Investigation of Agricultural Biomass Residues in Liquefaction Process

Leite B. S., Ferreira D. J. O., Leite S. A. F., Bastos F. S., Lins V. F. C., and Castro B. T.

***Abstract*—The use of agricultural biomass residues as an alternative of fossil derivatives have been extensively investigated in the last years due to environmental concerns. In this context, the liquefaction appears as an alternative to use these renewable sources to produce green materials. The present work aims to synthesize polyols from the cassava peels (CP), lemon bagasse (LB) and rice husk (RH) in order to obtain biopolyols suitable to produce polyurethane foams and add value to these residues. Besides the production of the green foams, this work has also the objective to evaluate how composition of the biomass (e.g.: solid, lignin and holocellulose content) can be related to the process yield and the characteristics of the biopolyol (e.g: hydroxyl number). The polyols were synthesized from the biomass liquefaction, using crude glycerol as solvent (a by-product of biodiesel industry) and sulfuric acid as catalyst. The liquefaction was performed using an autoclave, operated at 125 ℃ and 1.84 atm. Liquefaction yield varied from 38 to 91 %, according to biomass and process parameters used. It was observed that CP, which has the higher volatile solids content and the lower lignin plus holocellulose content, had the higher liquefaction yield. Polyol's hydroxyl number from RH had the lowest values and lower variation, according to process parameters. Liquefaction yield and hydroxyl number from LB presented great response to process parameters used.**

***Index Terms*—Valorization, polyol, lignocellulosic, lignin.**

I. INTRODUCTION

The uses of biomass and agricultural wastes as an alternative of fossil derivatives have been extensively investigated in the last years due environmental concerns. Several processes were developed in order to advance these renewable sources and generate green materials comparable to those petroleum-derived [1].

It is estimated that Latin America has the highest biomass potential, after considering food production and resource constraints [2]. Brazil is one of the most promising producers of biomass residues and has abundant renewable energy sources [3]. It is also one of the largest producers of citrus with a production of about 19 million tons in 2013. The juice industry makes use of only 40 to 50% of the fruit and its remainder is considered industrial residue [4].

Biomass liquefaction research is focused on the solvolysis of modified raw material at the early stage [5]. Among its products, bio-based polyols have suitable properties to produce polyurethane foams with comparable properties to the conventional ones. Liquefaction profitability dependents on the technology employed to alter the structure of lignocellulosic biomass and the feedstock used to produce the high value co-products. Most biomass liquefaction processes use petroleum-derived as biomass liquefaction solvents. The use of these fossil solvents increases the production cost and also contributes to the high carbon footprint of the polyols and polyurethanes from liquefaction process [6]. In this sense, several studies have shown that crude glycerol (co product of biodiesel production) can improve the properties of bio-based polyols and polyurethane (PU) foams derived from the liquefaction of lignocellulosic biomass [7]. Biomass products can significantly reduce greenhouse gases emission, compared to fossil-based products, although the maturity and economics of the processes and logistics are the main challenges for lignocellulosic biomass conversion [8].

Agricultural residues have large differences in their physical and chemical properties than wood. As a result, the optimum conditions that can be applied to the liquefaction of wood may be not suitable for the agricultural residues. Lemon bagasse, Rice husk and Cassava peels are a lignocellulosic residue combining cellulose, hemicelluloses and lignin and due to its characteristics it may be investigated for value-added chemicals productions [1], [9]-[13].

The aim of this work was to produce biopolyol from the lignocellulosic residues: lemon bagasse, rice husk and cassava peels and also to understand the influence of chemical composition and operation parameters on the liquefaction yield and hydroxyl number of three different biomass. Biomasses were characterized using Proximate Analysis, Lignin and Holocellulose Content and Nitrogen Total Kjeldahl. The polyols were synthesized from the biomass liquefaction, using crude glycerol as solvent and sulfuric acid as catalyst. The liquefaction was performed using an autoclave, operated at 125 ℃ and 1.84 atm. Biopolyols were characterized using Hydroxyl Number, functional groups, specific mass and viscosity.

