

Liquefaction of Kraft Lignin at Atmospheric Pressure

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Abstract: Kraft lignin was liquefied using polyethylene glycol #400 (PEG) and glycerol (G) in a weight ratio of 80/20 (w/w) and sulphuric acid (SA) as catalyst under atmospheric pressure at 160°C. The three independent variables: reaction time (60, 80 and 100 min), percentage of lignin (15, 20 and 25%, w/w), and catalyst concentration (0, 3 and 6%, w/w), were varied resulting in 27 experimental runs. The effect of these reaction conditions on the properties of the polyols was evaluated. The statistical analysis showed that only “the percentage of lignin” did not influence the properties of the liquefied products, however, reaction time and catalyst load were important parameters. The resulting liquefied products were characterized by FTIR analysis.

Keywords: Biopolyols; Kraft lignin; liquefaction; renewable resource; thermochemical conversion

1 Introduction

For many years, the world economy was mainly based on petrochemical resources. However, the exponential growth of population and the price of the petroleum encourage the scientific community to search for new renewable resources for the production of energy, fuel and chemicals.

Lignin is the main aromatic compound available in abundance in nature. It consists of phenylpropane units which are linked one each other mainly by β -O-4', as well as other ether and C-C linkages, such as α -O-4', 4-O-5', β - β ', 5-5' bonds. These structure forms a building blocks which results in a three-dimensional biopolymer [1,2]. Industrially, Kraft pulping process is the main source of lignin. This lignin is dissolved in the black liquor and it is considered as a waste in the process. Although, this lignin is burned to provide power to the plant, there is an excess of lignin that can be used as renewable resource. Lignin has great potential to substitute petrochemical phenol due to its aromatic structure, as in formulations of phenolic resins. However, lignin is less reactive than phenol, due to its macromolecule complex structure and few active sites. One strategy is to increase the active sites of lignin increasing the content of hydroxyl groups. Therefore, chemical modifications are necessary. Among the biomass conversion processes, the liquefaction is particularly attractive thermochemical conversion process, since it can be performed at relative short time, low temperature and at atmospheric pressure. The liquefaction can be carried out with polyhydric alcohols as solvent and with or without catalyst to convert the lignocellulosic material to a polyol rich in OH groups, making it much more reactive. Red pine wood [3], acid hydrolysis residue (AHR) of corn [4], enzymatic hydrolysis lignin (EHL) [5] and oil palm empty fruit bunch [6] are some of liquefied lignocellulosic materials mentioned in the literature using alcohols solvents and sulphuric acid as catalyst. In the literature, some works have been also reported about the potential use of Kraft lignin in liquefaction process using acid-based and metal oxide catalysts [7,8].

In the present work, the main objective is to study the influence of different liquefaction parameters (lignin load, catalyst concentration and reaction time) in the properties of obtained polyols by statistical analysis. Besides that, this work aims to impulse the valorisation of industry byproducts, Kraft lignin, for valuable biopolyols production. For that, Kraft lignin was liquefied under atmospheric pressure using polyethylene glycol and glycerol as solvent and sulfuric acid as catalyst. The effect of the amount of lignin, sulphuric acid as catalyst and the reaction time on the liquefied products were evaluated.

2 Materials and Methods

Materials: Kraft lignin (KL) was precipitated from black liquor provided by CMPC-Cellulose Riograndense (Brazil) using sulfuric acid. The chemicals polyethylene glycol#400 analytical grade, glycerol 99% for synthesis and sulfuric acids 96% technical grade were purchased of PanReac AppliChem. All reagents were used as received.

