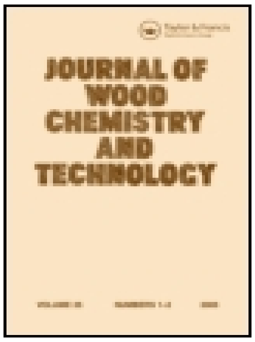

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KRAFT LIGNIN-BASED POLYOLS BY MICROWAVE: OPTIMIZING REACTION CONDITIONS

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Microwave liquefaction of precipitated Kraft lignin was carried out in polyethylene glycol (PEG) and glycerol (G) mixed with or without H_2SO_4 as catalyst. The influences of some independent variables on the yield and hydroxyl index were discussed. The viscosity, molecular distribution (GPC), and the types of volatiles measured by gas chromatography–Mass spectrometry (GC-MS) of all the liquefied products were determined. Response surface methodology (RSM) was used to optimize liquefaction conditions. Based on the results, lignin/solvents (wt%), catalyst/solvents (wt%), and reaction time were chosen as independent variables for a central composite design (CCD). The optimal liquefaction conditions were as: 20 wt% of lignin, 3 wt% of catalyst at 5 min with yield and hydroxyl number of 95.27% and 537.95 mg KOH.g^{-1}, respectively. Functional groups (measured by ATR-IR [attenuated total reflectance – infrared]) and the thermal degradation (TGA) of optimized bio-polyol and precipitated kraft lignin were determined.

KEYWORDS. Biopolymers, renewable source, catalysts, industrial waste

INTRODUCTION

For many years, commercial polyols used in formulations such as polyurethane and phenolic resins were only from petrochemical source. However, concerns about environmental pollution arising from fossil resources exploration and petroleum shortages have intensified biomass research as a possible substitute for commercial polyols.

Lignin is a three dimensional biopolymer widely available in nature, with around 300 billion tons that increase every year.[1] In addition, it is the only renewable raw material available in large volume with phenolic properties and is nontoxic.[2] The major source of industrial lignin is through the Kraft process, of which 90–95% of the lignin is solubilized in aqueous alkaline solution, part of it is burned in the furnace to generate energy, and the remainder is considered process waste. Aspects such as its aromatic properties, being a renewable source and its wide availability make Kraft lignin a strong candidate to substitute petroleum-based polyols in diverse formulations. However, in spite of these favorable aspects the lignin has a low reactivity due to complexity of its structure as drawback. Lignin is mainly constituted by three phenyl propane units—*p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S)—that are formed from dehydrogenation of their alcohols precursors: *p*-coumaryl, coniferyl, and sinapyl alcohols, respectively. The difference between

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Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lwct these phenyl propane units are on the *orto* positions (C3 and C5) of aromatic ring, which on the S units are occupied by methoxy groups, in contrast with H units, that have these positions free and on G units only one of these is occupied by methoxy group. In general, hardwood lignins are composed of S and G units with S/G ratio highly variable and softwood lignins are mainly composed of G units.[3] The concentration of these phenyl propane units and how they are linked to each other through C-O bonds (as β-O-4, α-O-4, 4-O-5) and C-C bonds (as β-5, β-β, 5–5) are strongly dependent on wood specie and environmental conditions. In addition, the extraction processes of lignin interfere in its reactivity functionalized to make it more reactive. The methods used to improve the reactivity of lignin usually involve the creation of new actives sites (as alkylation/dealkylation, animation, and hydroxyalkylation) or the functionalization of hydroxyl groups (as etherification, esterification, and phenolation).[4] Among the thermochemical conversions of biomass (in this case lignin), the liquefaction utilizes simultaneous solvolysis and depolymerization,[5] which can be carried out under mild reaction conditions (moderate temperature about 120–180°C and atmospheric pressure) producing a highly reactive dark liquid, rich in hydroxyl groups.[4, 6]

To prepare polyurethane (PU) films Kurimoto et al.[7] used different amounts of Sugi wood to liquefy (LW) in a constant ratio of glycerol:PEG:sulfuric acid (10:90:3). These authors verified a linear relation between crosslink density and the Tg of LW-PU film, which can be controlled by varying the amount of dissolved woody components at a constant [NCO]/[OH] ratio. Mahmood et al.[8] used hydrolysis lignin-based polyol in synthesis of foams (PU). First, the hydrolysis lignin (HL) was subjected to hydrolytic liquefaction (ethanol–water, 50/50, v/v) with the optimal conditions at 250°C, for 1 h and 20% of HL. Then, it was subjected to oxypropylation with propylene oxide and potassium glycerolate as an initiator at 150°C. Finally, the polyol with glycerol (a co-crosslinking agent), acetone as physical blowing agent, stannous octoate, and triethylene diamine as catalyst, surfactant, and water were used in the production of rigid foam PU. The authors concluded that the percentage of bio-contents of the LHL (liquefied hydrolysis lignin)-based polyols, as well as, the percentage of physical blowing agent have strong influence on the foam properties. In another study, Kraft lignin was liquefied and used to produce flexible foams.[9] The liquefaction of Kraft lignin with glycerol and PEG400 were realized in different lignin/glycerol/PEG400 ratio by microwave heating (at 180 W, 135°C, and 3 min). To produce flexible foam, these authors tested two chain extenders (polypropylene glycol triol or castor oil) for lowering the viscosity and the high OH value of the liquefied lignin.

In the field of phenol-formaldehyde (PF) resins, the chemically modified lignin has been used to substitute the non-renewable phenol in the synthesis of PF resins adhesives for wood which is the focus of our search. Fen et al.[10] used two type of barks (white birch bark, a typical hardwood and white spruce bark, a typical softwood) that were liquefied with water/ethanol (50/50, v/v) mixture at 300°C, 12.0 MPa of pressure for 15 min, to formulate phenol-formaldehyde resole adhesives. The so-called bio-crude were homogenized with water and NaOH (50 wt%) at 80°C for 60 min after formulated with near PF, previously prepared at phenol/formaldehyde ratio of 1:8. The formulations of bio-crude/neat PF varied in a weight ratio of 25:75, 50:50, and 75:25. They reported that the production of new formulated bio-phenol formaldehyde (BPF) adhesives was a success and that the type of the bark (species) interfered in the bio-crude/neat PF ratio to obtain a proper phenol-formaldehyde adhesive. The synthesis of Chinese fir-based adhesives was investigated.[11] First, the liquefaction was carried out with wood powder and a concentration of 25% NaOH solution into autoclave reactor at 200°C for 15 min. After, they used this liquid to prepare resin in weight ratios of Chinese fir to phenol:formaldehyde of 60/40, 55/45, and 50/50. The molar ratio of F to P was of 2:1, 2.5:1, and 3:1. The authors concluded that Chinese fir-based adhesives (CF/PF = 50/50, F/P = 2:1) properties complies with the requirement for exterior applications according JIS K6806-2003 standard.