II. EXPERIMENTAL

A. Sampling

The rice husk, cassava peels and lemon bagasse samples were collected between May and October of 2016 in the

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southeast region of Brazil (Florestal, Minas Gerais - Brazil). The samples were dried at 105 ℃ using an oven-dry until a constant weight was achieved. Then biomass cut in a knife mill to get fibers of 0.5 mm length for future chemical and physical analyses, which were performed in duplicate. The crude glycerol used as liquefaction solvent, was kindly provided by Petrobrás (Usina Darcy Ribeiro - Montes Claros - MG, Brazil) as received. Sulfuric acid (Synth) was used as catalyst for this reaction. The reactants used to perform the hydroxyl number of the polyols produced were 1,4-dioxane (Synth), imidazole (Synth), phtalic anydride (Synth) and sodium hydroxide (Synth). Polyurethane foams were synthesized using the polyols produced from lemon bagasse, isocyanate (Desmodur 44 V 20 of Bayer), surfactant (Tegostab 8460 supplied by Evonik), catalyst (Kosmos 19 commercialized by Evonik) and distillated water.

B. Proximate Analysis

Ash content was determined as the residue after combustion in a muffle furnace at 710 ℃ for 1 h. Volatile matter was the mass fraction released when 1.0 g of sample was heated in a muffle furnace at 850 ℃ for 7 min. The percentage of fixed carbon (FC) was the fraction that remains after subtracting the ash and the volatile matter content [14].

C. Lignin Content (Klason Lignin)

Klason Method was used to analyses lignin content [15]. Biomass sample (300 mg) was hydrolysed with H_2SO_4 72 % (m/v) for approximately 2 h. The acid was diluted to 4 % (m/v) and the sample was placed in an autoclave at 121 ℃ for 1 h. A vacuum filtration was performed in the autoclave solution using pre-weighed crucibles. The crucible with the filtered solid was placed in an oven at 105 ℃, until constant mass.

The insoluble lignin determination was performed in duplicate. Consequently, the result presented corresponds to the mean of the 4 samples results for the same condition studied. Eq(1) shows the calculation of the lignin insoluble percentage in biomass, where m_1 corresponds to the mass in grams of the empty crucible and m_2 corresponds to the mass in grams of the crucible with the filtrate, after the autoclave stage and m_3 corresponds to the mass ash after 1 hour in the muffle at 650 °C [15], [16].

$$\%\ \text{Insoluble Lignin} = \frac{(\text{m}_2 - \text{m}_3 - \text{m}_1)}{0.3} \text{x}\ 100 \qquad (1)$$

D. Holocellulose Content (Cellulose and Hemi-cellulose)

This fraction was obtained from extractive-free biomass by means of a sodium chlorite and glacial acetic acid treatment at 70 – 80 ℃. ASTM D-1104 standard (ASTM International, 1978) and the novel method were used for this purpose [17].

E. Nitrogen Total Kjeldahl (NTK)

The fraction of standard solution and samples were placed in the digestion tube, were added catalyst (96% K_2SO_4/4% $CuSO_4.5H_20$) and concentrated sulphuric acid. The tubes were placed on the Kjeldahl digester, previously heated at 370 °C. Heating was kept until white fumes appeared (approximately 10 min), then the digestion was continued for 30 min. The digestion residue obtained was cooled and diluted up to 10 mL with distilled and de-ionized water. By distillation, ammonium hydroxide was trapped as ammonium borate in a 4% boric acid solution (4 g of boric acid in 100 ml deionized water (w/v)) and total nitrogen was determined by titration with standardized HCL. All the measurements were performed at room temperature in triplicate [18].

F. Liquefaction Procedures (Polyol Synthesis)

The liquefaction process consists of the reaction between: biomass, solvent and catalytic agent on an specific time and the heat treatment was carried out in an autoclave [19]. For each run, according to the experimental factorial design (Section 2.4), a blend of 0.5 g of lemon bagasse together with solvent (Crude glycerol) and Catalytic agent (Sulfuric acid 95 wt%) was fed into the reactor (Erlenmeyer 250 mL). Reactions proceeded at fixed final temperature (120 ℃), with heating rate of 15 ℃/min, for a fixed time period and absolute pressure of 2 kgf/cm ²

The autoclave cooling and depressurizing time was about 30 minutes [20]. The product was collected for analysis and foam production according to the following sequences as shown in Fig. 1 [20].

