

Renewable Biopolyols from Residual Aqueous Phase Resulting after Lignin Precipitation

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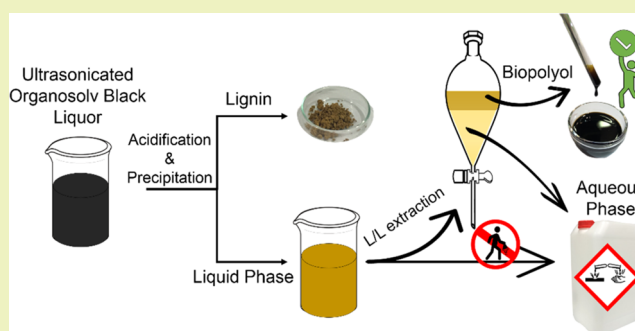
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ABSTRACT: The aim of this work was to obtain two biopolyols from the liquid residue resulting from the precipitation of lignin contained in two different black liquors, *Eucalyptus globulus* organosolv black liquor (EOBL) and *Pinus radiata* organosolv black liquor (POBL), thus adding value to this residue. Eucalyptus organosolv polyol (EOP) and Pine organosolv polyol (POP) were characterized to know their viscosity, hydroxyl number (I_{OH}), and functionality according to the corresponding standard American Society for Testing Materials (ASTM). The molecular weight of the biopolyols was measured through gel permeation chromatography (GPC); the chemical structure and composition were characterized by Fourier transform infrared (FTIR) and gas chromatography–mass spectrometry (GC-MS), respectively; and the thermal degradation (TGA) of the two biopolyols was determined. The biopolyols showed suitable properties to be employed in the production of polyurethanes (PU).

KEYWORDS: polyol, lignin, organosolv, black liquor, *Eucalyptus globulus*, *Pinus radiata*



INTRODUCTION

For eons, Earth has been able to sustain life through complex and interconnected ecosystems that human action is seriously altering. This fact has led many organizations and countries, as a result of an article published by the *BioScience* journal,¹ to declare a climate emergency in 2019. Oil, despite being one of the most important sources of pollution, has become an essential raw material for the global economy, not only as an energy source, whose consumption has increased 124% between 1976 and 2016,² but also in the manufacture of nonrenewable polymers such as polyurethanes (PU). PU are usually formed by polyaddition reactions³ between hard segments (isocyanates) and soft segments (polyols),⁴ and commonly, both are derived from petroleum. However, it is necessary to find new sources of raw materials that replace oil if society wishes to curb climate change.

Polyols are compounds that contain more than two hydroxyl groups in one molecule, which are usually petro-based compounds. However, many studies have been carried out to replace these petroleum-based polyols with lignin-derived biopolyols that can be produced by liquefaction reactions using polyhydric alcohols^{5,6} or through oxypropylation reactions.⁷

Lignin is one of the main compounds of lignocellulosic biomass and is also considered as the second most abundant renewable polymer after cellulose and the most abundant

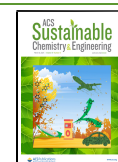
phenolic polymer on earth,⁸ which make it an ideal raw material for obtaining high-added-value chemical precursors.

Nowadays, the pulp and paper (P&P) industry is the main supplier of lignin, producing 97 of the 100 million tons of lignin annually.⁹ However, organosolv processes have proven to be more environmentally friendly than the processes used in P&P industry (kraft and sulfite processes), which has led them to gain relevance in the fractionation of lignocellulosic biomass in recent times.¹⁰ In fact, organosolv lignin percentage is expected to increase from the current 2–5% of lignin total production by 2025, mainly due to the boom in second-generation biorefineries for ethanol production.⁹ In both cases, lignin appears dissolved as a part of the black liquor generated after the biomass delignification reaction, which is usually burned to supply part of the energy necessities of the plant, thus losing the possibility of using lignin as a high-added-value chemical precursor.¹¹ Generally, lignin is precipitated from black liquor through the addition of inorganic acids and a posterior stage of membrane filtration,¹² obtaining, on the one

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hand, a solid lignin and, on the other hand, a liquid phase rich in degradation products of cellulose and hemicelluloses and also in lignin fragments (monomers, dimers, trimers, etc.) that are not retained by the filter.¹³ Generally, this liquid fraction is treated as a waste. However, the degradation compounds from lignin that are not recovered can be used for many purposes, such as polyol synthesis. Some studies have been carried out where lignin or modified lignin from eucalyptus or pine was used to produce polyol.^{14,15} Nevertheless, in all of those studies, the fraction that is used for biopolyols synthesis is the solid lignin recovered after its precipitation, and in some cases, this lignin is modified¹⁶ or depolymerized^{17,18} before its use as a polyol for polyurethane production. As far as we are concerned, the liquid fraction after precipitation of organosolv lignins that is still rich in lignin degradation products, independently of the employed biomass in the delignification process, has never been valorized for being used as a biopolyol.

The aim of this work is to valorize this liquid fraction by isolating these degradation products dissolved in it and study their properties as biopolyols for polyurethane production. For this purpose, the aqueous phase of two different black liquors that were previously ultrasonicated to reduce the molecular weight of the dissolved lignins, i.e., *Eucalyptus globulus* organosolv black liquor (EOBL) and *Pinus radiata* organosolv black liquor (POBL), were subjected to a liquid–liquid extraction. This extraction was carried out with ethyl acetate to separate an aqueous phase rich in sugar degradation products and an organic phase, which can be used as a biopolyol for diverse purposes, such as polyurethane manufacturing.

MATERIALS AND METHODS

Materials. The raw materials were obtained from two different companies both located in the Basque Country (Spain). *E. globulus* was kindly supplied from Papelera Guipuzcoana Zikuñaga S.A., while *P. radiata* sawdust was kindly supplied from Ebaki XXI S.A. Ethanol was purchased from Scharlab S.L., and ethyl acetate (high-performance liquid chromatography (HPLC) grade), sodium sulfate anhydrous ($\geq 99\%$), dimethylformamide (DMF, for HPLC, $\geq 99.9\%$), lithium bromide, 1,4-dioxane, pyridine (analytical grade), and phthalic anhydride (98%) were purchased from Fisher Scientific. Sulfuric acid (96%) (H_2SO_4) was obtained from Panreac.

