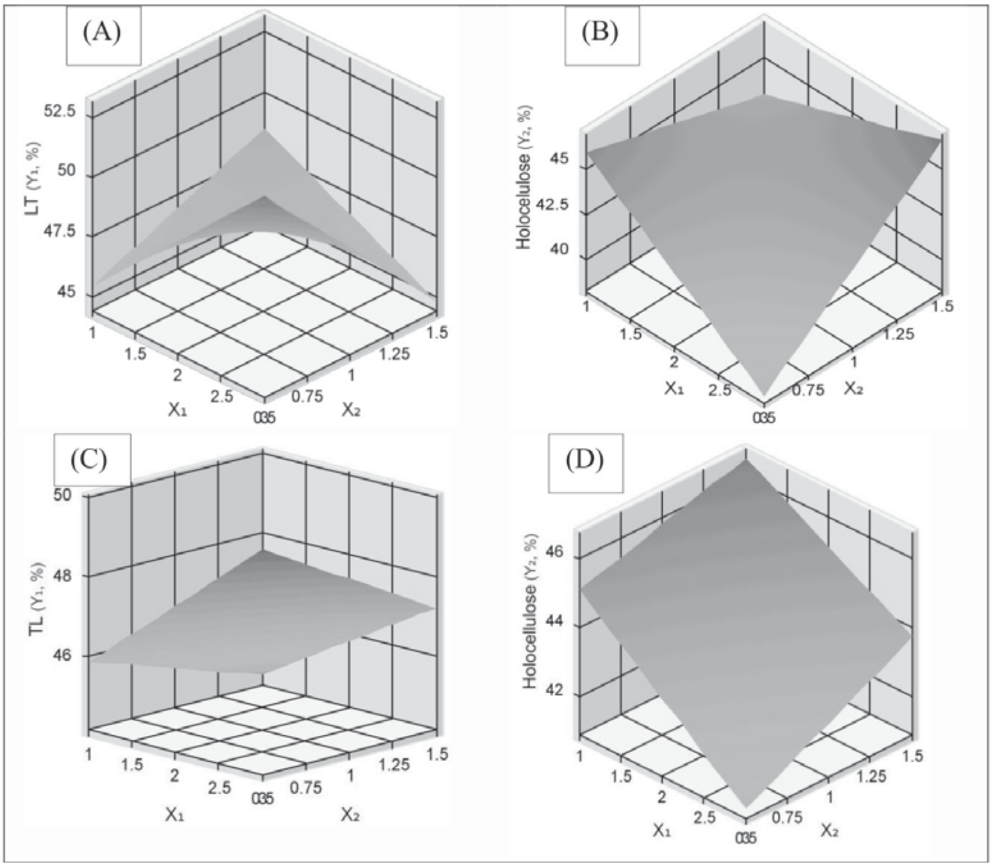


Source: Self-elaboration.

The points were randomly distributed near the line and showed excellent consistence; the model had no significant adjustment shortage. The prediction and experimental error values were lower than 0.53% in all models and it indicated that the mathematical model fitted well. The model's graph of residues suggested normal distribution (BRUNS; SCARMINIO; NETO, 2006).

Figures 4 (A) and (B) show the effects of hydrolysis times (1st and 2nd) on the TL and holocellulose yield in the endocarp, whereas Figures 4 (C) and (D) show the effects of hydrolysis times in the mesocarp for TL and holocellulose content. We observed maximized yield of approximately 53% and 46% by fixing the primary hydrolysis at 3 h (Figures 4 (A) and (B)) for secondary hydrolysis times 30 and 90 min in TL and holocellulose, respectively.

Figure 4. (A) Plot of Endocarp biomass in TL and (B) in the holocellulose parameters. (C) Plot of mesocarp biomass in TL and (D) in the holocellulose



Source: Self-elaboration.

Figures 4 (C) and (D) have opposite effects on TL and holocellulose, whereas the TL maximum time in the primary hydrolysis, associated with the minimum time of secondary hydrolysis, favors greater holocellulose yield. The minimum time in the primary hydrolysis associated with the maximum time in secondary hydrolysis provides maximum carbohydrate levels (45.97%).