The resulting reaction mixture was filtered to separate the residue and filtrate using ethanol to wash the residue. The residue was dried in an oven at 105 ℃ during 24 hours, and the resultant solid was used to calculate the liquefaction yield (Ly), showed (Eq 2):

$$Ly(\%) = \left(\frac{Biomass\ weight - Residue\ weight}{Biomass\ weight}\right) x\ 100 \qquad (2)$$

where biomass weight is the lemon weight (g) before the liquefaction process, residue weight is the insoluble lemon weight (after the liquefaction process). The liquid obtained from filtration was also dried at 75 ℃ to obtain the polyols.

G. Experimental Factorial Design

The Experimental Factorial Design was performed in order to appoint an initial pattern of work. The evaluation of the reaction conditions on liquefaction yield will be performed in a further work.

The variables investigated were: catalyst amount (wt%), time of reaction (hours) and molar ratio solvent/biomass (wt%), as shown in Table I. The study of factors affecting the liquefaction yield was evaluated involving a multivariate factorial design with central point for three variables at two levels (2^3).

TABLE I: LEMON BAGASSE LIQUEFACTION VARIABLES AND LEVELS USED IN THE 2^3 FACTORIAL DESIGN WITH CENTRAL POINT

Variables	-1	0	+1
X_1: catalyst amount (C)	2 %	5 %	7 %
X_2: time of reaction (t)	0.5 h	1.0 h	1.5 h
X_3: ratio solvent/biomass (R)	2:1	3.5:1	5:1

Series of experiment of three factors and two levels: 11 experiments, as shown in Table IV of Matrix of Planning of Experiments, were conducted.

H. Polyol Characterization

1) Hydroxyl number

Polyols hydroxyl number was determined according to the ASTM D4274 standard [1], as follows: one gram of each sample of liquefied product was esterified for 20 min at 110 °C with 25 mL of a phthalation reagent, a mixture of 150 g phthalic anhydride, 24.2 g imidazol, and 100 g dioxane. Then, 50 mL of 1,4 dioxane and 25 mL of distilled water were added to this polyol mixture.

Afterwards, it was titrated with a sodium hydroxide solution (1 mol.L^{-1}) until the equivalence point using a pH meter [21]. The hydroxyl number (mg KOH/g) was calculated from the difference in titration of blank and the sample solutions using the following equation Eq(3):

$$OH\ number\ \left(mg\frac{KOH}{g}\right)=\frac{(B-A)Nx56.1}{W} \tag{3}$$

where A is the volume of the sodium hydroxide solution required for titration of sample (mL); B is the volume of blank solution (mL);N is the normality of the sodium hydroxide solution and W is the weight of LM (g).

2) FTIR (fourier transform infrared) spectroscopy

Functional groups in the samples (*in nature*, solid residue, polyol and foam) were identified by FTIR spectra, obtained from a Perkin Elmer FTIR Spectrometer Frontier, with Universal ATR Sampling Accessory. The measurements were carried out within the mid-infrared area (4000 to 500 cm^{-1}).

Samples were directly spread on the surface of the ATR crystal (germanium) and analyzed in transmission mode. The resolution was set to 4 cm^{-1}, 16 scans were recorded and then corrected against the spectrum with ambient air as background. The spectra were treated by software Perkin Elmer Spectrum V 10.03.06.0100.

3) Specific mass

The specific mass was obtained by the technique of pycnometry, from the mass measurement that occupies the known volume of a pycnometer [22], using the relation presented in Equation 4.

$$\rho=\frac{biomass\ (kg)}{Pycnometry\ Volume\ (m^3)} \tag{4}$$

4) Viscosity

The viscosities of the polyols at 25 °C were measured experimentally using Brooksfield Viscosimeter (model DV-II). The triplicate measurements were recorded with an accuracy of ±0.001 MPa s [23].

I. Statistical Analysis

Data obtained from responses (yield liquefaction and hydroxyl number) were submitted to a variance analysis (ANOVA) in order to evaluate the variables and interactions that are significant to the process. ANOVA was performed using Microsoft Excel software and the Electronic Spreadsheets for Calculations of Experimental Planning [24].

