

Polyol and Foam Production from Lemon Bagasse Liquefaction

Brenno S. Leite^{*a}, Matheus T. D. Figueiredo^a, Sibeles A. F. Leite^a, Camila S. Carriço^b, Vânia M. D. Pasa^b

^aUniversidade Federal de Viçosa (UFV- Campus Florestal), Institute of Science and Technology, Rodovia LMG, 818 km 6 – CEP: 35.690-000, Florestal-MG, Brazil; tel. +55 31 35363308.

^bUniversidade Federal de Minas Gerais, Av. Antonio Carlos, 6627, Belo Horizonte MG, 31270-901 Belo Horizonte, Brazil. brennoleite@ufv.br

It is estimated that Latin America has the highest biomass potential, after considering food production and resource constraints. Brazil is one of the most promising producers of biomass residues and has abundant renewable energy sources. 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 only 40 to 50 % of the fruit and its remainder is considered industrial residue. Lemon bagasse is a lignocellulosic residue combining cellulose, hemicellulose and lignin and due to its characteristics it may be investigated for value-added chemicals productions. The aim of this work was to liquefy lemon bagasse using crude glycerol as solvent in order to investigate the polyols properties and its potential to produce green polyurethane foams. In this work, polyols were produced using agricultural residue (lemon bagasse previously dried and pulverized to 50 mesh), industry residue (crude glycerol, this solvent is a by-product of biodiesel industry) and sulfuric acid as catalyst. The reactions were performed at 120 °C during 1 hour at vapor pressure (1 kgf/cm²). An experimental factorial design was performed in order to evaluate how the catalyst amount, the time of reaction and the molar ratio solvent/biomass affect liquefaction yield. The polyols produced with best results were characterized by Fourier Transform Infrared Spectroscopy (FTIR), hydroxyl number and viscosity. The polyols infrared spectra showed the typical bands of lignocellulosic derivatives, which presented similar profiles to polyols obtained from other biomass liquefaction. The hydroxyl numbers indicate that these polyols are suitable to produce green rigid polyurethane foams.

1. Introduction

Recently significant efforts have been made to use renewable resources effectively through biorefinery processes for biomass conversion such as pyrolysis, gasification, and liquefaction (Ye et al., 2014).

It is estimated that Latin America has the highest biomass potential, after considering food production and resource constraints (Janssen and Rutz, 2011). Brazil is one of the most promising producers of biomass residues and has abundant renewable energy sources (Paula and Trugilho, 2011). 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 (Mendonça et al., 2006).

Lemon bagasse is a lignocellulosic residue combining cellulose, hemicelluloses and lignin and due to its characteristics it may be investigated for value-added chemicals productions. In this sense, liquefaction arises as an alternative to treat lemon bagasse. This process has some advantages such as simple operation, high production level, high energy conversion and powerful organic material treatment ability (Ye et al., 2014).

Biomass liquefaction research is focused on the solvolysis of modified raw material at the early stage (Nakano, 1994). Among its products, bio-based polyols have suitable properties to produce polyurethane foams with comparable properties to the conventional ones (Lee et al., 2000).

Liquefaction profitability depends 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 (Hu et al., 2014a). 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 (Hu et al., 2014b, Hu et al., 2014c).

In this sense, the main objective of this work was to produced polyols using the agricultural and industry residues, lemon bagasse and crude glycerol, in order to evaluate its potential to produce rigid foams.

2. Experimental

2.1 Sampling and Reagents

Lemon samples were collected between May and October of 2016 in the southeast region of Brazil (Florestal, Minas Gerais - Brazil). Lemon bagasse sample was dried at 105 °C 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), imidazol (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 distilled water.

2.2 Biomass Characterization

Ash content was determined as the residue after combustion in a muffle furnace at 710 °C for 1 h. Volatile matter was the mass fraction released when 1.0 g of sample was heated in a muffle furnace at 850 °C for 7 min. The percentage of fixed carbon (FC) was the fraction that remains after subtracting the ash and the volatile matter content (Rendeiro and Nogueira, 2008).