The analysis of the figures, once more, emphasized the fact that the NREL methodologies need to be adapted to each biomass. Accordingly, the secondary hydrolysis is at least 30 min longer than the standard reaction time, which led to better holocellulose results in both babassu residues. The 2-hour increase in the standard procedure led to maximum process yield in the endocarp, for example.

The equations using the regression coefficients and statistical results of all endocarp and mesocarp models are described in Table 6. The terms in bold represent the significant coefficients.

The interaction between variables was significant in all models involving babassu endocarps, but only the extractive model was significant in the mesocarp.

All $F_{calculated}$ were higher than $F_{tabulated}$ and it showed the statistical significance of the regression. It indicated that the mathematical models fit the experimental data well (BARROS; SCARMINIO; BRUNS, 2002).

The model fitting the observed responses was obtained through R^2 determination, thus indicating that more than 85% of the total variation was explained by the regression models.

Table 6. Regression equations and statistical parameters of the models at significance level 5% (p <0.05)

Equations	F_{cal}	p	R^2
$EEY = 3.14 - 0.24\,x_1 + 0.27\,x_2 - 0.98\,x_1\,x_2$	11.7	0.03	0.92
$MEY = 5.91 + 0.36\,x_1 - 1.29\,x_1^2 + 0.17\,x_2 + 0.38\,x_2^2 - 0.47\,x_1\,x_2$	23.3	<0.01	0.96
$ETL = 47.85 + 0.92\,x_1 - 1.24\,x_2 - 2.73\,x_1\,x_2$	13.3	0.03	0.93
$EHY = 43.51 - 0.92\,x_1 + 1.24\,x_2 + 2.73\,x_1\,x_2$	13.3	0.03	0.93
$MTL = 46.81 + 1.69\,x_1 - 1.01\,x_2 - 0.29\,x_1\,x_2$	6.1	0.08	0.86
$MHY= 44.09 - 1.69\,x_1 + 1\,x_2 + 0.29\,x_1\,x_2$	6.1	0.08	0.86

Source: Self-elaboration.

Legend: EEY: endocarp extraction yield; MEY: mesocarp extraction yield; ETL: endocarp total lignin; EHY: endocarp holocellulose yield; MTL: mesocarp total lignin; MHY: mesocarp holocellulose yield.

4 Conclusions

Brazilian biomasses, such as babassu residues are potential feedstocks to produce liquid and solid fuels. Its chemical composition is favorable under high carbohydrate and lignin levels.

The RSM was employed to identify the effects of extraction time, primary and secondary hydrolysis time and of ethanol concentration on extractives, hollocelulose and LT yield. The use of RSM to optimize analytical procedures was very useful because of its advantages to classical one-variable-a-time optimization such as the generation of large amounts of information from a small number of experiments and as the possibility of assessing the interaction effect between variables on the response.

The ethanol concentration 95%, at time reaction 5 h; and the ethanol concentration 98%, at time reaction 7 h, appeared to be the optimum reaction conditions to improve extractive yield in the endocarp and mesocarp, respectively. The optimum holocellulose conditions leading to maximum carbohydrate yield of at least 45% were 3 h and 90 min in the endocarp; and 1 h and 90 min, in the mesocarp.

The same experimental conditions (3 h and 30 min) applied to the endocarp and mesocarp provided the best TL contents. Therefore, we found low energy costs in both biomasses in a biorefinery process using optimized time between 1 h and 3 h.

Regarding the performance of the products of interest when it comes to cost, the best process concerned the carbohydrate contents.

The quality of the fitting models and their accuracy to predict the obtained experimental data was satisfactory.

The high value of the adjusted determination coefficient in the models (higher than $R^2 = 0.85$) and the no-significant difference between predicted and experimental values have demonstrated the validity of the herein proposed optimization models in statistical terms.

One of the modifications applied to the NREL methods was very useful for the biomass in question; it changed the primary and secondary hydrolysis time to improve sugars recovery.

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