Liquefaction of Kraft lignin: Kraft lignin was liquefied using polyhydric alcohols such as polyethylene glycol #400 (PEG) and glycerol (G) in a weight ratio of 80/20 (w/w) and sulfuric acid (SA) as catalyst under atmospheric pressure. The solvents and SA were added together into a neck flask reactor with magnetic stirrer, temperature control and condenser. When the temperature reached 160°C, the Kraft lignin was added into the flask and the time started to run. Then, the reactor was immersed in a cooled water bath to quench the reaction. Liquefied mixture was washed with acetone under vacuum. Solid residue was dried in oven at 105°C for 24 h and weighted to determine the process conversion yield. Acetone was removed by rotary evaporator under reduced pressure.

The independent variables such as reaction time (60, 80 and 100 min), percentage of lignin (15, 20 and 25%, w/w), and catalyst concentration (0, 3 and 6%, w/w) respect to the weight of solvents, were varied resulting in 27 experimental runs (Tab. 1) (elaborated through experimental design). The effect of these reaction conditions on the properties of the polyols were evaluated.

Table 1: Different reaction conditions (Rt = reaction time, Mass = percentage of lignin and Cat = percentage of catalyst) of liquefaction of Kraft lignin at 160°C and atmospheric pressure

Sample	Rt (min)	Mass (%)	Cat (%)	Sample	Rt (min)	Mass (%)	Cat (%)
1C	80	25	3	15C	100	25	3
2C	60	20	0	16C	100	15	3
3C	60	25	6	17C	80	15	6
4C	60	20	3	18C	80	15	3
5C	80	20	0	19C	100	15	6
6C	80	25	0	20C	60	25	0
7C	60	15	6	21C	80	20	3
8C	60	15	0	22C	100	25	0
9C	80	15	0	23C	60	15	3
10C	100	15	0	24C	60	20	6
11C	100	20	6	25C	100	25	6
12C	60	25	3	26C	80	25	6
13C	100	20	0	27C	100	20	3
14C	80	20	6				

The liquefaction yield was calculated as follows:

$$\text{Yield} = (1 - m/m_0) * 100 \quad (1)$$

where: Yield = yield of liquefied Kraft lignin (%); m_0 = amount of lignin used in liquefaction (g); m = solid residue of liquefaction (g).

Characterization of polyols: The acid number (An) and hydroxyl number (OHn) were determined by titration method according to the standard ASTM D974 [9] and ASTM D4274 [10], respectively. 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 changes in the chemical structure was evaluated by Spectrum Two FT-IR Spectrometer (ATR-IR), with a L1050231 Universal Attenuated Total Reflectance accessory using a Perkin-Elmer instrument with the angle of incidence at 45°. Spectra were recorded over 20 scans with velocity of 2 $\text{mm}\cdot\text{sec}^{-1}$, resolution of 4 cm^{-1} in a wavelength range from 4000 to 600 cm^{-1} .

3 Results and Discussion

The results of yield, OHn , An and viscosity of the 27 polyols, are shown in the Tabs. 2-4 and the standardized statistical effects of the reaction time, amount of lignin and catalyst and its interactions (reaction conditions) are shown in Fig. 1. As it can be observed in Tab. 2, the liquefaction yield varied from 61.97% with 15% of lignin, 6% of SA at 60 min, to 98.88% with 20% of lignin, 3% of SA at 60 min (Tab. 2). Barnes et al. [11] obtained yield around 95% for the liquefaction of organosolv lignin at higher temperature (300°C) using water and methylnaphthalene as solvent for 60 min. Jin et al. [5] obtained yield over 90% using SA as catalyst in a mass ratio range from 10 to 20 to EHL w/w, this ratio is bigger than those used in this study. On the other hand, in Fig. 1, it can be seen that only the catalytic interaction differs statistically into the yield of the polyols (Fig. 1(a)).