Organosolv Treatment. *E. globulus* and *P. radiata* sawdust were each subjected to an organosolv delignification process. A 1.5 L stainless 5500 steel Parr reactor with a 4848 Parr controller was used, employing a dissolution of 50% EtOH/water (w/w) for both reactions. For *E. globulus*, the reaction conditions were 200 °C and 75 min with constant stirring and a solid/liquid ratio of 1:6,¹⁹ while in the case of *P. radiata* sawdust, the reaction was carried out at 210 °C and 75 min with a solid/liquid ratio of 1:8.²⁰ A triplicate of each organosolv treatment was carried out employing 50 g of raw material. The liquid phase also called organosolv black liquor was separated from the remaining pulp through vacuum filtration employing filter papers with 7–12 μm retention capacity (Macherey-Nagel 640 w). The pretreated solids were first washed twice with ethanol/water solution (at the same concentration of the treatment) to remove adsorbed lignin from the pretreated solids and then washed only with water.

Ultrasonication Treatment. The obtained black liquors were subjected to an ultrasonication treatment with the aim of reducing the molecular weight and polydispersity index (PI) of the dissolved lignins, which were reserved for further applications. To do that, a Sonopuls ultrasonic homogenizer HD 3100 was used employing an output amplitude of 35% for 60 min at 35 °C.²¹

Black Liquor Characterization. EOBL and POBL were characterized to calculate different parameters. Density was calculated

by weighting a known volume of black liquors sample. Total dissolved solids (TDS) and inorganic matter (IM) were determined employing the corresponding TAPPI standards TAPPI T264 cm-97 and TAPPI T211 om-93. The organic matter (OM) was determined by the difference between TDS and IM.

Biopolyol Synthesis. The two different black liquors, i.e., EOBL and POBL, were acidified to precipitate lignin. To do this, two different volumes of acidified water (pH 2) were added to organosolv liquors. In both cases, lignin was separated from the liquid phase by membrane filtration employing a stainless steel holder of capacity 2 L and a nylon filter with a pore diameter of 0.22 μm . Then, the liquid phase was sent for liquid–liquid extraction with ethyl acetate to separate the organic phase (biopolyol) from the aqueous phase (residue). Four consecutive extractions were carried out employing a liquid phase/ethyl acetate ratio of 1:0.25 in each. Thus, the final relation between the liquid phase/ethyl acetate was 1:1 in all of the extraction processes. The organic phase was treated with anhydrous sodium sulfate to remove the possible traces of moisture, and finally, the ethyl acetate was evaporated in vacuum.

Biopolyol Characterization. The two biopolyols, Eucalyptus organosolv polyol (EOP) and Pine organosolv polyol (POP) obtained from EOBL and POBL, respectively, were analyzed to determine the chemical structure through Fourier transform infrared (FTIR) characterization employing a PerkinElmer Spectrum Two FTIR Spectrometer equipped with a universal attenuated total reflectance accessory with internal diamond crystal lens. The employed range was from 4000 to 600 cm^{-1} accumulating 18 scans in transmission mode with a resolution of 4 cm^{-1} .

In addition, to elucidate the chemical composition of the biopolyols, a sample of each biopolyol was dissolved in ethyl acetate (HPLC grade) and analyzed by GC-MS following the method described by Hernández-Ramos et al.¹³

The molecular-weight distribution (M_w , M_n , and M_w/M_n) of the biopolyols was calculated through a gel permeation chromatography (GPC) analysis. This analysis was carried out using a JASCO instrument equipped with an interface (LC.Net/ADC), a refractive index detector (RI-2031Plus), and two columns in series (PolarGel-M 300 mm \times 7.5 mm). The mobile phase employed was *N,N*-dimethylformamide with 1% lithium bromide, and the flow rate was 700 mm^3/min . The analyses were performed at 40 °C. The calibration was made using polystyrene standards (Sigma-Aldrich) ranging from 70 000 to 266 g/mol.

Thermal degradation of both samples was studied through TGA. The equipment employed was a TGA/SDTA RSI analyzer from Mettler Toledo. Approximately 5 mg of each sample was heated from 25 to 800 °C employing a heating rate of 10 °C/min with 10 mL/min of nitrogen flow as inert atmosphere.

The rheological behavior of the biopolyols was measured by means of rheological oscillatory and rotational tests. Oscillatory measurements were carried out using a rheometric scientific advanced rheometric expansion system (ARES). The storage and loss moduli (G' and G'' , respectively) were determined as a function of the frequency using a parallel-plate geometry of 25 mm by a frequency sweep from 0.1 to 100 rad s^{-1} at a fixed strain of 10% (25 °C). This strain was determined in the linear viscoelastic region (LVR) by a previously performed strain-sweep test. The synthesized biopolyols were also studied by rotational rheology to determine their viscosity (η) and shear stress (τ) as a function of the shear rate ($\dot{\gamma}$). Flow test was performed using a Haake Viscotester IQ (Thermo Fisher Scientific) using a parallel-plate geometry of 35 mm by shear rate sweep from 0.02 to 120 s^{-1} (25 °C).

ASTM D4274²² standard was followed to determine I_{OH} (hydroxyl number) that is defined as mg KOH/g of sample. Each biopolyol (0.5–1 g) was dissolved in 25 mL of a phthalation reagent composed of 115 g of phthalic anhydride dissolved in 700 mL of pyridine. This mixture was heated under reflux for 1 h at 115 °C. After this time, 50 mL of pyridine was added through a condenser. Then, the mixture was back-titrated with a 0.5 M sodium hydroxide (NaOH) solution employing a solution of 1% phenolphthalein in pyridine as an indicator. The hydroxyl number was calculated using eq 1

$$I_{\text{OH}} = \frac{(B - A) \times M \times 56.1}{W} + A_n \quad (1)$$

where I_{OH} is the hydroxyl number of the biopolyol (mg KOH/g); B and A are the volumes (mL) of the NaOH solution required for the titration of the blank solution and the biopolyol solution, respectively; M is the molarity of the NaOH solution; W is the amount of sample (g) to be analyzed; and A_n is the acidic number of the sample that was calculated based on ASTM D974,²³ where 0.4 g of sample was dissolved in 50 mL of a solvent mixture of 1,4-dioxane/water (4:1 v/v). A 1% phenolphthalein indicator solution (0.5 mL) in ethanol was added to this mixture, and it was titrated with 0.1 M KOH solution in ethanol to the equivalent point. The acidic number (mg KOH/g of sample) was calculated as follows using eq 2

$$A_n = \frac{(C - B) \times M \times 56.1}{W} \quad (2)$$

where C is the volume required for the titration of the KOH solution (mL), B is the titration volume (mL) of blank solution, M is the molarity of the KOH solution, and W is the amount of sample (g) to be analyzed.