Hypothesis tests were performed for a confidence level of 90 % and a level of significance (α) of 10 % [24]. Results of significance were reported using Pareto Chart, prepared using Statistica 7.0 software [25]. Data were also analyzed using Boxplot chart.

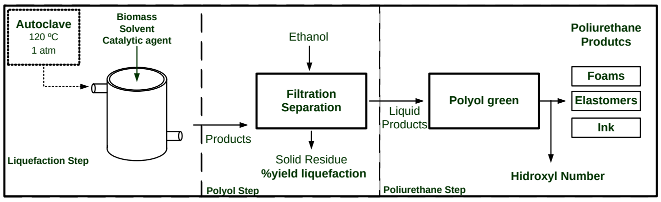

Fig. 1. Schematic flowchart by liquefaction process and foams production.

III. RESULTS AND DISCUSSION

The biomass liquefaction has the objective to transform carbonaceous solid materials into chemicals (as polyols), which depends on physical and chemical properties of the raw material. For this reason, proximate analysis (moisture, ash, volatile matter and fixed carbon content) estimate the use of the biomass to produce polyols, since they direct influence of the biomass composition.

The results from proximate analysis, lignin and holocelulose content and NTK are listed in Table II (% on an oven-dry weight basis).

TABLE II: RESULTS FOR PROXIMATE AND CHEMICAL ANALYSIS (DRY BASE) WITH THEIR RESPECTIVE STANDARD DEVIATIONS

Parameter (%wt)	Lemon Bagasse	Rice Rusk	Cassava Peels
VM	28.57 ±8.28	74.08 ±0.63	93.19 ±0.82
AC	7.17 ±2.72	12.75 ±0.08	2.91 ±0.06
FCC	68.71 ±9.79	13.77 ±0.45	3.31 ±0.84
NTK	1.34 ±0.02	0.38 ±0.02	0.93 ±0.08
MC	4.55 ±0.06	5.6 ±1.7	8.30 ±0.03
HC	35.7 ±0.4	44.7±2.5	10.4 ±0.5
LI	15.55 ±0.01	31.0 ±2.9	11.13 ±0.03
LS	1.60 ±0.22	2.26 ±0.03	0.87 ±0.47

VMC: Volatile Matter Content; AC: Ash Content; FCC: Fixed Carbon Content; NTK: Nitrogen Total Klason; MC: Moisture Content; HC: Holocelulose Content; LI: Lignin Insoluble; LS: Lignin Soluble

The chemical composition is also important information about the biomass, indicating as the content of carbon and hydrogen influence on the biomass liquefaction [10], [21].

Observing the results obtained for volatile matter content, it can be stated that the rice husk and cassava peels have high values of volatile material. However, the lemon bagasse presents low values of volatile material due to the mechanical process used to extract the juice. Thus, there is the reduction of volatile compounds. It was observed high content of volatile matter, which represents organic compounds of low chair that solubility rapidly, since, when exposed to heating.

The volatile matter (VM) can be considered as aromatic, pectin and flavonoid compounds (excluding moisture) that, when heated to a temperature of 493.15 K (120 °C) can be liquefied [9], [20].

The ash content represents the inorganic compounds, which was not solubilized in the liquefaction. The lemon bagasse presented 7 %wt, rice rusk presented 13 wt% and cassava peel presented 3 %wt of ash content, which represent the inorganic compounds and is expected of lignocellulosic residues. Generally, high amount of ash can cause the operational problems due to the formation of inorganic complexes, which reduce the liquefaction yields (biomass conversion) and hydroxyl number [21], [26], [27].

Fixed or non-combined carbon (FC) is the fraction remaining after volatile matter (organic compounds of high chair). The biomass samples were observed a fixes carbon content: 69 wt% for Lemon bagasse; 13 wt% for Rice husk and 3 wt% for Cassava peel. The high concentration of FC in the lemon bagasse may be interpreted according to the structure of the carbon chain of the fruit [8].