2.3 Liquefaction Procedures (Polyol Synthesis)

The liquefaction process consists of the reaction between: biomass, solvent and catalytic agent on an especific time and the heat treatment was carried out in an autoclave (Lee et al., 2016). For each run, according to the experimental factorial desing (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 °C), with heating rate of 15 °C/min, for a fixed time period and absolute pressure of 2 kgf/cm². The autoclave cooling and depressurizing time was about 30 minutes (Rafiquil et al., 2000). The product was collected for analysis and foam production according to the following sequences as shown in Figure 1 (Rafiquil et al., 2000).

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°C during 24 hours, and the resultant solid was used to calculate the liquefaction yield (Eq 1):

$$Liquefaction\ yield\ (\%) = \left(\frac{Biomass\ weight - Residue\ weight}{Biomass\ weight} \right) \times 100 \quad (1)$$

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°C to obtain the polyols.

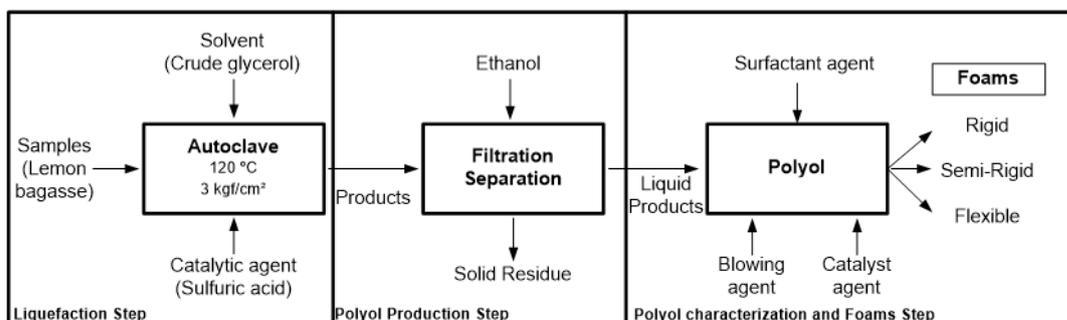


Figure 1: Schematic flowchart by liquefaction process and foams production

Table 1: Lemon bagasse liquefaction variables and levels used in the 2³ factorial design with central point

Variables	Levels		
	-1	0	+1
X1: catalyst amount (C)	2 %	5 %	7 %
X2: time of reaction (t)	0.5 h	1 h	1.5 h
X3: ratio biomass/solvent (R)	2:1	3.5:1	5:1

2.4 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 biomass/solvent (wt%), as shown in Table 1. The study of factors affecting the liquefaction yield was evaluated involving a multivariate factorial design with central point for three variables at two levels (2³).

2.5 Polyol Characterization

2.5.1 Hydroxyl Number

Polyols' hydroxyl number was determined according to the ASTM D4274 standard (Hassan & Shukry, 2008), 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 (Briones et al., 2011). The hydroxyl number (mg KOH/g) was calculated from the difference in titration of blank and the sample solutions using the following equation (Eq 2):

$$\text{Hydroxyl number (mg KOH / g)} = \frac{(B - A)N \times 56.1}{W} \quad (2)$$

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).

2.5.2 FT-IR (Fourier Transform Infrared) Spectroscopy

Functional groups in the samples (in natura, solid residue, polyol and foam) were identified by FT-IR spectra, obtained from a Perkin Elmer FT-IR 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.

2.6 Foam Production

Polyurethane foams were synthesized using the batch process method, by the mixture of polyol, surfactant, catalyst and blowing agent using a mechanical stirrer, Fisatom model 713 D, until the complete homogenization of the system. The foam formulation contained 2 % blowing agent, 2 % of surfactant and 2 % of catalyst in relation to the polyol weight. The isocyanate was added to this system and remained under agitation for 20 sec. The formulation was poured into a wooden mould with dimensions of 7.0 x 7.0 x 20.0 cm for the growth of the polymer foam, and the mould was kept closed for 24 hours at room temperature to perform curing.