In this work, newer techniques such as assisted microwave liquefaction, as mentioned above, have been studied[12–14] because it enables a volumetric heating in the system and a considerable reduction in reaction time. Thus, liquefied lignin under microwave may be considered a more environmentally friendly polyol. In this study the precipitated Kraft lignin was subjected to microwave liquefaction with polyhydric alcohols as solvent and sulfuric acid as catalyst. The aim was to obtain Kraft lignin-based polyols taking in account the high yield and an appropriate range of hydroxyl number to be used in future formulations such as phenolic resin adhesives.

EXPERIMENTAL

Materials

The black liquor from pulp and paper Kraft process was supplied by Cellulose Riograndense (CMPC), located in Guaíba/RS, Brazil. Hardwood (*Eucalyptus ssp.*) Kraft lignin was precipitated by adding concentrated sulfuric acid to the black liquor under manual stirring with glass stick until reaching pH6. After about 24 h at room temperature, the precipitated lignin was filtered and washed using acidified water (with sulfuric acid) until obtaining colorless filtrate. The precipitated lignin was dried on over for 24 h at 60°C and was used without further modification. The characterization of Kraft lignin followed the standard methods[15] and bibliographic procedures. The chemicals polyethylene glycol 400 analytical grade, glycerol 99%, NaOH, and sulfuric acid (99%) were purchased of PANREAC; dimethylformamide (DMF, for HPLC ≥ 99.9%), lithium bromide, tetrahydrofuran (THF, high performance liquid chromatography (HPLC) grade), pyridine and 1,4-dioxane analytical grade, and phthalic anhydride 98% were purchased from Fisher Chemicals, all were used without further purification.

Experimental Design

To determine the optimal conditions of Kraft lignin conversion into bio-polyol (based on yield and hydroxyl groups) a central composite design (CCD) was used. The factorial mathematical modeling [Equation (1)] allowed us to estimate the terms of first and second order of a polynomial, based on 27 experiments.

$$y = a_0 + \sum_{i=1}^{n} b_i X_{ni} + \sum_{i=1}^{n} c_i X_{ni}^2 \qquad (1)$$

where Y = dependent variable (yield and hydroxyl index); X = experimental value of variable studied;$_{\mathrm{ni}}$ = independent variable (X_t = time, X_m = mass, X_c = catalyst) normalized of −1 until 1; and a_0, b_i, c_i = are the linear and quadratic interception coefficients of the variables. Table 1 shows the normalized values from Equation (2) for each independent variables. Normalized values are used to better estimate the regression coefficients as the interrelations between the linear and quadratic terms are reduced.

$$X_n = 2 * \frac{X - \bar{X}}{X_{max} - X_{min}} \qquad (2)$$

where X_n = normalized value of independent variable (X_t = time, X_m = mass, X_c = catalyst); X = variable studied; $\bar{X}$ = average of the variable studied; X_{max} = maximum value of the variable studied, and X_{min} = minimum value of the variable studied.

Liquefaction under Microwave Heating

The liquefaction of Kraft lignin was performed in a CEM Microwave Discover System Model, with the temperature controlled (at 160°C) by internal sensor, magnetic stirring, and in the maximum power (300 W). A known amount of polyethylene glycol and glycerol mixed (80/20, w/w) as solvent, catalyst (H_2SO_4), and lignin were added into the vessel. The liquefaction was carried out for a certain time under microwave heating. The amount of H_2SO_4 and lignin were calculated

TABLE 1. Experimental conditions for liquefaction of Kraft lignin by microwave heating and the respective experimental results of dependent variables

Experiment N°	Time (min)	X_t	Catalyst (%)	X_c	Mass (%)	X_m	Yield (%)	I_{OH} (mg KOH.g^{-1})
01	30:00	1	0	−1	20	0	63.79	188.96
02	5:00	−1	3	0	15	−1	93.27	220.15
03	17:30	0	0	−1	20	0	64.94	424.52
04	30:00	1	6	1	20	0	81.67	609.12
05	30:00	1	6	1	15	−1	73.72	467.13
06	17:30	0	3	0	15	−1	94.82	1579.22
07	5:00	−1	6	1	15	−1	82.08	1189.87
08	30:00	1	0	−1	25	1	66.61	671.53
09	5:00	−1	0	−1	20	0	84.16	1152.04
10	17:30	0	0	−1	15	−1	68.06	1401.66
11	5:00	−1	3	0	20	0	95.27	537.95
12	5:00	−1	3	0	25	1	97.69	1147.78
13	17:30	0	3	0	20	0	88.37	1150.76
14	5:00	−1	6	1	25	1	91.90	265.60
15	30:00	1	0	−1	15	−1	69.97	333.05
16	30:00	1	3	0	20	0	95.74	973.31
17	5:00	−1	0	−1	25	1	74.19	1504.29
18	17:30	0	6	1	15	−1	90.65	1196.10
19	17:30	0	3	0	25	1	92.11	1175.69
20	30:00	1	6	1	25	1	80.86	1390.89
21	17:30	0	6	1	25	1	71.49	623.58
22	30:00	1	3	0	25	1	94.22	1651.24
23	17:30	0	0	−1	25	1	68.80	134.84
24	5:00	−1	0	−1	15	−1	75.75	1243.34
25	30:00	1	3	0	15	−1	93.41	1032.71
26	17:30	0	6	1	20	0	86.03	1000.42
27	5:00	−1	6	1	20	0	83.99	1425.34

as weight content (%) based on the quantity of liquefaction solvents. The independent variables (lignin, catalyst, and time) varied according to experimental design (Table 1). When reaction time was reached, the vessel was quickly immersed in cold water to stop the reaction. After cooling, the liquefied mixture was washed several times with acetone until filtrate was colorless and it was filtered under vacuum. Then the acetone was removed from the liquefied product using a rotary evaporator (at 45°C and 0.8 bar). The liquefied product was kept in a vial for later analyses. The residue (solid phase) was dried in oven at 105 ± 5°C for 12 h until constant weight. After it was conditioned in a desiccator and was weighed to determine the yield of liquefied product [Equation (3)]:

$$\eta = \left(1 - \frac{m}{m_o}\right) * 100 \tag{3}$$

where η = yield of liquefied lignin (%); m_o = amount of lignin used in liquefaction (g); and m = solid residue of liquefaction (g).