Finally, the high nitrogen content reduces the hydrocarbon yield during thermochemical conversion, in the sample were observed lower values of nitrogen, the high concentration of nitrogen reduces the hydrocarbon yield during the thermochemical conversion. The holocellulose and lignin content (insoluble and soluble) is important parameters in considering the application of material in polyols production and PU's foam production [8].

This increase of the molar mass and hydroxyl concentration were the effects responsible for increasing of the polyols viscosity. The increased entanglement of the polymeric chains hinders slipping between chains and, moreover, the incorporated hydroxyls enhance the effects of intermolecular interactions, causing an increase in viscosity [21], [28]-[31].

The results from physical chemical properties of the raw materials for crude glycerol and polyols are listed in Table III.

TABLE III: PHYSICAL CHEMICAL PROPERTIES OF THE RAW MATERIALS FOR CRUDE GLYCEROL AND POLYOLS

Samples	Specific Mass (g/mL)	Viscosity (mPa.s^{-1} at 30 ℃) ^{1}
Crude glycerol	1.29 ± 0.03	115 ± 0.23
Lemon Bagasse	1.38 ± 0.04	150 ± 0.01
Rice Husk	1.31 ± 0.02	140 ± 0.58
Cassava Peels	1.33 ± 0,038	160 ± 0.02

The increase in biomass Specific Mass and Viscosity, compared to crude glycerol, is one of the evidences of biopolyol synthesis (Table III). Also, FTIR were used to identify functional groups and confirm the liquefaction process (Fig. 2).

Therefore, FTIR spectrum was used for the characterization of the raw materials (lemon bagasse, rice husk and cassava peels) and products resulted from bagasse and cotton stalks liquefaction as shown in Fig. 4.

The bands at approximately 3400 cm^{-1} correspond to the vibration of the hydroxyl groups, and the bands at approximately 2920 and 2870 cm^{-1} were assigned to CH_2 and CH_3 stretches of aliphatic chains this increase is due to the rupture in the chemical backbone of the biomass and the functionalization place on cellulose. The bands between 1750 and 1650 cm^{-1} corresponds to the C=O stretching vibration in agreement with the existence of ketone, aldehyde, carboxylic, and esters groups. The bands at 1600 and 1515 cm^{-1} correspond to the vibration of the aromatic rings, and the bands at 1460–1420 cm^{-1}, due to the deformation of the CH on the aromatic ring, were also observed in the lignin spectrum; additionally, several absorption bands were observed below 1400 cm^{-1}, representing the contribution of various vibration modes [1], [6], [7], [21], [28]. Alcohols, ethers and esters at 1250 cm^{-1} and an increase and shift of the absorption in the C–O stretching region (1000–1100 cm^{-1}) at 1046 cm^{-1} reflects the corresponding increase in ether moieties resulting from the treatment. These absorption bands are in agreement with those published for liquefaction of several lignocellulosic materials [1], [32]. The spectra also show an important peak around 1400 cm^{-1}, which may be attributed to inorganic compounds groups.

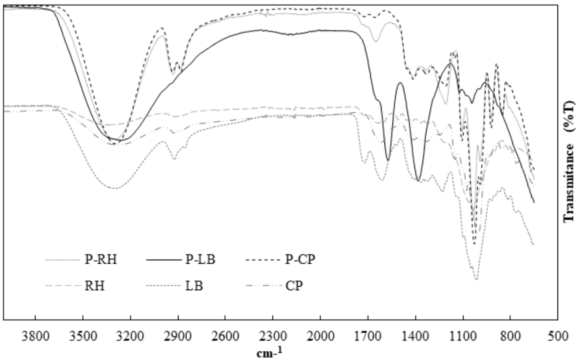

Fig. 2. Spectra of raw materials and polyol (P-RH: Polyol rice husk; P-LB: Polyol lemon bagasse; P-CP: Polyol cassava peels).

Table IV show the yield liquefaction and OH number results for the three biomass, this study was in agreement with the polyols requirements in view of its use in produce polyols suitable for preparation of semi-rigid and rigid polyurethane (between 300 and 1000 mg KOH. g^{-1}) [6], [7], [28], [30], [33].

