

LIGNOPOLYOLS DERIVED FROM ENZYMATIC GLYCEROLYSIS: CHARACTERIZATION AND PROSPECTIVE APPLICATIONS

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ABSTRACT

Lignin, a branched polymer derived from wood pulping in the paper industry, is typically associated with hemicellulose and cellulose in plant cell walls. Despite being underutilized in energy generation, its abundance of functional groups suggests potential in diverse applications, including as lignopolyols for polyurethane production. These lignopolyols underwent qualitative characterization for polyurethane use, with enzymatic glycerolysis favored over chemical catalysis due to its advantages like biodegradability and high selectivity. In this process, glycerol, castor oil, lignin, and properties such as viscosity and hydroxyl index were assessed. Lignopolyols catalyzed by enzyme N435 exhibited a higher hydroxyl index, indicating their suitability for polyurethane formation alongside other lignopolyols. Moreover, these lignopolyols displayed lower viscosity when catalyzed by N435, possibly due to the enzyme recovery process, impacting rheological properties. FTIR analysis revealed a correlation between increased hydroxyl content and lignin proportion in the reaction mixture. This study underscores the potential of lignin in diverse applications and the efficacy of enzymatic glycerolysis for lignopolyol synthesis.

Keywords: Lignopolyols. Lignin. Transesterification. Enzymatic glycerolysis. Lipases.

1 INTRODUCTION

The search for sustainable and renewable materials has become increasingly important due to environmental concerns and the need to reduce reliance on non-renewable sources.¹ In this context, lignin, a byproduct of the wood pulping process in the paper and cellulose industry, has emerged as a promising alternative source for the production of lignopolyols, which can be used, for example, in the manufacture of polyurethane foams. Lignin possesses a complex molecular composition rich in functional groups, which holds the potential to substitute non-renewable resources in polyurethane (PU) production, thus helping to reduce industrial waste and making processes more sustainable and economical. Additionally, this approach is essential for developing green products.²

Enzymatic lignin glycerolysis is a novel and promising technique for producing lignopolyols from renewable raw materials. In this process, lignin is mixed with alcohol and an ester, catalyzed by a specific enzyme that breaks lignin's chemical bonds. As documented in the literature, the use of enzymes offers several advantages over conventional methods, including higher efficiency and lower energy consumption.³

Thus, this study aimed to investigate enzymatic lignin glycerolysis as a viable route for producing high-value green chemicals based on lignin and to evaluate their physicochemical properties to determine their potential as a renewable source and future application in PU production.

2 MATERIAL & METHODS

Lignopolyols were obtained by enzymatic glycerolysis using castor oil, commercial glycerol and lignin in a solvent-free system. The methodology was adapted from.⁴ The lignopolyols were synthesized in a jacketed glass reactor using castor oil, glycerol in a 1:6 molar ratio, lignin (0, 5, 10 and 15 wt.%) related to castor oil and glycerol, Tween 80 was applied as surfactant (16% in relation to castor oil), glycerol and lignin and 9% of biocatalyst (Commercial immobilized lipase Novozym® 435, from *Candida antarctica* - immobilized on a macroporous anionic resin, 1.4 wt.% water or free Cal B lipase). The substrates and lipase were mixed and kept at 70 °C, 600 rpm for 2 h. After the reaction, the immobilized enzyme was recovered by vacuum filtration using a Buchner funnel and filter paper. The polyols were washed several times until the enzymes are recovered with solution methanol:water (v/v ratio of 80:20). In sequence, the immobilized enzymes and polyols were dried overnight (60 °C).

The lignopolyols were characterized by Fourier Transform Infrared Spectroscopy (FTIR) using a Shimadzu IR Prestige 21. The evaluation was performed by transmittance in the region of 4000 cm⁻¹ - 750 cm⁻¹ with a resolution of 4 cm⁻¹ and 32 scans. The hydroxyl value followed the procedure presented in Fernandes et al.⁵ The pH was measured on pHmeter (KASVI K39-2014B); water content was evaluated using coulometric Karl Fischer (Hanna Instruments model HI 904) and the viscosity parameters of the biopolyols were observed through rotational tests using an Anton Paar MCR 72 plate rheometer (PP25) at room temperature (-20 °C), set at a shear rate of 218 s⁻¹ for 360 s.

3 RESULTS & DISCUSSION

The lignopolyols obtained in this investigation underwent physicochemical analysis to evaluate the effects of different biocatalysts and lignin ratios. Table 1 presents the data obtained from this phase of the study. Notably, the biopolyols containing lignin in the reaction medium observed an alkaline pH environment, which favored enzymatic glycerolysis. Additionally, the hydroxyl numbers of biopolyols incorporating lignin were higher, with particular emphasis on those catalyzed by Novozym 435. This immobilized enzyme demonstrated excellent stability against fluctuations in the reaction medium. Furthermore, the moisture content of the biopolyols was assessed using the sample with the highest moisture content to enable comparison with biopolyols having similar moisture levels. Table 1 provides insights into the moisture content of lignopolyols prior to measurement, utilizing the PN0 biopolyol as a reference.⁶ The polyols catalyzed by the immobilized enzyme (N435) exhibited lower viscosity values due to the recovery of the biocatalyst by a methanol:water mixture (80:20), which may have affected the rheological and viscosity properties of these polyols; however, values obtained in this study are similar to polyols mentioned in the literature.⁷

Table 1 Physicochemical properties of biopolyols obtained via enzymatic glycerolysis..