Acid Values and Hydroxyl Number Determination

The acidity (An) which can interfere in the hydroxyl index (I_{OH}) of the lignin-based polyol was determined by titration method according to standard American Society for Testing Materials (ASTM) D974.[16] 0.4 g of polyol was dissolved in 50 mL of solvent (1.4-Dioxane/water, 4:1, v:v), and phenolphthalein indicator solution 1% in ethanol was added and titrated with 0.1 M KOH solution in ethanol. The amount of milligrams of KOH required to neutralize the acid in one gram of sample was calculated as follows in Equation (4):

$$A_n = \frac{(\mathrm{C} - \mathrm{B}) * M * 56.1}{\mathrm{W}} \tag{4}$$

where An = acid number (mg KOH. g^{-1}); B = volume of the 0.1 M KOH solution in ethanol to titrate the blank (mL); C = 0.1 M KOH solution in ethanol to titrated the sample (mL); M = molarity of the 0.1 M KOH solution in ethanol; 56.1 = molecular weight of KOH; and W = amount of sample (g).

The I_{OH} of liquefied lignin was determined according to standard ASTM D4274[17] as follows: 0.5–1.0 g samples was dissolved in 25 mL of phthalation reagent (115 g of phthalic anhydride dissolve in 700 mL of pyridine) under reflux for 1 h at 115°C. Then, 50 mL of pyridine were added through the condenser. The mixture was titrated with 2 N sodium hydroxide solution (NaOH) using 1% phenolphthalein solution in pyridine as the indicator. The hydroxyl index (hydroxyl number) is defined as the amount of KOH in milligram equivalent to the OH content in 1 g of liquefied product (mg KOH.g^{-1}). Corrected hydroxyl number was calculated using Equation (5):

$$I_{OH} = \frac{(B - A) * N * 56.1}{W} + A_N \qquad (5)$$

where I_{OH} = hydroxyl number (mg KOH. g^{-1}); A = volume of the 2 N NaOH solution to titrate the sample (mL); B = volume of the 2N NaOH solution to titrate the blank (mL); N = normality of 2N NaOH solution; 56.1 = molecular weight of KOH; W = amount of sample (g); and An = acid number (mg KOH. g^{-1}).

Characterization of Liquefied Lignin

Viscosity and Molecular Weight. Dynamic rheological behavior of the polyols was measured with a Rheometric Scientific Advanced Rheometric Expansion System (ARES), using parallel-plate geometry (25 mm diameter), and the upper plate was set at the separation distance (gap) of 0.5 mm. Frequency sweep measurements were carried out at 25°C from 0.1 to 500 rad s^{-1} at a fixed strain. The average molecular weight (Mw) and the polydispersity (PDI) of precipitated Kraft lignin and polyols were analyzed by gel permeation chromatography (GPC). The analysis was carried out using a JASCO instrument equipped with an interface (LC-NetII/ADC) and a refractive index detector (RI-2031 Plus). Two PolarGel-M columns (300 × 7.5 mm^2) and PolarGel-M guard (50 × 7.5 mm^2) were employed. The flowrate of 0.7 mL.min^{-1} and the analyses were carried out at 40°C. The samples were dissolved in DMF and filtered with a filter of 0.2 μL. The calibration was made using polystyrene standards (Sigma Aldrich) ranging from 70.000 to 266 g.mol^{-1}.

Gas Chromatography–Mass Spectrometry (GC-MS). GC-MS analysis was carried out in split mode (10:1) on Agilent 7890A gas chromatograph coupled to a 5975C mass spectrometer using helium as the carrier gas at a flow rate of 1 mL.min^{-1}. Separation was performed using anon-polar HP5-MS fused silica capillary column (30 m × 0.25 × 0.25 μm film thickness). Ionization voltage of mass spectrometer in the EI-mode was equal to 70 eV and ionizations source temperature was 250°C. The samples were diluted in ethyl acetate (HPLC Grade). The temperature program started at 50°C, held 2 min, then, the temperature is raised to 120°C at 10 C.min^{-1}, held 8 min, raised to 280°C at 10 C.min^{-1}, held 8 min. Finally, the temperature was elevated to 300°C at 10°C.min^{-1} and held for 10 min. Compounds were qualitatively identified by comparison of the retention time and mass spectra with available library data (Agilent Techno.). Only those peaks with over 70% of certainty are included. Quantitation was performed by internal calibration curve and the percentage of additional compounds was calculated by the area normalization method. The quantitative results of the compounds were expressed in ppm.

The Optimized Reaction Condition. Surface response methodology is used to show the interaction between the independent variables (time, lignin, and catalyst) in relation to the liquefaction yield and hydroxyl number. The functional groups of optimized polyol were compared with precipitated Kraft lignin by ATR-IR spectroscopy using JASCO model FT/IR-4100 type A equipped with a device of attenuated total reflectance (ATR PRO450-S) with the angle of incidence at 45°. The spectrum was recorded in transmittance mode as a function of wave number (3900–600 cm^{-1}) for 40 scans with a velocity of 2 $mm.sec^{-1}$ and resolution of 4 cm^{-1}. The thermal degradation of both (precipitated Kraft lignin and optimized polyol) were analyzed using an equipment TGA/SDTA RSI Mettler Toledo. Samples ($\sim$5 mg) were heated at 25°C up to 800°C at the rate 10°$C.min^{-1}$, using a constant nitrogen flow (10 $mL.min^{-1}$) as inert atmosphere during the experiment.

RESULTS AND DISCUSSION

Precipitated hardwood Kraft lignin presented the following composition: moisture content 6.07%, 53.7% of ash, and acid insoluble lignin 46.12%. Soluble lignin 8.33% was determined by ultraviolet-visible (UV)-vis spectroscopy. The total sugar was 0.76% ppm (glucose 0.15%, xylose 0.55%, and arabinose 0.06%) and acidic substances 0.21% ppm were determined by HPLC. The Kraft lignin at pH 6 used in this study showed 46.12% purity, lower than those found by Gordobil et al.[18] (58.6% at pH 2), but higher than that verified by Santos et al.[19] (26.88% at pH 6). Usually the impurities in lignin are based on residual ash and carbohydrates. Here, ash is the main impurity in lignin (53.70%). The value of this is higher than that found by Gordobil et al.[18] (22.40%), however, Santos et al.[19] reported higher impurity (71.62%) in Kraft lignin at pH 6 due to the presence of Na_2SO_4 and other salts (not identified in the library) detected by using X-ray diffraction. This can explain the higher ash content in our Kraft lignin precipitated with concentrated sulfuric acid.