RESULTS AND DISCUSSION

Black Liquor. Black liquors were characterized, and the results are outlined in Table 1. As it was expected, there were

Table 1. Characterization of the Black Liquors

	black liquor	
	<i>E. globulus</i>	<i>P. radiata</i>
pH	3.600 ± 0.035	3.787 ± 0.031
density (g/mL)	0.926 ± 0.003	0.911 ± 0.001
TDS	5.527 ± 0.373	2.313 ± 0.021
IM	0.027 ± 0.003	
OM	5.509 ± 0.367	2.313 ± 0.021
lignin (%)	2.970 ± 0.103	1.425 ± 0.076

no significant differences in the pH and density values between both raw materials. Otherwise, although in the case of POBL a small amount of IM is observed, it can be concluded that in both cases, the TDS corresponded to the OM. However, in the case of POBL, it was observed that lignin accounted for 61.62% of the organic matter, while in the case of EOBL, this percentage was 53.92%. The rest of the organic matter can be attributed to degradation products derived from the hemicellulosic fraction and to the extractives that were also solubilized in the liquor.

Biopolyol. As mentioned above, a triplicate of the organosolv treatments was performed for each raw material. The average yields of biopolyols obtained were $5.45 \pm 0.533\%$ (EOP) and $5.24 \pm 0.285\%$ (POP) with respect to the initial raw material.

The chemical structures of EOP and POP were analyzed by FTIR spectroscopy. The chromatograms obtained by this technique are shown in Figure 1a,b. As can be seen in Figure 1a, both biopolyols showed a broad band at 3400 cm^{-1} , which corresponds to O–H stretchings of phenolic or alcoholic units. The characteristic vibration of aliphatic C–H bonds ($3000\text{--}2840 \text{ cm}^{-1}$) was also visible.²⁴ On the other hand, in the fingerprint region ($1800\text{--}800 \text{ cm}^{-1}$) shown in Figure 1b, carbohydrates and lignin had their characteristic absorption peaks. Regarding the characteristic peaks of lignin, some small differences were observed that can be attributed to the different nature of the feedstock which was employed, since softwood is mostly composed of G units while hardwood is usually formed by an equal amount of S and G units. In this sense, the signals from 1330 to 815 cm^{-1} are referred to the bands that correspond to G units ($1270, 815 \text{ cm}^{-1}$), S units ($1330, 1114 \text{ cm}^{-1}$), and both G and S units (1026 cm^{-1}).^{25–27} It was also remarkable that the signal at wavenumber 1270 cm^{-1} , which corresponds to G ring plus C=O stretching in G units, was much more intense in the case of POP than in EOP, where it appeared like a shoulder. Furthermore, the signal corresponding to the C–H group in G units (815 cm^{-1}) was only visible in the sample coming from pine, while in the case of eucalyptus, it disappeared. These confirm that the biopolyol from pine was richer in G units as it was expected for a softwood while biopolyol from eucalyptus had more S units. This was also verified through GC-MS analysis of biopolyols. The signal that corresponds to C=O in S units (1330 cm^{-1}) was only present in EOP, while the aromatic deformation of C–H in S units (1114 cm^{-1}) gave a small signal also in the case of POP. It was also visible that the band at 1026 cm^{-1} associated with the aromatic ring in G units was more intense in the case of POP than EOP as it was expected. Finally, a variation in the intensity of the bands corresponding to the C=O stretching in conjugated arylketones (1674 cm^{-1}) and C–H deformation (1460 cm^{-1}) could also be observed.²⁵ In the first one, the signal increased in POP, while in the second, the opposite occurred. As mentioned above, carbohydrate-related peaks also appeared in the fingertip region. Thus, peaks

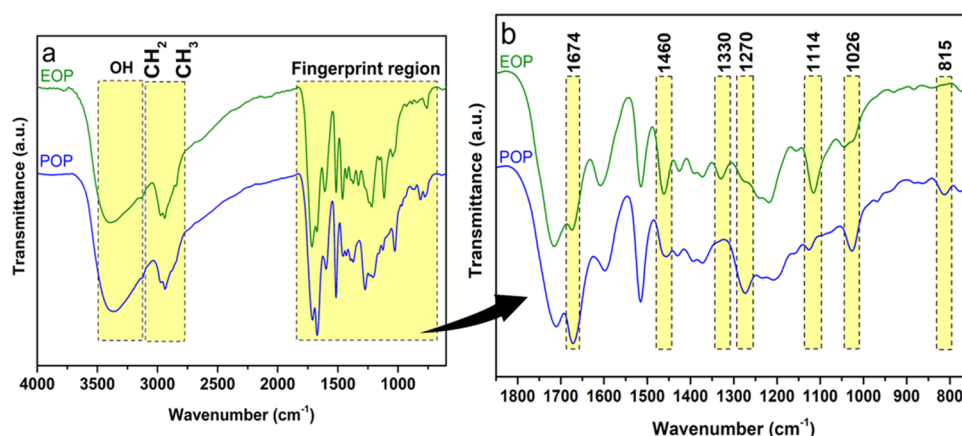


Figure 1. FTIR spectra (a) and Fingerprint region of FTIR spectra (b) of EOP and POP.

at 1603, 1424, 1114, and 1026 cm^{-1} were indicative of the existence of carbohydrate-derived compounds.²⁸

The chemical composition of biopolyols was determined by GC-MS, whose chromatograms are shown in Figure 2. For a