Evaluating the results presented in Table IV, it was observed a high yield for the three biomass used in this study: about 88.37% for lemon bagasse; 79.02% by weight for rice husks and 91.99% by weight for cassava peels. The hydroxyl numbers and liquefaction yield obtained in this study were in the same range with those obtained during the liquefaction of different lignocellulosic materials [1], [28], [34].

It can be said therefore that the applied liquefaction conditions for lemon bagasse, rice husk and cassava peels produce green polyols appropriate for manufacture of several types of polyurethane products. The influence of the operational parameters and the biomasses characteristics on the liquefaction process will be described bellow.

From analysis of variance (ANOVA) only the catalyst was significant (*p*-value <0.1) for the variables' responses for lemon bagasse. The factors investigated were not significant for rice husk. Evaluating the cassava peels, it was observed that the time and solvent/biomass ratio were significant for hydroxyl number. To visualize the effect of the independent variables on the evaluated responses, Pareto chart were constructed. Pareto analysis is a statistical technique used in decision-making for selecting and prioritizing a small number of items capable of producing large effect on improving processes.

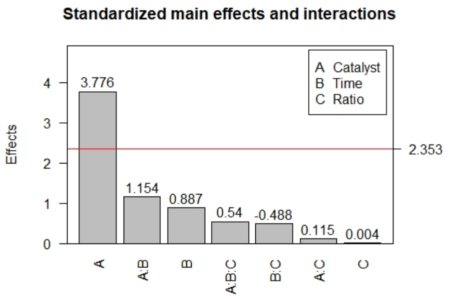

Fig. 3. Pareto plot of the standardized effects of the factors under the liquefaction yield using the Lemon bagasse.

As shown in the Pareto chart (Fig. 3) the catalyst was the main response of the high values from the yield liquefaction for lemon bagasse.

This result was expected, since the process aims at breaking and solubilizing the solid molecules in the organic solvent. Therefore, the catalyst assists in the breaks of the carbon chains [8], [20], [31] .When, we analyses the other results, it is observed that both variables (ratio and time) and interactions were not significant to increase the yield liquefaction.

TABLE IV: PHYSICAL CHEMICAL PROPERTIES OF THE RAW MATERIALS FOR CRUDE GLYCEROL AND POLYOLS

Design Points	Coded independent variable levels[a]			Lemon Bagasse		Rice Husk		Cassava Peels	
	Catalystic Agent X_1 (%)	Time (hours)	Solvent/biomass ratio (w/w%)	Liquefaction yield (%)	Hydroxyl number (mg/g)	Liquefaction yield (%)	Hydroxyl number (mg/g)	Liquefacti on yield (%)	Hydroxyl number (mg/g)
1	2	0.5	2:1	32.19	289.35	75.88	419.96	49.98	256.67
2	7	0.5	2:1	65.06	256.12	35.78	280.60	88.36	300.30
3	2	1.5	2:1	40.41	296.54	58.71	353.42	80.34	109.83
4	7	1.5	2:1	86.52	795.37	68.51	440.02	89.69	475.28
5	2	0.5	5:1	42.09	463.46	79.02	690.02	62.17	622.45
6	7	0.5	5:1	65.79	772.46	65.78	295.17	59.81	579.48
7	2	1.5	5:1	28.12	443.75	64.59	390.19	91.99	305.95
8	7	1.5	5:1	88.37	829.46	60.51	375.08	88.27	105.50
9	5	1.0	3.5:1	77.62	795.78	38.32	198.94	78.22	483.88
10	5	1.0	3.5:1	55.54	624.99	53.10	386.94	84.88	443.46
11	5	1.0	3.5:1	40.69	475.26	38.69	162.95	49.98	256.67

[a] Refer to Table I for uncoded levels of independent variables

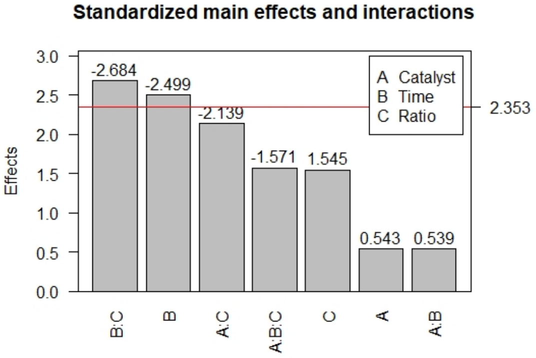

Fig. 3. Pareto plot of the standardized effects of the factors under the production of the number of hydroxyls using the Cassava peels.