3. Results and Discussion

The biomass liquefaction has the aim to transform carbonaceous solid materials into chemicals (as polyols), which depends on physical and chemical properties of the raw material. The polyol are strongly dependent on biomass characteristic and liquefaction conditions, these properties give important indications about the liquefaction process and information about the quality of the polyol (Briones et al., 2011).

For this reason, proximate analysis (volatile matter, ash and fixed carbon content) estimate the use of the biomass to produce polyols, since they direct influence of the biomass composition, such as carbon content. The results for proximate analysis are shown in Table 2 (% on an oven-dry weight basis).

Table 2: Results for Proximate Analysis (dry base) with their respective standard deviations.

Proximate Analysis (wt%)	Lemon Bagasse
Volatile Matter Content	28.57 ± 8.28
Ash Content	7.17 ± 2.72
Fixed Carbon Content	68.71 ± 9.79

It was observed high content of volatile matter (about 28 wt%), which represents organic compounds of low chain that easily solubilized into solvent. These low-chain organic components contribute to the chemical composition of the polyols.

The ash content represents the inorganic compounds, which was not solubilized in the liquefaction. The evidence of the existence of these inorganic compounds in the lemon bagasse was the ash content obtained from the proximate analysis. Lemon bagasse presented 7 wt% of ash content, which represent the inorganic compounds and is expected of lignocellulosic residues. Generally, high amount of ash can causes low reaction yields and operational problems due to the high amount of residues insoluble after the main biomass conversion (Briones et al., 2011, Eriksson et al., 2009, Juhaida et al., 2010). Therefore, the greater the amount of ash, the lower the yield (Rafiqul et al., 2000; Ye et al., 2014).

Fixed or non-combined carbon (FC) is the fraction remaining after volatile matter (organic compounds of high chair). This samples of lemon bagasse showed a fixes carbon content of proximally 69 wt% that is a higher value in comparison with other lignocellulosic biomass (Rambo et al., 2015). High VM/FC ratio increases the degree of reactivity of the biomass. The liquefaction in presence of acid leads to decomposition of cellulose and hemicellulose into small compounds due to acid hydrolysis and other oxidation reactions takes place on cellulose. The intensity of carbonyl in these compounds may reflect the degree of compounds carbon decomposition and yield process.

Considering the high organic content (approximately 92 %wt), it can be said that lemon bagasse consists mainly by cellulose, hemicellulose and lignin, that increases the availability of hydroxyl groups in the polyols.

Table 3 summarizes the results of the liquefaction yield and the hydroxyl number of the Conditions 1 and 2 that represents the higher (88.4 %wt) and lower (28.1 %wt) liquefaction yield, respectively. The analysis of the full result show that the conditions used to get higher liquefaction yields were higher catalyst content, time of reaction and molar ratio solvent/biomass.

The hydroxyl numbers reported in this study (Table 3) were in agreement with the polyol requirements used to produce semi-rigid and rigid polyurethanes (hydroxyl groups between 320 and 830) (Vilar, 2002; Carriço et al., 2016, Cateto et al., 2009).

FTIR spectrum (Figure 2) was used for the characterization of the raw materials (and products resulted from bagasse liquefaction). 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 $\text{C}=\text{O}$ 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 (Briones et al., 2011; Carriço et al., 2016; Hassan et al., 2008; Hu et al., 2014b). Alcohols, ethers and esters at 1250 cm^{-1} and an increase and shift of the absorption in the $\text{C}-\text{O}$ 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 (Giannakopoulou et al., 2010; Hassan et al., 2008). The spectra also show an important peak around 1400 cm^{-1} , which may be attributed to inorganic compounds groups (Carriço et al., 2016, Vilar, 2002).