Table 2: Values of the yield of the polyols

Catalyst (%)	Time (min)	Yield (%)		
		Weight of lignin (%)		
		15	20	25
0	60	68.32	68.41	96.70
	80	81.58	78.62	94.13
	100	81.68	67.78	70.30
3	60	95.70	98.88	95.40
	80	97.90	97.26	93.19
	100	98.17	96.80	92.10
6	60	61.97	95.88	79.79
	80	82.67	81.54	94.98
	100	72.24	72.43	84.63

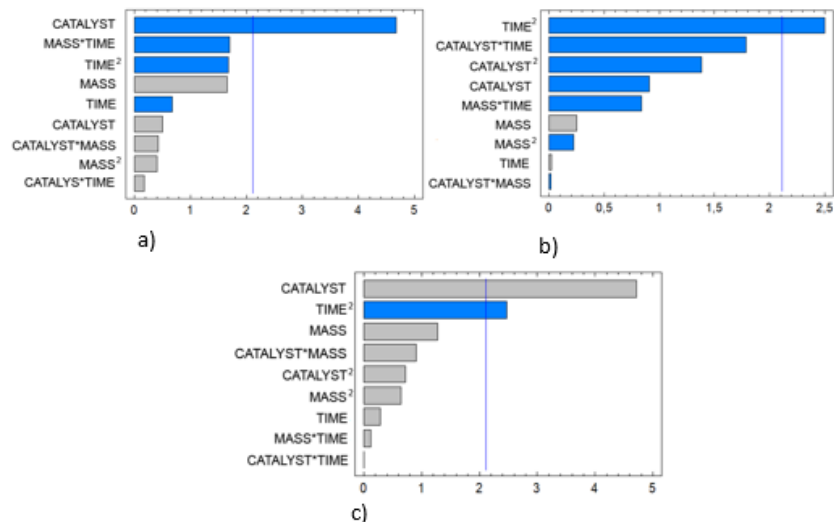


Figure 1: Second-order linear model: standardized Pareto chart showing the effects of the independent variables (time, mass, catalyst) and its interactions on the: a) yield, b) hydroxyl groups and c) viscosity of the polyols. The vertical line represents the significance at 95% ($p < 0.05$)

The different reaction conditions promoted a wide range on the hydroxyl number values in the polyols (Tab. 3). The resulting OH groups in the polyols is generally associated with the conversion reaction and the amount of acid groups formed during the reaction time. At 15% of lignin, the OHn value increased from 402 mg KOH/g to 2556.47 mg KOH/g without catalyst and increasing the reaction time from 60 min to 100 min. Under this condition, the liquefaction yield was similar at 80 and 100 min of reaction time (81%, Tab. 2). However, the number of acid (An) formed over 80 min (16.63 mg KOH/g) is much higher than at 100 min (6.04 mg KOH/g). In this case, the hydroxyl groups were more consumed to form acid substances at 80 min (1827.66 mg KOH/g) than at 100 min (2556.47 mg KOH/g). However, at 15% of lignin, 3% of catalyst and at 100 min, the OH groups were diminished considerably (where acid groups were also reduced). In this sample the low OH groups could be due to the dehydration reaction [12].

Table 3: Hydroxyl number (OHn) and acid number (An) of the polyols

Catalyst (%)	Time (min)	(mg KOH/g)					
		Weight of lignin (%)					
		15		20		25	
		OHn	An	OHn	An	OHn	An
0	60	402.43	8.28	983.09	10.84	1687.97	10.06
	80	1827.66	16.63	2314.11	14.77	1363.59	50.49
	100	2556.47	6.04	904.61	7.57	1773.06	11.96
3	60	2092.55	17.29	924.97	23.17	1582.62	12.48
	80	2399.51	24.25	2351.04	13.95	2354.60	12.64
	100	544.83	12.42	1731.10	14.22	1672.99	14.23
6	60	733.45	13.54	2173.90	33.35	1280.53	28.30
	80	1372.81	26.31	1716.15	37.03	1550.40	34.00
	100	1275.65	44.44	902.34	6.39	558.74	15.85

The viscosity of the polyols is shown in Tab. 4. The values were ranged from 0.1361 Pa.s (without catalyst, 20% of lignin at 60 min) to 1.8456 Pa.s (6% of SA, 25% of lignin at 80 min). Statistically this property was influenced by both reaction time and catalyst (Fig. 1(c)).