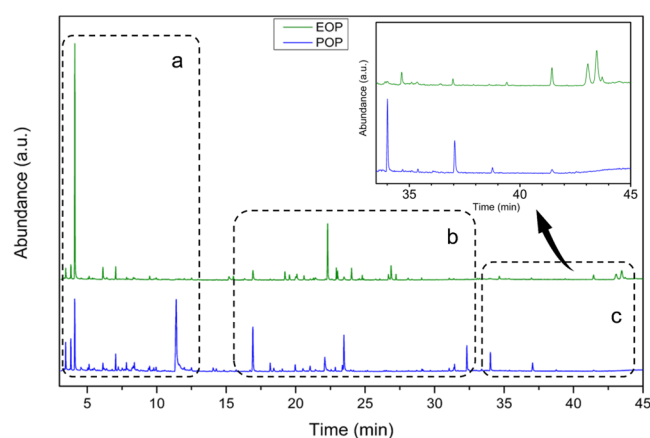


Figure 2. GC-MS chromatograms of EOP and POP.

better understanding, the chromatograms were delimited in three zones, namely, a, b, and c. The first zone a corresponded to carbohydrate degradation compounds, which confirmed the presence of these compounds in both samples, as mentioned in the previous section. It was possible to observe some differences between both samples due to the origin of the raw materials. Thus, in the case of EOP, the most abundant peak corresponded to furfural and no HMF was observed. Since hardwood hemicelluloses are mainly constituted by pentoses, they are mostly decomposed in furfural. On the other hand, in the case of POP, which comes from softwood, the main peak corresponded to HMF, that is, the principal degradation compound of hexoses.¹³ Other degradation compounds such as ethyl glycolate and ethyl lactate from esterification of glycolic and lactic acid were observed.

In contrast, regions identified as b and c represented the compounds generated by the depolymerization of lignin during the organosolv delignification process in which the α and β ether bonds of lignin are hydrolytically broken.²⁹ First, the zone noted as b is the region where the monomeric compounds of lignin were visible. As it was previously mentioned, there were differences between EOP and POP due to the origin of the feedstocks. Hence, EOP was richer in S-derived compounds, such as syringaldehyde among others, which was the most abundant. However, as it was expected, G-derived compounds were also appreciable, although in lesser proportion. On the other hand, G-derived compounds were majority in POP, as summarized in Table 2.

Finally, in the last region c, the presence of dimers and trimers could be observed, although with a low abundance due to the low volatility of these compounds. Nevertheless, this could indicate that biopolyols may contain bigger compounds derived from lignin depolymerization, which were not visible in GC-MS.

EOP and POP were thermogravimetrically analyzed to study the relationship between chemical structure and degradation. The TGA thermograms of each biopolyol and the corresponding derivative thermogravimetry (DTG) curves are shown in Figure 3. The latter, DTG curves, revealed clear differences between both biopolyols. First, the EOP showed three peaks

Table 2. Identification of the Products from EOP and POP Observed in GC-MS Chromatograms^{a,b}

RT (min)	COMPOUND	EOP	POP	Origin
3.451	Ethyl glycolate	✓	✓	C
3.823	Ethyl lactate	✓	✓	C
4.107	Furfural	✓	✓	C
6.129	5-Methylfurfural	✓	✓	C
7.042	Ethyl 2-acetoxy-2-methylacetoacetate	✓	✓	C
11.045	Hydroxymethylfurfural (HMF)	×	✓	C
16.992	Vanillin	✓	✓	G
22.101	Dihydroconiferyl alcohol	×	✓	G
22.305	Syringaldehyde	✓	×	S
22.934	4-propenyl syringol	✓	×	S
23.014	Homosyringaldehyde	✓	×	S
23.475	Coniferyl aldehyde	×	✓	G
24.025	Syringylacetone	✓	×	S
26.863	Sinapyl aldehyde	✓	×	S
34.011	4,4'-stilbenediol,3,3'-dimethoxy-(E)	×	✓	G ^b
37.053	3,4-Divanillyltetrahydrofuran	×	✓	G ^b
38.755	Secoisolaricresinol	×	✓	G ^b
41.443	4,4'-stilbenediol,3,3',5,5'-tetramethoxy-	✓	×	S ^b
41.451	Dibenzylbutyrolactone	×	✓	G ^b
43.265	Syringaresinol	✓	×	S ^b

^aC, carbohydrate; G, guaiacol; S, syringol. ^bTwo phenolic rings.

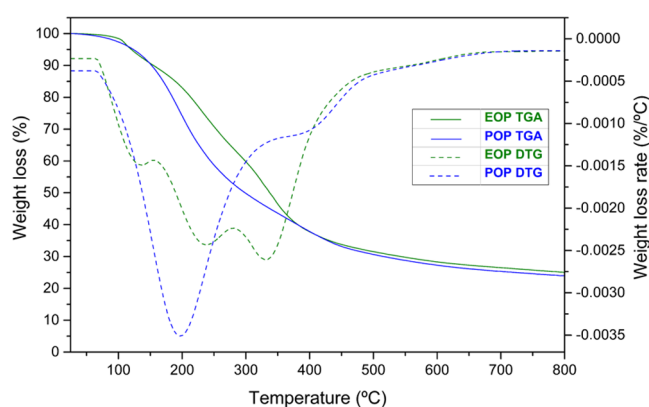


Figure 3. TGA thermograms and DTG curves of EOP and POP.

that corresponded to two degradation zones. The first degradation zone, which represents a total mass loss of 37.64%, was located in the temperature range of 120–260 °C, and it can be associated with the degradation of monomeric compounds from lignin³⁰ and the degradation of carbohydrates.³¹ This region had two maximum degradation peaks, one at 130 °C, which is associated with the most volatile compounds accounting for 10.33% of the mass loss, and the other at 236 °C, which is related to the monomeric compounds with higher boiling points³⁰ and represented a mass loss of 27.31%. The last degradation zone (300–500 °C) had a maximum degradation peak at 331 °C and the largest mass loss with 29.76% of the total mass. This zone is usually attributed to the degradation of lignin; hence, it could be attributed to dimers, trimers, and oligomers, which are expected to be in the biopolyol.³² POP, for its part, even though had the same two degradation areas, did not show the same peaks. Thus, in the first degradation zone, which accounted for 52.14% of mass loss, it showed a single maximum degradation peak at 200 °C. However, in the zone identified as the degradation zone of larger lignin molecules, the maximum degradation peak at about 380 °C is shoulder-shaped and represented only 16.2% of the total mass loss. In

both cases, as the temperature was increased over 500 °C, a loss of mass of about 75% took place, and total residue of 25.07 and 23.96% were left, respectively.