Table 3: The comparison of liquefaction yield of the different ratios and hydroxyl number

Conditions	Parameters reaction			Liquefaction yield (% wt)	Hydroxyl number (mg KOH g^{-1})
	Catalyst (%)	Time (h)	Solvent/biomass		
1	7	1.5	5:1	88.4	830
2	2	0.5	3.5:1	28.1	320

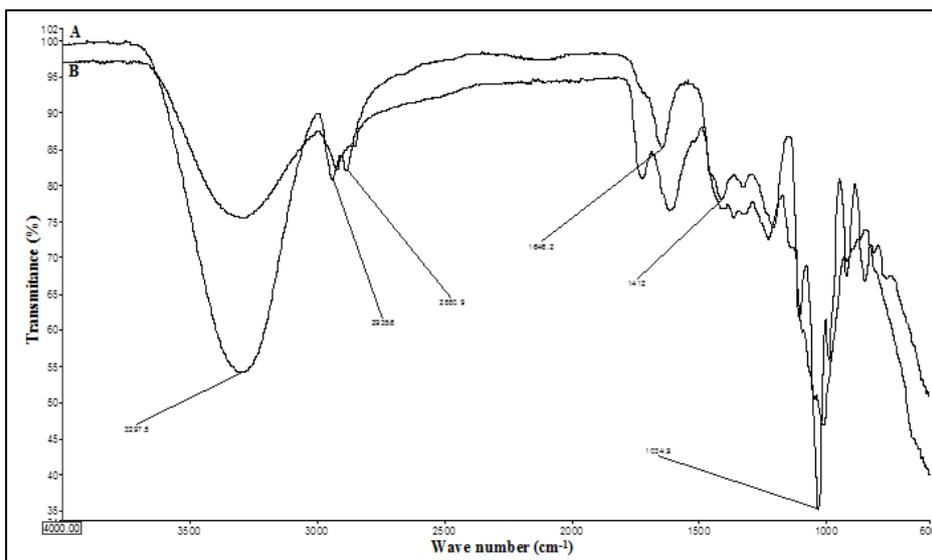


Figure 2: FT-IR spectral analysis of the (A) polyol and (B) Lemon bagasse.

Foams were produced using the polyol obtained in the Condition 1 liquefaction process (Figure 3). A qualitative analysis showed these innovative foams produced from lemon bagasse and crude glycerol (from biodiesel industry) are rigid and presented a good dimensional stability. Further investigation will be done in order to evaluate their mechanical properties and thermal stability and their potential to be used as insulating and packing materials. 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 (Rambo et al., 2015).



Figure 3: Rigid Foam produced using the lemon bagasse (Condition 1 from liquefaction process)

4. Conclusion

The feedstock analysed in this study is abundant and promising for biorefining opportunities in Brazil. The physicochemical characterization indicated that in general, all of the lemon bagasse exhibit parameters for polyol production, such as high carbon content, high lignin content and low ash content. The liquefaction process to convert lemon bagasse in polyols is simple, fast and cheap and presented high yields using crude glycerol (a co product from biodiesel production), which is a satisfactory result to use raw materials to produce chemicals. The polyols obtained have a potential use to produce rigid polyurethane foams. This study shows possibilities of use agricultural residues as renewable feedstock in biorefineries for the production of bio-products. Its use for production to low cost polyols by chemical conversion and their possible incorporation as precursors into polymer formulations could entail a much valorization of the residue (by-product), economic and environmental improvements for the agriculture.

Acknowledgements

Universidade Federal de Viçosa (UFV), Fundação de Amparo à Pesquisa de Minas Gerais –FAPEMIG and Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPQ.