Effect of Reaction Conditions on the Liquefied Lignins

Reaction Time. The influence of reaction time on the average results of the polyols are summarized in Table 2. The polyols showed similar yield (around 80%), however, the heating mechanism of microwave increases the reaction rate and lignin decomposition reactions take place in a short time[20,21] which may explain the highest value obtained in the initial stages (86.48% at 5 min) of liquefaction. After this time, the re-polymerization and condensation reactions of lignin fragments increase the residue in the reaction medium[22] and decrease the yield of the liquefied lignin. Sequeiros et al.[23] obtained similar results with 5 min in the liquefaction of organosolv lignin from olive pruning by microwave. Zheng et al.[24] obtained yields close to 100% at 2 min of liquefaction of wood meal *Pinus sp.*

TABLE 2. Effect of reaction time on the liquefied lignins. Conditions: PEG#400:G = 80:20 (w/w), lignin/solvent (15, 20, and 25 wt%), catalyst/solvent (0, 3, and 6 wt%) at 160°C and 300 W

Time (min)	Yield (%)	Hydroxyl number (mg $KOH.g^{-1}$)	Acid number (mg $KOH.g^{-1}$)
05:00	86.48 (8.48)	965.13 (490.58)	24.89 (14.63)
17:50	80.58 (11.99)	1096.31 (366.98)	25.59 (13.60)
30:00	80.00 (12.33)	813.10 (488.82)	27.23 (17.21)

The values in parentheses are the standard deviation.

By definition, the acid number indicates the number of acid functional groups per gram of polyol is one of the important properties thereof due to these functional groups may react with catalysts or other carboxyl groups of copolymers, thus interfering in the reaction of the hydroxyl groups. The average values of acid substances increase as the reaction time increase (Table 2). Results similar to acidity were found by Zheng et al.[24] in the liquefaction of wood in polyhydric alcohols by microwave. This can be attributed to dehydration and/or oxidation reactions of alcohols and depolymerized lignin.[24]

The hydroxyl group content is very important in a polyol because it is related to available active sites to react, for example, with methylol groups for the formulation of phenolic formaldehyde adhesives resin. The hydroxyl groups on average increased from 965.13 to 1096.31 mg $KOH.g^{-1}$ with increasing the time from 5:00 to 17:50 min and decreasing to 813.10 mg $KOH.g^{-1}$ at 30:00 min. This behavior was expected because when the reaction time is long, dehydration, oxidation, and self-condensation reactions of depolymerized lignin are dominant in the reaction medium and may consume many hydroxyl.[25] This might explain the reduction of OH groups while the acid value increases at 30:00 min (Table 2). The results obtained by Kunaver et al.[26] showed almost linear decrease of the values of hydroxyl number (about 800 to 1300 mg KOH.g^{-1}) of the liquefied spruce wood with time. The produced polyols were mixed at different loading (20% and 30%) with melamine-formaldehyde or melamine-urea-formaldehyde resin precursors for particle board preparation.

Lignin: Solvent (wt%). Table 3 shows that the percentage of lignin based on weight of solvents adopted in this study had no influenced on the yield of polyols that was constant (around 82%). Zheng et al.[22] observed that in the liquefaction under microwave heating, the solvent:wood weight ratio did not influenced the liquefaction yield (less 1%).

Acid number has the maximum average values (29.54 mg KOH.g-1) with 15 wt% of lignin and an increase to 25 wt% decreased the amount of acidic substances in the reaction medium to 21.99 mg KOH.g^{-1}. This may occur due to the greater amount of depolymerized lignin reacting with the solvents. In the presence of lower lignin:solvent (15 wt%) oxidation and dehydration reactions appear to be dominant due to the higher value of acid number.

The hydroxyl number decreased from 962.58 to 829.14 mg KOH.g^{-1} with increasing the lignin:solvent from 15 to 20 wt%. However, 25 wt% of lignin increased the hydroxyl number to 1082.83 mg KOH.g^{-1}. This increase can be due to both the increase of lignin and the smaller amount of acidic substances (Table 3).

TABLE 3. Effect of lignin:solvent (wt%) on the liquefied lignins

Mass (%)	Yield (%)	Hydroxyl number (mg KOH.g^{-1})	Acid number (mg KOH.g^{-1})
15	82.41 (10.85)	962.58 (494.46)	29.54 (19.12)
20	82.66 (11.45)	829.14 (406.17)	26.18 (12.09)
25	81.99 (12.14)	1082.83 (462.36)	21.99 (12.42)

Conditions: PEG#400:G = 80:20 (w/w), reaction time (5:00, 17:30, 30:00 min), catalyst:solvent (0, 3 and 6 wt%) at 160°C, 300 W.

The values in parentheses are the standard deviation.

TABLE 4. Effect of catalyst:solvent (wt%) on the liquefied lignins

Catalyst (%)	Yield (%)	Hydroxyl number (mg KOH.g^{-1})	Acid number (mg KOH.g^{-1})
0	70.70 (6.40)	914.91 (509.12)	11.83 (5.68)
3	93.89 (2.62)	1052.09 (451.95)	24.74 (6.53)
6	82.49 (6.81)	907.54 (425.46)	41.14 (11.73)

Conditions: PEG#400:G = 80:20 (w/w), reaction time (5:00, 17:30, 30:00 min), lignin:solvent (15, 20, 25 wt%), at 160°C, 300 W.

The values in parentheses are the standard deviation.

Catalyst: Solvent (wt%). The experiments carried out without catalyst showed the lowest yield (70.70%, Table 4). With the addition of 3% of sulfuric acid the yield of liquefied lignin increased to 93.88%, representing an increase of 23.18% in the average yield. During the lignin liquefaction process, the solvolysis reactions are very important for the decomposition of lignin. In addition, the use of catalyst provides higher reaction rates, at relatively moderate temperature (160°C) and with less residue in the reaction medium.[27] Zheng et al.[24] obtained only 10.49% of yield on wood meal liquefaction without catalyst and with addition of 0.5% sulfuric acid these authors had the best yield (99.94%). Zhuang et al.[28] found maximum yield on algae liquefaction using 6% sulfuric acid.

Acid number increases with the addition of catalyst (11.83–41.14% without and with 6% of catalyst, respectively, Table 4). This can be explained by the strong acidity and oxidation characteristics of sulfuric acid that influences the formation of acidic substances in the polyols.