The molecular-weight distribution of each biopolyol was analyzed to determine M_w , M_n , and PI. As expected, due to the origin of biopolyols, both showed low-molecular-weight compounds ranging from 848 to 235 g/mol. Since the detection limit of the equipment is around 230 g/mol, hemicellulose degradation compounds, such as furfural and HMF among others, and lignin-derived small monomers are outside the detection range. However, it can be concluded that biopolyols were also composed of dimers and oligomers from the depolymerization of lignin during the delignification process. Furthermore, the average molecular weights and polydispersity index (PI) of both biopolyols were very similar, as summarized in Table 3. As regards the PI, which is an

Table 3. M_w (g/mol), M_n (g/mol), and PI Values of EOP and POP

biopolyol	M_w (g/mol)	M_n (g/mol)	PI
EOP	648	437	1.493
POP	563	357	1.579

important factor to consider, since it has a direct effect on the applicability of the biopolyol,³³ EOP and POP showed low values, 1.493 and 1.579, respectively. This indicated a homogeneous molecular-weight distribution for both biopolyols. Furthermore, these values were very similar to those of industrial polyethers and polyesters, 1.05 and 1.3 respectively.³³

As can be seen in Figure 4, there were three clear signals in both chromatograms with virtually equal retention times in

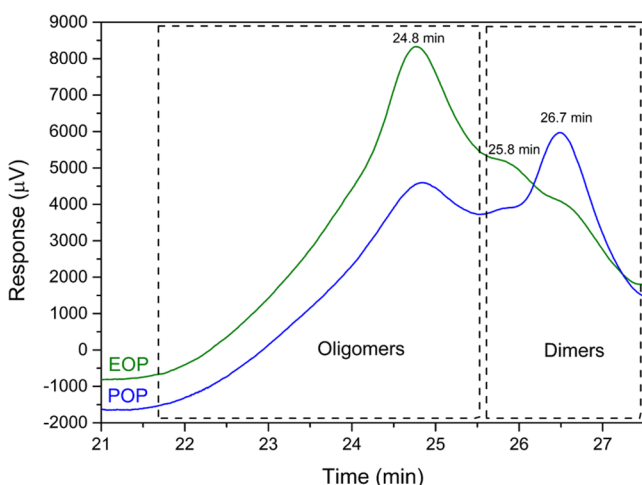


Figure 4. Molecular-weight distribution of EOP and POP.

both cases (24.8, 25.8, and 26.7 min). Nevertheless, there were differences in the intensities of these signals, indicating that the distribution of molecular weights was different in each case. Thus, the first peak (24.8 min) was more intense in the case of EOP, which indicated a higher concentration of trimers and oligomers ($M_w \approx 815$ g/mol) than in the POP, which was in accordance with the results from TGA analysis. Signals displayed at 25.8 and 26.7 min retention times corresponded to areas with molecular weights of around 274 and 235 g/mol, respectively, indicating the presence of dimers in biopolyols.

The latter signal showed an intense peak in POP, whereas in the EOP chromatogram, it was only a shoulder. This would indicate a higher number of dimers in POP than in EOP. However, taking into account the obtained results, it can be concluded that the molecular weights of both biopolyols are in the required range (200–8000 g/mol) for PU production.³⁴

The acidic number (A_n), hydroxyl number (I_{OH}), and functionality of biopolyols are summarized in Table 4.

Table 4. A_n , I_{OH} , and Functionality of EOP and POP

biopolyol	A_n (mg KOH/g)	I_{OH} (mg KOH/g)	functionality
EOP	85.06 ± 2.51	618.07 ± 9.79	4.81
POP	64.34 ± 1.69	587.63 ± 0.63	3.74

As can be seen, two biopolyols presented an elevated A_n , 85.06 and 64.31 mg KOH/g for EOP and POP, respectively. These high A_n values were due to the generation of organic acids, such as formic, levulinic, acetic, glycolic, and lactic acids, during the organosolv delignification process. A low A_n value is preferable since acid groups can react with the amine groups of the catalyst decreasing the efficiency of the reaction.³⁵ However, polyols from lignocellulosic biomass usually presented high A_n values, which can be greater than 40 mg KOH/g.³⁴ To solve this problem, biopolyols could be neutralized using bases such as NaOH or MgOH before their employment to produce PU.³⁶

Otherwise, the EOP and POP I_{OH} values were 618.07 mg KOH/g and 587 mg KOH/g, respectively. Similar values of I_{OH} were obtained by other authors through liquefaction of lignin.^{5,15,37,38} Gosz et al.¹⁵ used Kraft pine lignin to produce biopolyols through liquefaction obtaining I_{OH} values of 610–670 mg KOH/g. Similarly, da Silva et al.⁵ employed Kraft lignin to obtain biopolyols with 660 mg KOH/g when employing lactic acid as a catalyst. Otherwise, I_{OH} values of 538 mg KOH/g were achieved through liquefaction of commercial lignin by Mohammadpour et al.³⁸ These relatively high values can be explained by the presence of compounds with abundant OH-reactive groups, such as dimers and oligomers from lignin, among others. These lignin-derived compounds were formed during the delignification process, during which lignin molecules were broken into smaller fragments that were solubilized in the medium.³⁹ On the other hand, the presence of these lignin-derived compounds explains the functionality values that were obtained. The I_{OH} and functionality values indicate that the biopolyols could be used for the manufacture of PU, such as rigid foams, rigid coatings, and elastoplastics, which required polyols with I_{OH} values from 250–1000 mg KOH/g and functionalities of 3–8.³

Finally, the rheological behavior of biopolyols was analyzed. First, an oscillatory test was carried out to determine the viscoelastic properties of the two biopolyols. For this purpose, a comparison was made between the loss module or viscous module (G'') and the storage or elastic module (G') used to measure the degree of liquid and solid of the biopolyol, respectively.⁴⁰ Figure 5a,b shows that the two polyols had liquid behavior since G'' presented higher values than G' over the entire frequency range. In addition, as it was expected taking into account the molecular weights of the two biopolyols (Table 3), the values of EOP modules were higher than those obtained from POP since they decrease as M_w is reduced.⁴¹