As it can be observed, viscosity was increased when the catalyst load increased. The highest change was observed in the samples liquefied at 15% and 25% of lignin at 80 min process time, where viscosities were increased from 0.190 to 1.336 Pa.s and from 0.291 to 1.846 Pa.s, respectively. This can be attributed to condensation and repolymerization reactions that can occur at high catalyst concentrations [13]. The reaction time also increased the viscosity of the samples up to 80 min, where at further reaction times (100 min) the viscosity decreased. Kurimoto et al. [14] found viscosities between 0.33 and 31.00 Pa.s with reaction time range from 30 to 90 min.

Table 4: Values of the viscosity of the polyols

Catalyst (%)	Time (min)	Viscosity (Pa.s)		
		Weight of lignin (%)		
		15	20	25
0	60	0.183	0.136	0.267
	80	0.190	0.261	0.291
	100	0.196	0.238	0.282
3	60	0.556	0.203	0.512
	80	0.445	0.619	0.386
	100	0.426	0.328	0.605
6	60	0.272	0.791	0.644
	80	1.336	0.869	1.846
	100	0.440	0.688	0.700

Effect of the independent variables (reaction time, lignin, catalyst) on the polyols

The average results of yield, OHn and viscosity as a function of reaction conditions (time, mass and catalyst) are shown in Tab. 5.

Reaction time: Fig. 1 shows the influence of reaction time on the features evaluated of polyols. Take into account the reaction time, the average values of liquefaction yield range from 89% (80 min) to 81% (100 min) (Tab. 5). This decrease maybe due to the recondensation polymerization of the lignin fragments over the time [4,15]. ANOVA analysis showed that the reaction time is not significantly different ($p > 0.05$), therefore, this parameter did not influence the yield of the polyols. However, it affected the hydroxyl numbers, where at 60 min was about 1317.15 mg KOH/g and the highest value was obtained at 80 min with 1916.65 mg KOH/g (Tab. 5). The reaction time of 60 min seems not enough to promote greater active sites (OH). In contrast, at 100 min, the low average value of OH groups could be due to condensation and repolymerization of the lignin fragments [5]. Statistically, the average values of OH groups of the polyols as a function of the reaction time were significantly different (ANOVA, $p < 0.05$). On the other hand, the liquefied lignin showed average viscosity of 0.396, 0.694 and 0.433 Pa.s at 60, 80 and 100 min, respectively. Kurimoto et al. [14] found viscosities between 0.33 and 31.00 Pa.s. Viscosities results were significantly different (ANOVA, $p < 0.05$) as a function of reaction time.

Lignin load: The percentage of 15%, 20% and 25% (w/w) of lignin provided average yields of 82.25%, 84.20% and 89.03%, respectively (Tab. 5). Apparently, more lignin provides higher yields, although these values are not statistically different (ANOVA, $p > 0.05$). Jo et al. [16] used the same percentages (15, 20 and 25%) of mass and obtained higher yields (around 94%) using 15% of palm kernel cakes in the

liquefaction. As it can be observed in Tab. 5, when lignin load is increased from 15 to 20%, the *OHn* values were increased (1446.98 to 1555.70 mg KOH/g, respectively) and then, remained constant at 25% of lignin. It appears that 15% of the lignin was not sufficient to react with the solvents. However, over 20% of lignin, reactions of self-condensation seem to be dominant. The increase in lignin from 15 to 25% promoted a 38% increase in viscosity of liquefied lignin, from 0.449 to 0.615 Pa.s. However, Pareto diagram (Fig. 1) shows that the lignin content did not influence the viscosity of the polyols. Kurimoto et al. [14] verified the same trend of viscosity growth (from 0.33 to 31.00 Pa.s) with the increase of Sugi wood concentration (*Criptomeria japonica* D. Don) from 9.6 to 29.8%, respectively.