The amount of hydroxyl groups increased from 917.91 to 1052.09 mg KOH.g^{-1} with the increment of 0–3% sulfuric acid in the reaction medium. Addition of 6% sulfuric acid decreases the hydroxyl number (907.54 mg KOH.g^{-1}) showing values similar to those without catalyst (Table 4).

Characterization of Liquefied Lignin

Viscosity and Molecular Weight. Viscosity is also an important characteristic in a polyol and is intrinsically linkage with the

TABLE 5. Weight-average (M_w), number-average (M_n) molecular weight and polydispersity (PDI) of liquefied lignins and precipitated lignin

Experiment	M_w	M_n	PDI	Experiment	M_w	M_n	PDI
1M*	1241	434	2.8573	15M*	1116	440	2.5389
2M**	2080	603	3.4468	16M**	2723	666	4.0905
3M*	1019	442	2.3074	17M*	1816	496	3.6573
4M***	3202	660	4.8476	18M***	2784	648	4.2937
5M***	3170	633	5.0050	19M**	2822	669	4.2199
6M**	2063	578	3.5659	20M***	5240	673	7.7810
7M***	3476	649	5.3553	22M**	2234	562	3.9775
8M*	1366	481	2.8381	23M*	1688	496	3.4025
9M*	1508	470	3.2087	24M*	1087	440	2.4716
10M*	1187	445	2.6691	25M**	837	526	1.5923
11M**	1775	505	3.5129	26M***	3433	649	5.2859
13M**	2691	645	4.1704	KL	7474	965	7.7418
14M***	2505	601	4.1660				

*Without catalyst **3% of catalyst ***6% of catalyst.

molecular weight. In our study, the viscosities of the polyols were analyzed taking in account the independent variable that was statistically different (Table 7). The viscosities of polyols are presented as a function of catalyst variable in Figure 1. The results of all polyols without catalyst showed lower viscosity (average of 0.093 Pa.s) than those with the catalyst (average 0.223, and 0.311 Pa.s for 3% and 6% H_2SO_4, respectively).

Gel permeation chromatography was used to study the molecular weight distribution of the precipitated lignin and of the polyols under different reaction conditions by microwave heating (Table 5 and Figure 2). The polyols 12M**, 21M***, and 27M*** were not analyzed because we did not have enough quantity. The chromatograms of the polyols and precipitated lignin, in general, show three distinct molecular weight groups (Figure 2). The first group (A) represents the peaks with the higher molecular weights eluting between 20.0 and 23.5 min. The second group (B) has peaks with lower molecular weight eluting between 23.5 and 26.3 min, and the third group (C) shows peaks with the lowest molecular weight range between 26.3 and 28.0 min. In some cases, as the precipitated lignin and the polyols 4M***, 5M***, 11M**, and 14M***, the lowest molecular weight appear subdivided in other group (D) eluting between 28.0 and 29.0. All polyols analyzed showed M_w and M_n less than the precipitated lignin (M_w = 7474 and M_n = 965) suggesting a high degree of depolymerization by microwave heating. As a normal trend in polymer degradation polydispersity (PDI) also decreased[29] compared with precipitated lignin, except the polyol 20M*** that presents PDI = 7.7810 which is very similar to precipitated lignin (PDI = 7.7418, Table 5).

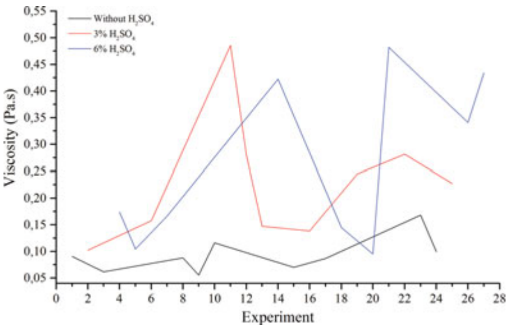

FIGURE 1. Influence of catalyst:solvent (wt%) on the viscosity of polyols. Conditions: PEG#400:G = 80:20 (w/w), reaction time (5:00, 17:30, 30:00 min), lignin:solvent (15, 20, 25 wt%), at 160°C, 300 W.

The influence of catalyst (only independent variable statistically significant, Table 7) on the molecular weight distribution of the polyols is shown in Figure 2. Reaction conditions without and with 3% catalyst (Figure 2a and b, respectively) do not appear to have affected the molecular weight distribution in the polyols, as

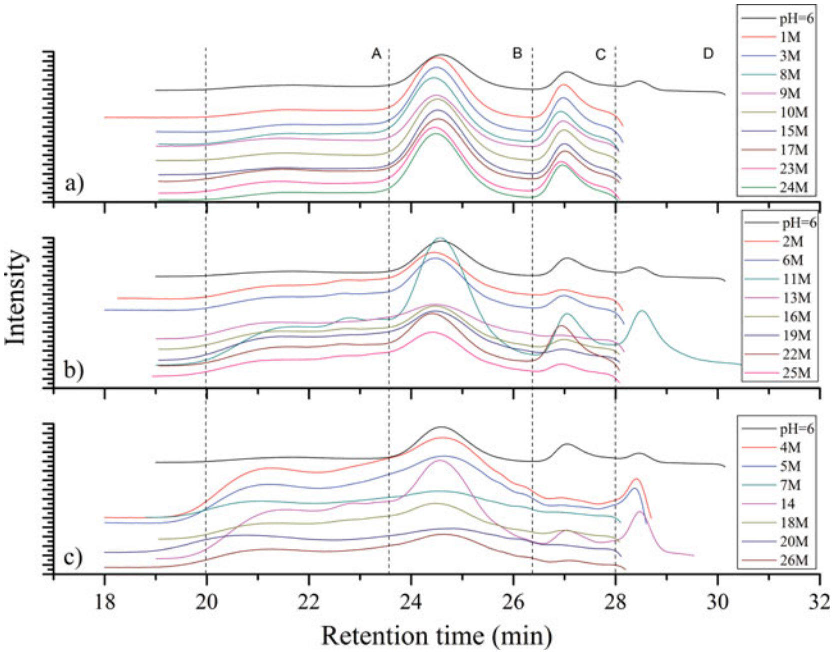

FIGURE 2. GPC chromatograms of the polyols and Kraft lignin as a function catalyst. Molecular weight range (a) 10470 – 1072 g.mol^{-1} (eluting between 20.0 and 23.5 min) ; (b) 1072 – 241 g.mol^{-1} (eluting between 23.5 and 26.3 min); (c) 241 – 253 g.mol^{-1} (eluting between 26.3 and 28.0 min); and (d) 435 – 332 g.mol^{-1} (eluting between 28.0 and 29.0 min). Conditions: reaction time (5:00, 17:30 and 30:00 min), lignin/solvent (15, 20 and 25 wt%) at 160°C and 300 W.