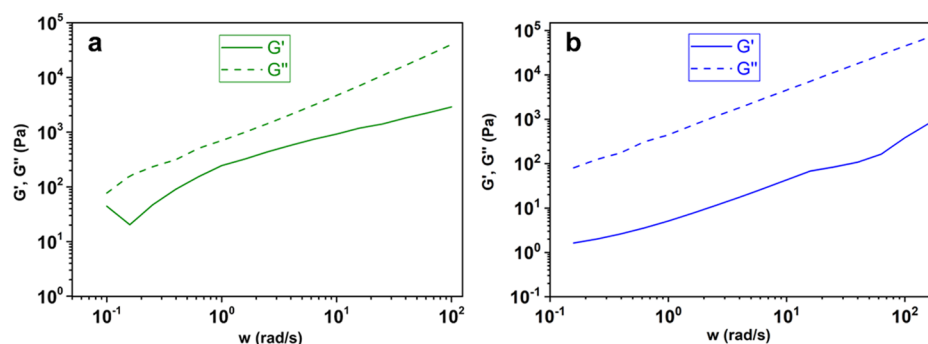


Figure 5. Storage (G') and loss (G'') moduli (Pa) as a function of ω (rad/s) of EOP (a) and POP (b).

In addition, a rotational test was performed to analyze the fluid behavior through the study of the relation between viscosity (η), shear stress (τ), and shear rate ($\dot{\gamma}$). The parameters were adjusted to the power-law equation (eq 3)

$$\tau = \kappa \cdot \dot{\gamma}^n \quad (3)$$

where both n and κ are adjustment parameters that depend on the nature of the fluid and the measurement conditions and have been called consistency index (κ) and flow index (n). The former is related to the apparent viscosity of the fluid at a shear rate of 1 s^{-1} , presenting higher values as the viscosity of the sample increased,⁴² whereas the latter indicates the fluid's behavior. Thus, the fluid is Newtonian if $n = 1$, pseudoplastic when $n < 1$, and dilatant when $n > 1$. A summary of the data obtained by the software is shown in Table 5, and the corresponding flow curves are presented in Figure 6a.

Table 5. Power-Law Linear Functions Based on the Rheological Data from EOP and POP

biopolyol	κ (Pa·s ^{<i>n</i>})	n	R^2
EOP	0.016710	0.9650	0.9983
POP	0.005897	0.9226	0.9418

As can be seen from the study of the data summarized in Table 5, both rheograms showed a good fit as indicated by the R^2 values. In addition, the n values were very close to unity, indicating that both biopolyols behaved as Newtonian fluids. This behavior can be observed in Figure 6a, where the viscosity had a constant value regardless of the applied strain rate. Thus, it can be said that consistency index is simply the constant viscosity, η .⁴³

Nevertheless, to confirm the Newtonian behavior of the biopolyols, the relation between shear stress (τ) and shear rate ($\dot{\gamma}$) was studied and represented in Figure 6b. It was possible to confirm that both had a linear relation as it is expected from a Newtonian fluid where the slope of the line must correspond to the viscosity. This was confirmed since the slopes of the lines in Figure 6b were exactly the same as the κ values reported in Table 5. Thus, EOP had a viscosity of 0.0168 Pa·s, while the viscosity of POP was 0.0059 Pa·s. These values are very low, but they are in accordance with those obtained by other authors^{5,37} and below 300 Pa·s, which resulted suitable values for PU production.⁴⁴ The higher viscosity values in EOP could be explained by its higher molecular weight compared to POP since viscosity is intrinsically related to the molecular weight.⁶

CONCLUSIONS

In summary, two biopolyols were obtained from the aqueous residue resulting from the precipitation of the lignin contained in the organosolv liquors. Yields of 5.43 and 5.24% for EOP and POP were obtained with respect to the initial raw material, respectively. The average molecular weights of these biopolyols were 648 and 563 g/mol, and their polydispersity indexes were 1.493 and 1.579, respectively, which were very similar to those of industrial polyether and polyester polyols (1.05 and 1.3, respectively). On the other hand, the I_{OH} and functionality values were 618 mg KOH/g and 4.81 in the case of EOP and 587 mg KOH/g and 3.74 in the case of POP, respectively. However, due to the origin of the biopolyols, the acidic numbers of both biopolyols were elevated. Finally, the study of the rheological behavior of the biopolyols revealed that both biopolyols behaved as Newtonian fluids with viscosity values of

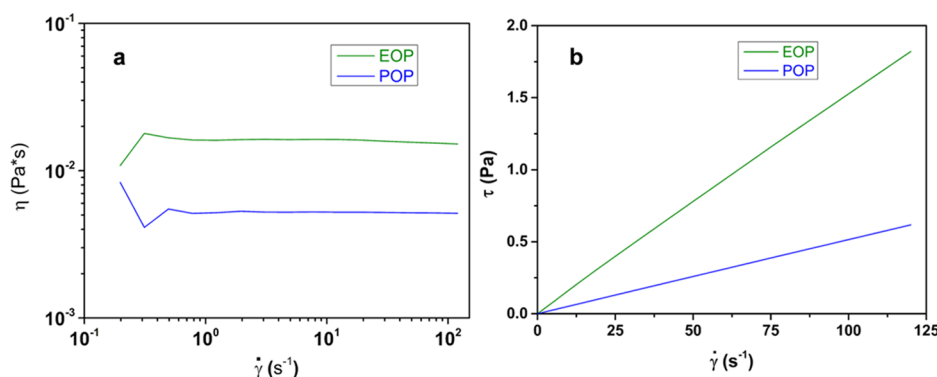


Figure 6. (a) Viscosity (η) VS shear rate ($\dot{\gamma}$) and (b) shear stress (τ) VS shear rate ($\dot{\gamma}$) of EOP and POP.