A shown Pareto chart, Fig. 4, it was observed the influence of time and solvent/biomass ratio on the hydroxyls number. The hydroxyl numbers decreased with higher reaction time and ratio. The decreases in hydroxyl number are thought to be due to the complexation or repolimerizaton of the lignin with solid residues or liquefied compounds [1], [9] [35]. However, it is highlight that the hydroxyl number is an important parameter for the polyols since it determines the polyurethane product.

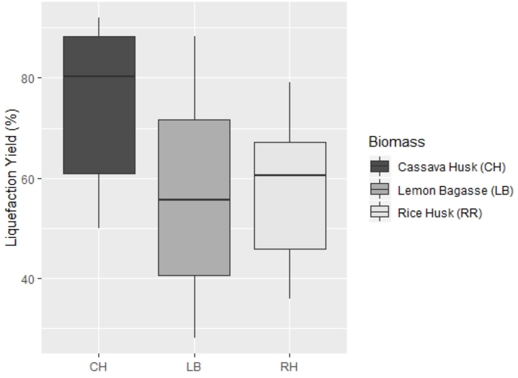

Fig. 5. Boxplot of the distribution of the liquefaction yields using the biomass Lemon Bagasse (LB),Rice Husk (RH) and Cassava Peels (CP).

Boxplot (Fig. 5) presents the average liquefaction yield of the three biomasses. It shows the higher yield for the cassava peels. Since the operational parameters were the same for all biomasses used, it can be stated that the composition influenced the yield. Cassava peel and rice husk have a higher volatile matter content.

The volatile matter represents organic compounds of low chair that solubility rapidly when exposed to heating and contribute to the liquefaction yield. Although the rice husk also presents higher amount of volatile matter, the amount of lignin and ash present in this biomass may have decreased the yield [9].

Boxplot (Fig. 6) presents the average hydroxyl number of the three biomasses. From this chart it can be seen that rice husk presented smaller variation when compared to the other biomass. In this case, regardless the operating parameters used, the hydroxyl number has a well defined range

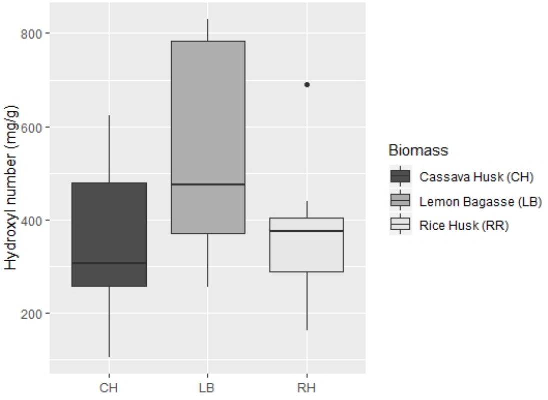

Fig. 6. Boxplot of the hydroxyl number distribution using the biomass cassava peels (CH), lemon bagasse (LB) and rice husk (RH).

Lemon bagasse and cassava peel had more spread results from hydroxyl number. These results indicate hydroxyl number from these biomass can be stated according operational parameters. Hence, the liquefaction from theses biomasses can be investigated and set to fit a larger variety of products (foam, ink, elastomers).

IV. CONCLUSION

Lemon bagasse, rice husk and cassava peel are suitable to produce biopolyol. From the results presented, it was observed that the composition of the lignocellulosic biomass influences the characteristics of the polyols and the yield of the process. It was also observed that among the variables investigated in this study, the catalyst was significant parameter for the yield.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

B.S. Leite, S.A.F. Leite and B.T. Castro conducted the liquefaction process and the biomass characterization. B.S. Leite, D.J.O. Ferreira and V.F.C. Lins writing and reviewing the paper and S.A.F Leite and F.S. Bastos conducted the statistical analysis; all authors had approved the final version.

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