both conditions (without and 3% of catalyst) showed a similar pattern, except the polyol 11M** (Figure 2b) which shows a peak in the group D. The molecular weight distribution of polyols without (∗) catalyst comprises, in average, 80% of structures low molecular such as phenolic methylols (dimers, trimers, and oligomers). These structures of low molecular weight comprises between 61.73% (19M**) and 74.70% (13M**) of the polyols with the addition of 3% of catalyst. On the other hand, an increase of 6% of catalyst causes changes in the behavior of molecular weight distribution of the polyols (Figure 2c). Maybe it is possible that the liquefaction from purer Kraft lignin gives a polyol with lower molecular weight and PDI. It is to be mentioned that the molecular weight is one of the properties required in the polyol and varies depending on its application.

GC-MS of Polyols. To further investigate the influence of independent variables on polyols the volatile compounds of the polyols were investigated. The polyols presented traces of alcohols, acids, aldehydes, ketones, esters, ethers, and aromatic derivatives as principal chemical species formed from solvolysis reactions (polyethylene glycol and glycerol) and Kraft lignin mixture (Table 6). The polyols 12M** and 21M*** were not analyzed because they did not have enough quantity. Esters compounds such as ethyl 2-methyl butyrate and ethyl valerate were identified in almost all samples, except the last one, which was not found in the samples 16M**, 19M**, 22M**, and 25M**. In alcohols compounds, glycerol was found in all samples in the absence of catalyst and in sample 14M*** (with 6% of catalyst). With 3% of catalyst just the samples 13M** and 16M** do not contain glycerol. The others alcohols compounds are mainly formed in the presence of 6% catalyst, as well as, the ethers. The aromatic compounds identified were mainly lignin derivatives. In this group only the *n*-xylol was identified in all samples (with and without catalyst) except in sample 10M∗. Traces of lignin units such as syringol and guaiacol were identified. The syringol were found in all samples except in samples 2M**,

TABLE 6. Composition analysis of liquefied lignins under different catalyst loading

Name of compound	RT[a] (min)	Mw	Without catalyst	With catalyst
Acids				
Acid vanileic	16.04	168	Only 23M*	ND
Lauric acid	17.90	200	ND	Only 4M***
Esters				
Ethyl butyrate	3.40	116	Except 8M*, 23M*, 24M*	Only 11M**
Butyl acetate	3.53	116	Except 8M*, 23M*, 24M*	Except 20M***
Ethyl 2-methyl butyrate	3.95	130	All	All
Ethyl valerate	4.56	130	All	Except 16M**, 19M**, 22M**, 25M**,
Methyltriglycol acetate	5.74	206	ND	Only 5M**, 7M**
2-(2-Hydroxyethoxy)ethyl acetate	7.72	148	ND	Only 27M***
Aldehydes/Ketones				
Mesityl oxide	3.41	98	ND	Except 11M**
Acetaldehyde-di-sec-butylacetal	9.85	174	ND	Only 2M**
4-Methyl-2,5-dimethoxybenzoldehyde	18.15	180	Only 8M*	ND
Syringaldehyde	19.57	182	Only 3M*, *M*, 10M*, 24M*	Only 11M**
Alcohols				
Glycerolformal	4.31	104	ND	Only 11M**
4-Methylmannitol	4.58	196	ND	Only 19M**, 25M**
Diethylene glycol	5.59	106	ND	Only 2M**, 13M**, 20***, 26M***, 27M***
Glycerol	7.31	92	All	Except 13M** and, 16M**. Only14M***
Glycerol acetone	5.11	132	ND	Except 20M***, 26M***, 27M***
Methyl carbitol	5.07	120	ND	Only 4M***, 5M***, 7M***, 20M***, 26M***, 27M***
Methyltriglycol acetate	5.74	206	ND	Only 5M***, 7M***
Trielethylene glicol mononetyl ether acetate	5.70	206	ND	Only 4M***, 5M***, 7M***, 14M***, 18M***, 20M***, 26M***, 27M***
Triethyelene glycol	10.43	150	Only 1M*, 24M*	Only 2M**, 6M**, 4M***, 5M***, 7M***, 20M***, 26M***, 27M***
Diethyl glicol butyl ether	9.14	162	ND	Only 4M***
Methoxytriglycol	9.80	164	ND	Only 4M***, 5M***, 20M***, 26M***, 27M***
Tetraethylene glycol	17.18	194	Only 1M*, 24M*	Only 2M**, 25M**, 4M***, 5M***, 20M***, 26M***, 27M***
2-[2-(2-(2-Methoxyethoxy)ethoxy)ethoxy]ethanol	17.00	208	ND	Only 20M***

(*Continued on next page*)

TABLE 6. Continued

Name of compound	RT^a (min)	Mw	Without catalyst	With catalyst
Pentaethylene glycol	21.13	238	Only 1M*, 24M*	Only 26M***,27M***
Hexaethylene glycol	24.01	282	Only 23M*, 24M*	Only 25M**, 4M***, 27M***
Octaethyelene glycol	24.14	370	Only 1M*, 24M*	Only 26***
β-Sitosterol	38.75	414	Only 23M*, 24M*	ND
Ethers				
Propane,1,1-diethoxy	4.87	132	ND	Only 13M**
p-Thioxane	4.44	104	ND	Only 7M***, 20M***
15-Crown-5 ether	12.82	220	ND	Only 13M**, 19M**
12-Crown-4	12.70	176	ND	Only 4M***, 5M***, 7M***, 14M***, 18M***, 20M***, 26M***, 27M***,
18-Crown-6	25.14	264	ND	only 13M**, 7M***, 14M***, 18M***
Aromatic compounds				
n-Xylol	4.24	106	Except 10M*	All
Guaiacol	7.37	109	Only 23M*	Only 19M**, 22M**
o-Acetyl-*p*-cresol	10.89	150	ND	Except 2M**, 13M**, 16M**, 19M**
p-Ethylguaiacol	11.70	152	Only 23M*	ND
Syringol	13.92	154	All	Except 2M**, 16M**, 25M**, 18M***, 26M***
Benzene-1,2,3-trimethoxy-5-methyl	17.52	182	Only 15M*, 17M*, 23M*	ND
Acetosyringone	20.50	196	Except 15M*, 17M*	Only 11M**, 19M**, 22M**, 14M***
Others				
DMSO	3.76	78	Only 23M*, 24M*	Only 25M**, 4M***
Acetonyldimethylcarbonil	3.88	116	All	Except 25M**
1,2-Methyl-2-cyclopentenone	4.70	96	ND	Only 7M***, 20M***, 26M***, 27M***
Acetin	7.44	134	Only 24M*	ND
1,3-Dioxolane-4-metanol,2-ethyl	6.82	132	ND	Only 19M**
4,4,6-Trimethyl-3,7,9-trioxabicyclo[4,2,1]nonane	7.97	172	ND	Only 2M**
1,2-(3,4-Dimethoxyphenyl)-6-methyl-3,4-chromonediol	18.16	316	Only 9M*	ND