0.0168 and 0.0059 Pa·s for EOP and POP, respectively. All of these characteristics indicated that both biopolyols were suitable for the manufacture of polyurethanes. Therefore, the aqueous residue from organosolv black liquors was successfully valorized.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Ripple, W. J.; Wolf, C.; Newsome, T. M.; Barnard, P.; Moomaw, W. R. World Scientists' Warning of a Climate Emergency. *Bioscience* **2019**, *70*, 1–7.
- (2) Kumar, N.; Sonthalia, A.; Pali, H. S.; Sidharth Next-Generation Biofuels-Opportunities and Challenges. In *Innovations in Sustainable Energy and Cleaner Environment*; Gupta, A. K.; De, A.; Aggarwal, S. K.; Kushari, A.; Runchal, A. K., Eds.; Springer: Singapore, 2020 171–191.
- (3) Li, Y.; Luo, X.; Hu, S. Introduction to Bio-based Polyols and Polyurethanes. In *Bio-Based Polyols and Polyurethanes*; SpringerBriefs in Molecular Science; Springer International Publishing: Cham, 2015; pp 1–13.
- (4) Crescentini, T. M.; May, J. C.; McLean, J. A.; Hercules, D. M. Mass Spectrometry of Polyurethanes. *Polymer* **2019**, *181*, No. 121624.
- (5) da Silva, S. H. F.; Egiús, I.; Labidi, J. Liquefaction of Kraft Lignin Using Polyhydric Alcohols and Organic Acids as Catalysts for Sustainable Polyols Production. *Ind. Crops Prod.* **2019**, *137*, 687–693.
- (6) da Silva, S. H. F.; dos Santos, P. S. B.; Thomas da Silva, D.; Briones, R.; Gatto, D. A.; Labidi, J. Kraft Lignin-Based Polyols by Microwave: Optimizing Reaction Conditions. *J. Wood Chem. Technol.* **2017**, *37*, 343–358.
- (7) Abid, A.; Brosse, N.; Ziegler-Devin, I.; Gabsi, S. Production and Characterization of Rigid Polyurethane Foam by Oxypropylation of Organosolv Lignin Extracted from Exhausted Olive Pomace. *J. Polym. Res.* **2020**, *27*, No. 266.
- (8) Kirk, T. K.; Farrell, R. L. Enzymatic “Combustion”: The Microbial Degradation of Lignin. *Annu. Rev. Microbiol.* **1987**, *41*, 465–501.
- (9) Bajwa, D. S.; Pourhashem, G.; Ullah, A. H.; Bajwa, S. G. A Concise Review of Current Lignin Production, Applications, Products and Their Environment Impact. *Ind. Crops Prod.* **2019**, *139*, No. 111526.
- (10) Brosse, N.; Hussin, M. H.; Rahim, A. A. Organosolv Processes. In *Biorefineries*; Wagemann, K.; Tippkötter, N., Eds.; Advances in Biochemical Engineering/Biotechnology; Springer International Publishing: Cham, 2017; Vol. 166 pp, 153–176.
- (11) Erdocia, X.; Prado, R.; Corcuera, M. Á.; Labidi, J. Effect of Different Organosolv Treatments on the Structure and Properties of Olive Tree Pruning Lignin. *J. Ind. Eng. Chem.* **2014**, *20*, 1103–1108.
- (12) Lauwaert, J.; Stals, I.; Lancefield, C. S.; Deschaumes, W.; Depuydt, D.; Vanlerberghe, B.; Devlamynck, T.; Bruijninckx, P. C. A.; Verberckmoes, A. Pilot Scale Recovery of Lignin from Black Liquor and Advanced Characterization of the Final Product. *Sep. Purif. Technol.* **2019**, *221*, 226–235.
- (13) Hernández-Ramos, F.; Fernández-Rodríguez, J.; Alriols, M. G.; Labidi, J.; Erdocia, X. Study of a Renewable Capping Agent Addition in Lignin Base Catalyzed Depolymerization Process. *Fuel* **2020**, *280*, No. 118524.
- (14) Carriço, C. S.; Fraga, T.; Pasa, V. M. D. Production and Characterization of Polyurethane Foams from a Simple Mixture of Castor Oil, Crude Glycerol and Untreated Lignin as Bio-Based Polyols. *Eur. Polym. J.* **2016**, *85*, 53–61.
- (15) Gosz, K.; Kosmela, P.; Hejna, A.; Gajowiec, G.; Piszczuk, Ł. Biopolyols Obtained via Microwave-Assisted Liquefaction of Lignin: Structure, Rheological, Physical and Thermal Properties. *Wood Sci. Technol.* **2018**, *52*, 599–617.
- (16) Alinejad, M.; Nikafshar, S.; Gondaliya, A.; Bagheri, S.; Chen, N.; Singh, S. K.; Hodge, D. B.; Nejad, M.; Henry, C. Lignin-Based Polyurethanes: Opportunities for Bio-Based Foams, Elastomers, Coatings and Adhesives. *Polymers* **2019**, *11*, No. 1202.
- (17) Gharib, J.; Pang, S.; Holland, D. Synthesis and Characterisation of Polyurethane Made from Pyrolysis Bio-Oil of Pine Wood. *Eur. Polym. J.* **2020**, *133*, No. 109725.
- (18) Mahmood, N.; Yuan, Z.; Schmidt, J.; Xu, C. Depolymerization of Lignins and Their Applications for the Preparation of Polyols and Rigid Polyurethane Foams: A Review. *Renewable Sustainable Energy Rev.* **2016**, *60*, 317–329.
- (19) Yáñez-S, M.; Matsuhira, B.; Nuñez, C.; Pan, S.; Hubbell, C. A.; Sannigrahi, P.; Ragauskas, A. J. Physicochemical Characterization of Ethanol Organosolv Lignin (EOL) from *Eucalyptus Globulus*: Effect of Extraction Conditions on the Molecular Structure. *Polym. Degrad. Stab.* **2014**, *110*, 184–194.
- (20) Domínguez, J. C.; Santos, T. M.; Rigual, V.; Oliet, M.; Alonso, M. V.; Rodríguez, F. Thermal Stability, Degradation Kinetics, and Molecular Weight of Organosolv Lignins from *Pinus Radiata*. *Ind. Crops Prod.* **2018**, *111*, 889–898.
- (21) Wells, T.; Kosa, M.; Ragauskas, A. J. Polymerization of Kraft Lignin via Ultrasonication for High-Molecular-Weight Applications. *Ultrason. Sonochem.* **2013**, *20*, 1463–1469.
- (22) ASTM D4274-99. *Standard Test Methods for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols*; ASTM International, 2000.
- (23) ASTM D974-12. *Designation: Standard Test Method for Acid and Base Number by Color-Indicator Titration 1*; ASTM, 2013; pp 1–7.
- (24) Chi, Z.; Wang, Z.; Liu, Y.; Yang, G. Preparation of Organosolv Lignin-Stabilized Nano Zero-Valent Iron and Its Application as Granular Electrode in the Tertiary Treatment of Pulp and Paper Wastewater. *Chem. Eng. J.* **2018**, *331*, 317–325.