Catalyst load: Tab. 5 shows that the experiments performed without catalyst had the lowest average yield (78.64%). However, at 3% of SA there was an increase of 22.28% of the yield, with average of 96.16%. The catalyst plays an important role in liquefaction yield by facilitating the decomposition of lignin and retarding the condensation reactions. At higher catalyst load (6 w/w), the concentration of liquefied products was very high and the condensation reactions were dominant [4]. Here, it was observed that the yield is lower in the absence of SA than at higher concentrations (6% w/w). ANOVA analysis shows that the yield values are statistically different as a function of catalyst ($p < 0.05$). The *OHn* of liquefied lignins synthesized in absence of SA increased from 1534.78 mg KOH/g to 1739.36 mg KOH/g with 3% of SA. Then, *OHn* decrease again to 1284.88 mg KOH/g with 6% of SA. The highest *OHn* value with 3% SA should be related to the high conversion of lignin to polyol. Liquefaction performed in absence of catalyst, with 3% and with 6% of SA, resulted in polyols having an average viscosity of 0.227, 0.453 and 0.843 Pa.s, respectively. As it can be observed, the viscosity was increased when the catalyst load increased. This can be attributed to condensation and repolymerization reactions that can occur at high catalyst concentrations [13]. In the liquefaction of crude glycerol for 90 min at 180°C, Lou et al. [17] obtained viscosity of 0.37 Pa.s with 4% of SA.

Table 5: Effect of the independent variables (reaction time, lignin and catalyst) on the average values of yield, *OHn* and viscosity of the polyols

	Yield (%)	<i>OHn</i> (mg KOH/g)	Viscosity (Pa.s)
Reaction time (min)			
60	84.56	1317.15	0.396
80	89.12	1916.65	0.694
100	81.79	1324.42	0.433
Lignin (%)			
15	82.25	1467.26	0.449
20	84.20	1555.70	0.459
25	89.03	1536.05	0.615
Catalyst (%)			
0	78.64	1534.78	0.227
3	96.16	1739.36	0.453
6	80.68	1284.88	0.843

FTIR analysis: The changes in the chemical structures of the polyols and Kraft lignin were analyzed by FTIR spectroscopy (Fig. 2). All spectra of the polyols showed similar peaks, however, they presented some differences in intensity. The spectrum of liquefied lignins showed marked changes compared with Kraft lignin. The increase broad band in the region 3665-3144 cm^{-1} is related to the stretching OH groups. This increase was expected due to aliphatic OH contributions from polyhydric alcohols and aromatic OH groups from Kraft lignin depolymerisation. Besides that, the peaks at 2937 cm^{-1} and 2869 cm^{-1} related to the asymmetric and

symmetric C-H stretching in the methylene and methyl groups, increased. The strong peak of methylene may be due to the structure of PEG and G. For methyl groups, may be due to the phenylpropane units from Kraft lignin. The appearance of the peak at 1247 cm^{-1} , assigned to C-O in phenol hydroxyl groups, confirms that Kraft lignin had participated in the liquefaction reaction [5]. The peak at 1350 cm^{-1} is related to the stretching OH in plane deformation. The appearance of a peak in the region between 1709 and 1732 cm^{-1} is attributed to C=O in the unconjugated ketones, carbonyl and ester groups stretching [13,18].