All = mean that the compound was identified in all samples in relation to catalyst loading, Except = when the compound was not identified in relation to catalyst loading, Only = mean that the compound was identified just in mentioned sample in relation to catalyst loading, ND = no detected * = Without catalyst **= 3% of catalyst ***= 6% of catalyst.

16M**, 25M**, 18M***, and 26M***, on the other hand, the guaiacol units were found only in samples 25M*, 19M**, and 22M**. The acetosyringone was found in almost all samples in the absence of catalyst, except in samples 15M* and 17M*. Traces of acetosyringone were detected in samples 11M**, 19M**, 22M** and 14M***. The presence of these compounds, mainly, syringol, guaiacol, and acetosyringone demonstrate that in the absence of catalyst, in

TABLE 7. Compounds volatile identified quantitatively in the polyols.

Experiment	Glycerol (ppm)	Guaiacol (ppm)	Syringol (ppm)	Acetosyringone (ppm)
3M*	0.64	ND	1.26	1.26
4M***	4.18	ND	ND	ND
5M***	0.05	ND	ND	ND
7M***	0.05	ND	ND	ND
8M*	0.05	ND	5.00	1.56
9M*	0.07	ND	ND	ND
10M*	0.07	ND	ND	ND
14M***	0.14	ND	ND	ND
15M*	0.11	ND	5.88	ND
17M*	0.16	ND	3.93	ND
18M***	0.08	ND	ND	ND
20M***	1.39	ND	ND	ND
22M**	146.47	ND	ND	1.15
23M*	ND	2.83	13.33	ND
25M**	170.40	ND	ND	ND
26M***	34.71	ND	ND	ND
27M***	16.52	ND	ND	ND

*Without catalyst **3% of catalyst ***6% of catalyst ND = not detected.

TABLE 8. Yield variance analysis (ANOVA) of polyols by microwave heating.

Source	Sum of squares	Df	Average square	F rate	P value
Main effect					
A: Catalyst	2418.39	2	1209.19	34.51	0.0001*
B: Mass	2.11036	2	1.05518	0.03	0.9704
C: Time	231.164	2	115.582	3.30	0.0902
Interactions					
AB	14.4611	4	3.61527	0.10	0.9782
AC	111.755	4	27.9388	0.80	0.5592
BC	114.17	4	28.5425	0.81	0.5501
Residue	280.291	8	35.0364		
Corrected total	3172.34	26			

F = rate are based on average square residual error
*Significant at 95% confidence level.

general, the depolymerization of lignin is not complete and with 6% of catalyst the depolymerization is more severe.

Table 7 shows the volatiles identified quantitatively. It can be verified based on the catalyst variable that in general, both in the absence and with 6% catalyst the glycerol did not completely react. Although samples 22M** and 25M** (with 3% catalyst) showed the highest amounts of glycerol. The quantitative identification of lignin derivatives (guaiacol, syringol, and acetosyringone) in the liquefaction without catalyst is corroborated with the yield results based on the variable catalyst.

Optimized Reaction Condition of Liquefied Lignin

Both yield and hydroxyl number of polyols were analyzed as a function of the independent variables (reaction time, lignin:solvent, and catalyst:solvent) to determine the best reaction conditions. Experiments were carried out following the experimental design mentioned above and shown in Table 1.

The results of independent variables analyzed (by ANOVA (analysis of variance)) in relation to yield showed that only the catalyst is significantly different ($p < 0.05$, Table 8). The adjusted model for the yield as a function of catalyst explains 81.14% ($R_{2aj} = 81.14\%$) of the evaluated data. Equation (6) predicts the behavior yield of polyols:

$$yield = 69.1337 + 14.330 * cat - 2.01419 * cat^2 \tag{6}$$

Figures 3 and 4 show the response surface for the yield as a function of catalyst vs. mass and/or catalyst vs. time, respectively. It

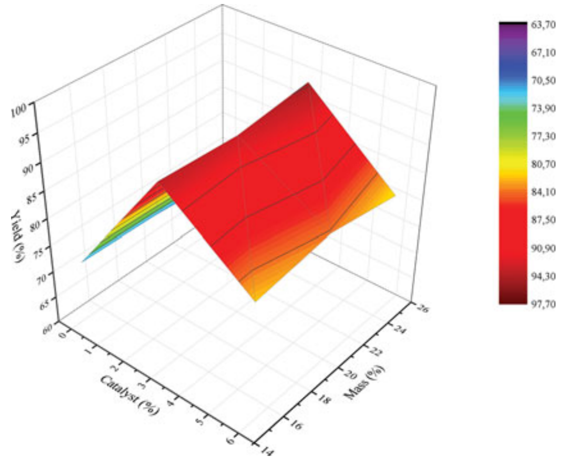

FIGURE 3. Influence of the independent variables (catalyst vs. mass) on the yield of polyols.

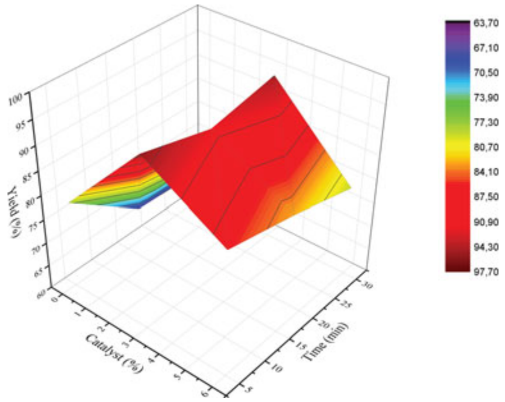

FIGURE 4. Influence of the independent variables (catalyst vs. time) on the yield of polyols.

TABLE 9. Hydroxyl number variance analysis (ANOVA) of polyols by microwave heating.