References

- Amutha K.; Sivakumar G., 2013, Analytical analysis of synthesized biosilica from bioresidues. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, v. 112, p. 219–222.
- Carriço C. S.; Fraga T.; Pasa V. M. D., 2016, Production and characterization of polyurethane foams from a simple mixture of castor oil, crude glycerol and untreated lignin as bio-based polyols. *European Polymer Journal*, v. 85, p. 53–61.
- Cateto C.A., Barreiro M.F., Rodrigues A.E., Belgacem M.N., 2009, Optimization study of lignin oxypropylation in view of the preparation of polyurethane rigid foams, *Ind. Eng. Chem. Res.* 48, 2583–2589.
- Eriksson G., Hedman H., Boström D., Pettersson E., Backman R., Öhman M., 2009, Combustion characterization of rapeseed meal and possible combustion applications, *Energy Fuels* 23, 3930–3939.
- Garcia R. et al. 2014. Spanish biofuels heating value estimation. Part II: Proximate analysis data. *Fuel*, v. 117, n. PARTB, p. 1139–1147.
- Giannakopoulou K., Lukas M., Vasiliev A., Brunner C., Schnitzer H., 2010, Conversion of rapeseed cake into bio-fuel in a batch reactor: effect of catalytic vapour upgrading, *Microporous Mesoporous Mater.* 128, 126–135.
- Bonzel H.P., Bradshaw A.M., Ertl G., Eds., 1989, *Physics and Chemistry of Alkali Metal Adsorption*. Elsevier, Amsterdam, the Netherlands.
- Hassan E. barbary M., & Shukry N., 2008, Polyhydric alcohol liquefaction of some lignocellulosic agricultural residues. *Industrial Crops and Products*, 27(1), 33–38.
- Hu S., Li Y., 2014a, Polyols and polyurethane foams from base-catalyzed liquefaction of lignocellulosic biomass by crude glycerol: Effects of crude glycerol impurities, *Ind. Crop. Prod.* 57, 188–194.
- Hu S., Li Y., 2014c, Polyols and polyurethane foams from acid-catalyzed biomass liquefaction by crude glycerol: Effects of crude glycerol impurities, *J. Appl. Polym. Sci.* 131, 9054–9062.
- Hu S., Luo X., Li Y., 2014b, Polyols and Polyurethanes from the Liquefaction of Lignocellulosic Biomass, 4096, 66–72.
- Janssen R., Rutz D.D., 2011, Sustainability of biofuels in Latin America: risks and opportunities, *Energy Policy* 39, 5717–5725.
- Juhaida M.F., Paridah M.T., Hilmi M.M., Sarani Z., Jalaluddin H., Mohamad Zaki A.R., 2010, Liquefaction of kenaf (*Hibiscus cannabinus* L.) core for wood laminating adhesive, *Bioresour. Technol.* 101, 1355–1360.
- Lee J.-H. et al., 2016, Crude glycerol-mediated liquefaction of empty fruit bunches saccharification residues for preparation of biopolyurethane. *Journal of Industrial and Engineering Chemistry*, v. 34, (2016), p. 157–164.
- Lee S.H., Yoshioka M., Shiraishi N., 2000, Liquefaction of corn bran (CB) in the presence of alcohols and preparation of polyurethane foam from its liquefied polyol, *J. Appl. Polym. Sci.* 78, 319–325.
- Mendonça L. M. V. L. et al., 2006, Caracterização da composição química e do rendimento dos resíduos industriais do limão Tahiti (*Citrus latifolia* Tanaka). *Ciência e Tecnologia de Alimentos*, v. 26, n. 4, p. 870–874.
- Nakano T., 1994, Mechanism of thermoplasticity for chemically modified wood. *Holzforschung* 48, 318–324.
- Paula L.E.R., Trugilho, P.F, 2011, A. Napoli, M.L. Bianchi, Characterization of residues from plant biomass for use in energy generation, *Cerne* 17, 237-246.
- Rafiqul I., Lugang B., Yan Y., & Li T., 2000, Study on co-liquefaction of coal and bagasse by Factorial Experiment Design Method. *Fuel Processing Technology*, 68(1), 3–12.
- Rambo M. K. D., Schmidt F. L., & Ferreira M. M., C.2015, Analysis of the lignocellulosic components of biomass residues for biorefinery opportunities. *Talanta*, 144, 696–703.
- Rendeiro G., Nogueira M., 2008, *Combustão e Gasificação de Biomassa Sólida: Soluções Energéticas para a Amazônia*. Brasília.
- Smidt E. et al., 2002, Characterization of waste organic matter by FT-IR spectroscopy: Application in waste science. *Applied Spectroscopy*, v. 56, n. 9, p. 1170–1175
- Vilar W., 2002, *Química e Tecnologia dos Poliuretanos*, Vilar Consultoria, São Paulo.
- Ye L., Zhang J., Zhao J., Tu S., 2014, Liquefaction of bamboo shoot shell for the production of polyols. *Bioresource Technology*, 153, 147–153.