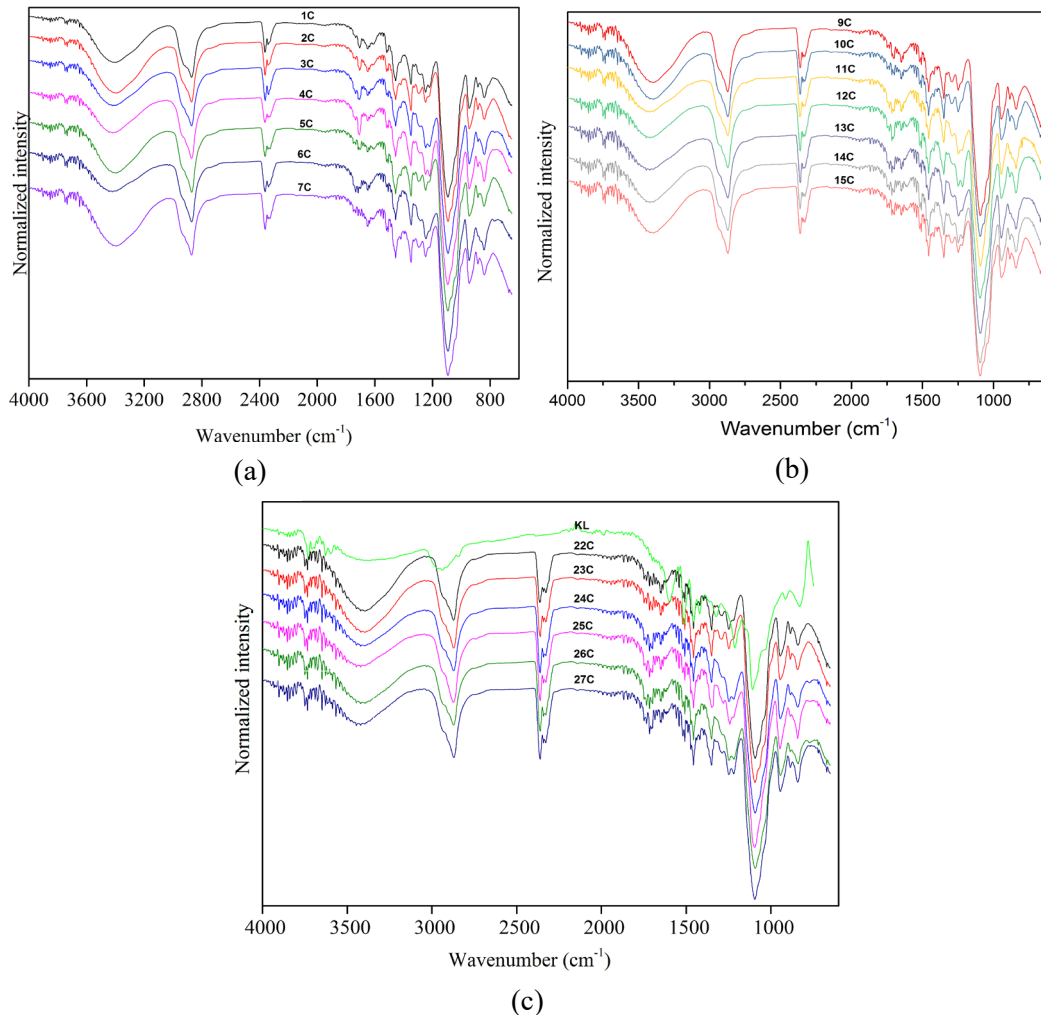


Figure 2: FTIR spectrum of polyols a) 1C to 7C, b) 8C to 14C and c) 22C to 27C and Kraft lignin

4 Conclusions

In this work, the influence of the reaction time, catalyst load and Kraft lignin percentage in the liquefied products properties was analyzed. The obtained results indicated that the obtained yield of liquefied lignins (61.97-98.88%) was statistically affected by catalyst loading, where hydroxyl number (values around 402.43-2556.47 mgKOH/g) was influenced by reaction time. However, the viscosity of liquefied lignins (range between 0.183-1.846 $\text{Pa}\cdot\text{s}$) was influenced by reaction time and catalyst load. Finally, the lignin percentage had no influence on polyols properties. Therefore, it can be concluded that the most important parameters that affect the polyol properties, are the catalyst load and liquefaction time. On the other hand, the liquefied lignins presented marked changes in FTIR spectra comparing with the precipitated Kraft lignin. This confirms that Kraft lignin participates in the liquefaction reaction.

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