- (25) Chen, L.; Wang, X.; Yang, H.; Lu, Q.; Li, D.; Yang, Q.; Chen, H. Study on Pyrolysis Behaviors of Non-Woody Lignins with TG-FTIR and Py-GC/MS. *J. Anal. Appl. Pyrolysis* **2015**, *113*, 499–507.
- (26) Fernández-Rodríguez, J.; Erdocia, X.; Sánchez, C.; González Alriols, M.; Labidi, J. Lignin Depolymerization for Phenolic Monomers Production by Sustainable Processes. *J. Energy Chem.* **2017**, *26*, 622–631.
- (27) Jiang, X.; et al. Thermogravimetry-FTIR Analysis of Pyrolysis of Pyrolytic Lignin Extracted from Bio-Oil. *Chem. Eng. Technol.* **2012**, *35*, 827–833.
- (28) Morales, A.; Hernández-ramos, F.; Sillero, L.; Fernández-marín, R.; Dávila, I.; Gullón, P.; Erdocia, X.; Labidi, J. Multiproduct biorefinery based on almond shells: Impact of the Delignification stage on the manufacture of valuable products. *Bioresour. Technol.* **2020**, *315*, No. 123896.
- (29) Zhang, Z.; Harrison, M. D.; Rackemann, D. W.; Doherty, W. O. S.; O'Hara, I. M. Organosolv Pretreatment of Plant Biomass for Enhanced Enzymatic Saccharification. *Green Chem.* **2016**, *18*, 360–381.
- (30) Jensen, M. M.; Djajadi, D. T.; Torri, C.; Rasmussen, H. B.; Madsen, R. B.; Venturini, E.; Vassura, I.; Becker, J.; Iversen, B. B.; Meyer, A. S.; Jørgensen, H.; Fabbri, D.; Glasius, M. Hydrothermal Liquefaction of Enzymatic Hydrolysis Lignin: Biomass Pretreatment Severity Affects Lignin Valorization. *ACS Sustainable Chem. Eng.* **2018**, *6*, 5940–5949.
- (31) Girometta, C.; Dondi, D.; Baiguera, R. M.; Bracco, F.; Branciforti, D. S.; Buratti, S.; Lazzaroni, S.; Savino, E. Characterization of Mycelia from Wood-Decay Species by TGA and IR Spectroscopy. *Cellulose* **2020**, *27*, 6133–6148.
- (32) Morales, A.; Gullón, B.; Dávila, I.; Eibes, G.; Labidi, J.; Gullón, P. Optimization of Alkaline Pretreatment for the Co-Production of Biopolymer Lignin and Bioethanol from Chestnut Shells Following a Biorefinery Approach. *Ind. Crops Prod.* **2018**, *124*, 582–592.
- (33) D'Souza, J.; Camargo, R.; Yan, N. Biomass Liquefaction and Alkoxylation: A Review of Structural Characterization Methods for Bio-Based Polyols. *Polym. Rev.* **2017**, *57*, 668–694.
- (34) Hu, S.; Luo, X.; Li, Y. Polyols and Polyurethanes from the Liquefaction of Lignocellulosic Biomass. *ChemSusChem* **2014**, *7*, 66–72.
- (35) Hu, S.; Li, Y. Polyols and Polyurethane Foams from Base-Catalyzed Liquefaction of Lignocellulosic Biomass by Crude Glycerol: Effects of Crude Glycerol Impurities. *Ind. Crops Prod.* **2014**, *57*, 188–194.
- (36) Jiang, W.; Kumar, A.; Adamopoulos, S. Liquefaction of Lignocellulosic Materials and Its Applications in Wood Adhesives—A Review. *Ind. Crops Prod.* **2018**, *124*, 325–342.
- (37) Briones, R.; Serrano, L.; Labidi, J. Valorization of Some Lignocellulosic Agro-Industrial Residues to Obtain Biopolyols. *J. Chem. Technol. Biotechnol.* **2012**, *87*, 244–249.
- (38) Mohammadpour, R.; Mir Mohamad Sadeghi, G. Effect of Liquefied Lignin Content on Synthesis of Bio-Based Polyurethane Foam for Oil Adsorption Application. *J. Polym. Environ.* **2020**, *28*, 892–905.
- (39) El Hage, R.; Brosse, N.; Sannigrahi, P.; Ragauskas, A. Effects of Process Severity on the Chemical Structure of Miscanthus Ethanol Organosolv Lignin. *Polym. Degrad. Stab.* **2010**, *95*, 997–1003.
- (40) Tseng, Y. C.; Hsieh, Y. C.; Chin, N. Y.; Huang, W. Y.; Hou, S. S.; Jan, J. S. Synthesis, thermal properties and rheological behaviors of novel Poly(Ethylene Glycol) segmented Poly(Arylene Ether)s. *Polymer* **2020**, *196*, No. 122426.
- (41) Behera, K.; Chang, Y. H.; Chiu, F. C.; Yang, J. C. Characterization of Poly(Lactic Acid)s with Reduced Molecular Weight Fabricated through an Autoclave Process. *Polym. Test.* **2017**, *60*, 132–139.
- (42) Chimene, D.; Peak, C. W.; Gentry, J. L.; Carrow, J. K.; Cross, L. M.; Mondragon, E.; Cardoso, G. B.; Kaunas, R.; Gaharwar, A. K. Nanoengineered Ionic-Covalent Entanglement (NICE) Bioinks for 3D Bioprinting. *ACS Appl. Mater. Interfaces* **2018**, *10*, 9957–9968.
- (43) Parcheta, P.; Datta, J. Structure-Rheology Relationship of Fully Bio-Based Linear Polyester Polyols for Polyurethanes - Synthesis and Investigation. *Polym. Test.* **2018**, *67*, 110–121.
- (44) Cateto, C. A.; Barreiro, M. F.; Rodrigues, A. E.; Belgacem, M. N. Optimization Study of Lignin Oxypropylation in View of the Preparation of Polyurethane Rigid Foams. *Ind. Eng. Chem. Res.* **2009**, *48*, 2583–2589.