Source	Sum of squares	Df	Average square	F rate	P value
Main effect					
A: Catalyst	111,302	2	59,651	0.45	0.6539
B: Mass	289,876	2	144,938	1.09	0.3817
C: Time	361,583	2	180,791	1.36	0.3105
Interactions					
AB	676,507	4	169,127	1.27	0.3571
AC	1.76272	4	440,681	3.31	0.0702
BC	1.00115	4	250,288	1.88	0.2073
Residue	1.0647	8	133,087		
Corrected total	5.27584	26			

F = rate are based on average square residual error.

was observed that the response surface is convex and well-defined nature, suggesting that the optimal response value based on the combined effects (catalyst vs. mass and catalyst vs. time) can be obtained for several combinations of the variables.

Interaction between catalyst vs. mass (Figure 3) shows significant changes in the yield of polyol relative to the catalyst, unlike the mass variable that remained practically unchanged. Since mass variable does not influence significantly in yield results, a greater amount of lignin in the reaction medium means less solvent, which can be economically attractive. Thus, the optimal reaction conditions for yield as a function of catalyst vs. mass were determined in the presence of 3 wt% sulfuric acid and 20 wt% lignin.

Figure 4 shows the yield based on the interaction of the catalyst vs. time. As can be seen the catalyst have more influence than the time on the yield. Considering the catalyst vs. time variables, the optimum reaction conditions for the yield were determined with 3 wt% sulfuric acid at 5 min of reaction by microwave heating.

Although the statistical results of hydroxyl number as a function of independent variables were not statistically significant ($p > 0.05$, Table 9), it was taken into account to determine the optimal conditions of liquefaction because it is one of the important properties of liquefied product. The higher variety of hydroxyl values in this work, may be due to the higher ash content (different salts) present in the Kraft lignin precipitated at moderate pH. Polyol with hydroxyl number between 800 and 800 1300 mg KOH.g^{-1} are reported in the literature as suitable for formulations such as formaldehyde resin.[26]

Based on yield and hydroxyl number of liquefied lignins the optimized conditions of liquefaction was lignin 20 wt% and catalyst 3 wt% at 5 min (experiment n° 11).

Characterization of Optimized Liquefied Lignin

ATR-IR Analysis. Analysis of the ATR-IR spectra of the precipitated Kraft lignin and optimized lignin-based polyol (experiment n° 11M) are shown in Figure 5. Structural changes are observed in the spectra polyol (11M*) in the region between 3500–3300 cm^{-1} band related to the stretching vibration O-H of the hydroxyl group increased. Stretching vibration peaks at 2930–2880 cm^{-1} are assigned to vibrations of aliphatic C-H bonds of methylene and methyl groups, which increase in polyol spectrum. The increase of these peaks might be due to the polyethylene glycol and glycerol (methylene) and the degradation of lignin in the presence of sulfuric acid (methyl).[29,30] The intensity of the peak at 1110 cm^{-1} increased due to vibration caused by the deformation of the C-H bonds in the syringyl structure.

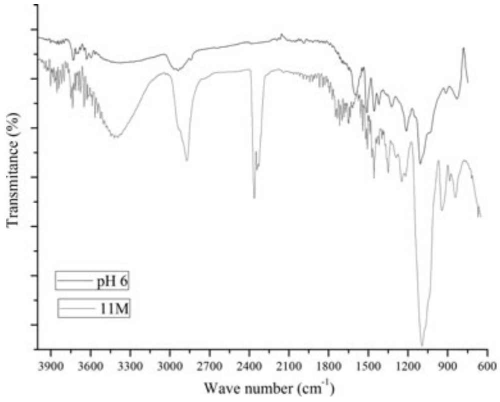

FIGURE 5. FT-IR spectra of the precipitated lignin and optimized lignin-based polyol (experiment n° 11M**).

TGA. The thermal properties of Kraft lignin and optimized Kraft lignin-based polyol (11M*) were investigated. The weight loss as a function to the temperature of thermal degradation (precipitated lignin and polyol 11M*) and the weight loss rate curves are shown in Figure 6a and b, respectively. First step of weight loss that refer to moisture content occurred for both precipitated lignin and polyol ranging from 40°C to 125°C. DTG curves of Kraft lignin showed a slight weight loss ranging from 185°C to 260°C corresponding to the decomposition of hemicellulose.[31] This confirm the low sugar content (0.76% ppm) found in Kraft lignin. However, optimized polyol showed a broad peak ranging from 230°C to 298°C due to the decomposition of liquefaction solvents glycerol and polyethylene glycol.

The maximum weight loss ratio to Kraft lignin was observed at 303°C while to polyol 11M occurred at 382°C. The range of weight loss at about 260–425°C is related to the structural decomposition of lignin with the break down of the inter-units linkages.[28]

CONCLUSIONS

Precipitated Kraft lignin was liquefied using polyhydric alcohols with or without catalyst by microwave heating. Liquefied lignins showed lower Mw and PDI than precipitated lignin. The volatile compounds present in the liquefied lignins are mainly due to the solvolysis and lignin derived. In general, the polyols have suitable hydroxyl groups and can be used directly as precursors in phenolic resin adhesives synthesis. The optimized reaction conditions were determined based on the yield and hydroxyl groups of liquefied lignins. The results showed that between the three independent variables chosen (time, lignin and catalyst) only the catalyst affects the yield significantly. With respect to the hydroxyl number, the independent variables were not statistically different. But based on yield and hydroxyl number, the liquefaction with 20 wt% of lignin and 3 wt% of catalyst at 5 min is the optimal reaction conditions.

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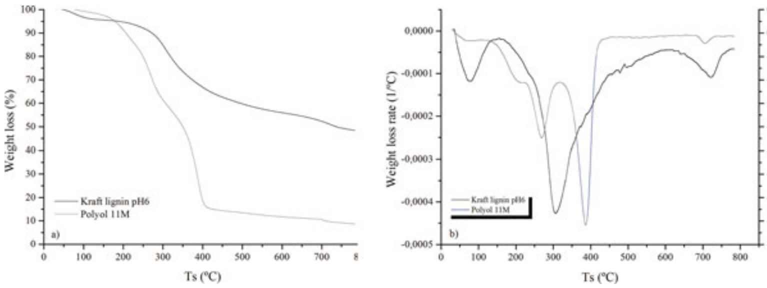

FIGURE 6. Profile of thermal degradation of precipitated lignin at pH 6 and optimized polyol: a) TGA curves and b) DTG curves.

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