Sample	Hydroxyl value (mg·KOH/g)	pH	Viscosity (m·Pas) *
PC0	537 ± 10	5.3	136
PC5	698 ± 111	8.8	2065
PC10	480 ± 45	8.8	3431
PC15	559 ± 26	9.4	4618
PN0	321 ± 91	4.0	565
PN5	979 ± 214	8.5	715
PN10	1229 ± 164	8.4	278
PN15	1154 ± 245	8.4	59

The sample codes refer to P: polyol; N or C: catalysts N435 or CalB-free and 0; 5; 10; 15: percentage by mass of lignin in the polyol.

* Viscosity values relative to the end of the rheological analysis (when subjected to shear).

FTIR analysis facilitates the visualization of vibrations associated with the primary constituents comprising biopolyols (Fig. 1). In all spectra, peaks were evident within the regions of 3382 cm⁻¹, 2932 cm⁻¹, 2855 cm⁻¹, and 1715 cm⁻¹, attributed to hydroxyl groups, (-CH) stretching, (-CH₂) stretching, and carbonyl or carboxyl groups, respectively.^{8,9} Peaks indicative of phenolic groups, signifying the presence of lignin in the biopolyol, are discernible within the range of 1579 cm⁻¹ to 1569 cm⁻¹. The intensity of these peaks correlates with the increasing proportion of lignin in the polyol.^{10,11} While bands situated at 1118 cm⁻¹ and 1042 cm⁻¹ signify aromatic (-CH) strains of the guaiacol units.¹²

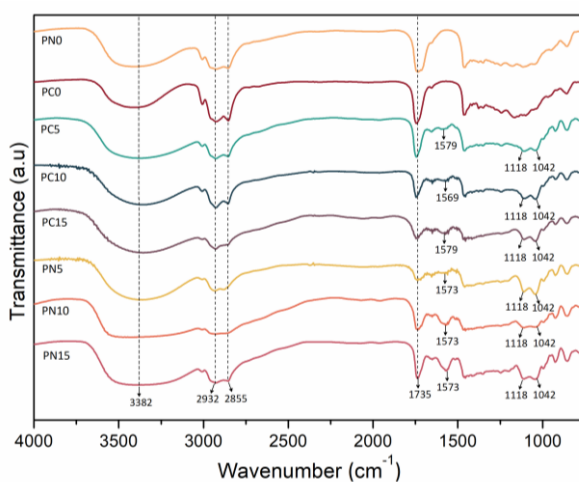


Figure 1 FT-IR spectra of biopolyols with lignin and without lignin.

4 CONCLUSION

Enzymatic glycerolysis-derived lignopolyols have shown a high hydroxyl index, indicating many hydroxyls (-OH) groups for binding in polyurethane formation. The elevated functional hydroxyl content allows for the production of polyurethanes with increased crosslinking, enhancing mechanical strength. Thus, enzymatic glycerolysis emerges as a promising technique worthy of further exploration for lignopolyol production, catering to various applications from construction materials to the footwear industry.

REFERENCES

- HARIDEVAN, H., EVANS, D. A. C., RAGAUSKAS, A. J., MARTIN, D. J., ANNAMALAI, P. K. 2021. Green Chem. 23. 8725-

8753.

- ² ARAUJO, T. R., BRESOLIN, D., de OLIVEIRA, D., SAYER, C., de ARAÚJO, P. H. H., de OLIVEIRA, J. V. 2023. Eur. Polym. J. 188. 111934.
- ³ BRESOLIN, D., BOLZAN, A., SAYER, C., DE ARAÚJO, P. H. H., DE OLIVEIRA, D. 2021. J Polym Environ. 29. 3900-3908.
- ⁴ VALÉRIO, A., ROVANI, S., TREICHEL, H., DE OLIVEIRA, D., OLIVEIRA, J. V. 2010. Bioproc Biosyst Eng. 33. 805-812.
- ⁵ FERNANDES, E., VICENTE, J., CRUZ, R., NELE, M., NUNES, E., COSTA-FÉLIX, R. 2014. Polym Testing. 33. 16-20.
- ⁶ GURGEL, D., BRESOLIN, D., SAYER, C., FILHO, L. C., DE ARAÚJO, P. H. H. Ind Crops Prod. 164. 113377.
- ⁷ GOSZ, K., KOSMELA, P., HEJNA, A., GAJOWIEC, G., PISZCZYK, L. 2018. Wood Sci Technol. 52. 599-617.
- ⁸ MOHAMMADPOUR, R., MIR MOHAMAD SADEGHI, G. 2020. J. Polym. Environ. 28. 892-905.
- ⁹ TAVARES, L. B., BOAS, C. V., SCHLEDER, G. R., NACAS, A. M., ROSA, D. S., SANTOS, D. J. 2016. Express Polym. Lett. 10. 927-940.
- ¹⁰ MA, Z., WANG, J., ZHOU, H., ZHANG, Y., YANF, Y., LIU, X., YE, J., CHEN, D., WANG, S. 2018. Fuel Process. Technol. 181. 142-156.
- ¹¹ MULLER, L. C., MARX, S., VOSLOO, H. C. M., CHIYANZU, I. 2019. Polym. Renew. Resour. 10. 3-18.
- ¹² GÓMEZ-FERNÁNDEZ, S., UGARTE, L., CALVO-CORREAS, T., PEÑA-RODRÍGUEZ, C., CORCUERA, A., ECEIZA, A. 2017. Ind. Crops Prod. 100. 51-64.

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