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Valorisation of crude glycerol in the production of liquefied lignin bio-polyols for polyurethane formulations

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ABSTRACT

Bio-polyols, produced by liquefying lignin with polyhydric alcohols, offer a promising alternative to conventional polyols for polyurethane production. To enhance the sustainability on the production of these bio-polyols, this study proposes the use of crude glycerol and microwave-assisted liquefaction as substitutes for conventional methods and commercial glycerol. This approach reduces the energy requirements of the reaction while also adding value to this by-product. The synthesis of bio-polyols with suitable properties to produce elastic and rigid polyurethane was carried out using previously optimised reaction conditions. Organosolv lignins obtained from *Eucalyptus globulus* and *Pinus radiata* were employed, using polyethylene glycol and crude glycerol as solvents and sulphuric acid as a catalyst. Several parameters of the bio-polyols were analysed, including hydroxyl number (I_{OH}), acid number (A_n), and functionality (*f*), suggesting that the bio-polyols were suitable for polyurethane synthesis. Bio-polyols formulated to produce rigid polyurethanes exhibited I_{OH} values of 554 and 383 (mg KOH/g), A_n values of 1.91 and 4.21 (mg KOH/g), and functionalities of 4.16 and 3.14 for *Eucalyptus globulus* and *Pinus radiata* lignin. In the case of bio-polyols for elastic polyurethanes, the values were 228 and 173 (mg KOH/g) (I_{OH}), 20.94 and 25.09 (mg KOH/g) (A_n), and functionalities of 3.51 and 2.08.

1. Introduction

The impact of human activity has become so relevant that the Nobel Prize winner, Paul J. Crutzen, proposed a new term to place it in a geological context [1]. This new term, the Anthropocene, even though it has not been officially established by academia, is now in vogue. However, the mere fact that the scientific community has acquired and maintained it so far, makes it clear how important the human footprint on the environment is. The use of petroleum, not only as fuel but also as a feedstock for the manufacture of different materials, represents one of the main causes of the degradation of the environment. For this reason, the scientific community is looking for new sources of raw materials that could totally or partially substitute the use of petroleum.

Among petroleum derived materials, PUs, first synthesised by Dr. Otto Bayer in 1937, have become one of the most versatile man-made synthetic materials [2]. Such versatility lies in their excellent mechanical, chemical, and physical properties, such as abrasion resistance, elasticity, biocompatibility, durability, or toughness [3]. PUs can be used for the manufacture of a variety of products, such as foams, elastomers, paints, coatings, adhesives or medical applications [4]. PUs are cross-linked materials formed by a poly-addition reaction between isocyanates (with more than one isocyanate group per molecule) and molecules with two or more OH reactive groups called polyols [5]. In 2019, the polyol market generated around USD 26.2 billion and it is expected to reach USD 34.4 billion by 2024 [6]. Although the polyols employed nowadays to synthesise PUs are generally petroleum-derived compounds, it is possible to substitute them with lignocellulosic biomass-derived materials to produce more eco-friendly PUs that satisfy the requirements of new and more rigorous legislation [7].

Lignocellulosic biomass is formed mainly by cellulose,

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hemicellulose, and lignin forming a composite matrix [8], and it is considered a sustainable raw material source to produce high valued-added commodities [9]. Cellulose, the earth's most abundant renewable biopolymer, can be used in different industrial fields. Probably its most well-known application, apart from pulp production, is the conversion to bioethanol to be used as biofuel. Nevertheless, its remarkable properties, such as high abrasion resistance, biocompatibility, biodegradability and chemical stability, make it suitable to be used for the manufacture of composites [10], in medical applications, food packaging and photoelectric materials, among others [11]. Meanwhile, hemicelluloses can be used to produce xylooligosaccharides and furfural [12]. Finally, lignin, which is considered as the most abundant renewable phenolic polymer [13], is usually burned to supply energy to paper mills where it is generated as waste [14]. However, due to its phenolic nature, high availability, low cost, and the presence of aliphatic and phenolic OH groups, lignin can be used to create high value-added bio-based products, including bio-based polyols [15]. Nevertheless, despite the large number of OH group present in the lignin molecule, chemical modifications of its structure are usually necessary, as many of these groups are not accessible because of being sterically hindered, which significantly decreases the reactivity of this molecule [16]. In this work, different lignin modification strategies have been tested to obtain these polyols, of which, oxyalkylation and liquefaction with polyhydric alcohols are the most relevant ones [17].

Lignin liquefaction reaction is typically carried out under atmospheric pressure and acidic conditions (H_2SO_4) employing mild temperatures(150–170 °C), a reaction time around 90 min, and using PEG and CG as solvents [18]. Hence, as conventional lignin liquefaction methods entail high energy expenses attributed to lengthy residence times and elevated temperatures, it becomes imperative to investigate alternative approaches that are more eco-friendly. The aim is to diminish operational costs and optimise the aforementioned factors to enhance the industrial feasibility of the process. In this regard, microwave-assisted irradiation presents itself as a compelling substitute for traditional lignin liquefaction techniques. By enabling rapid and uniform heating, it reduces reaction time and subsequently lowers energy consumption [19]. Generally, technical grade petroleum derived-glycerol is used for the liquefaction process. There is, however, a large amount of glycerol that is generated as a by-product in the biodiesel industry. In fact, for every 10 t of generated biodiesel, 1 t of crude glycerol is produced. Once purified, this glycerol can be used in the food, pharmaceutical and cosmetic industries [20]. Nevertheless, due to the large surplus of CG caused mainly by the booming of biodiesel industry, the price of the refined product decreased in recent years [21], thus making it unprofitable for small plants [22]. It is therefore necessary to find an industrial use for this waste, such as reactant it in the liquefaction of lignin to produce polyols. Different studies have been carried out in this field, where CG was successfully employed to synthesise bio-polyols from lignocellulosic biomass [18,23,24] or lignin [25–29]. Hence, the combination of using the application of both microwave-assisted reaction and the utilisation of crude glycerol in the lignin liquefaction process can be a significant step forward in incorporating lignin into the polyurethane industry. However, unlike conventional methods where temperatures, times, and reactant concentrations are well established, it is necessary to continue research in order to establish suitable reaction conditions. For this reason, in the present study, *Eucalyptus globulus* and *Pinus radiata* organosolv lignin samples were liquefied employing PEG and CG through microwave irradiation technology. The optimised reaction conditions were obtained from a previous work [30]. The produced bio-polyols were characterised to evaluate relevant parameters for their use as polyurethane precursors. Thus, hydroxyl number index (I_{OH}), acid number (A_n), molecular weight (M_w), polydispersity index (PI), functionality (*f*) as well as liquefaction yield and rheological behaviour were determined.

2. Materials and methods

2.1. Materials

Eucalyptus globulus and *Pinus radiata* were kindly supplied by Papelera Guipuzcoana Zikuñaga S.A. and Ebaki XXI S.A. The vegetable oil employed to obtain the CG was sunflower oil used for cooking and collected from the canteen of the Gipuzkoa Engineering School in Eibar, University of the Basque Country, UPV/EHU. Sulphuric acid (96 %), KOH (85 %) and PEG400 were purchased from Panreac. Ethanol and methanol were obtained from Scharlab S.L. The rest of technical reagents were supplied by Fisher Scientific, i.e., sodium sulphate anhydrous (≥99 %), dimethyl-formamide (DMF, for HPLC ≥%99.9), ethyl acetate (HPLC grade), lithium bromide, 1,4-dioxane, pyridine (analytical grade) and phthalic anhydride (%98).

2.2. Lignin obtention procedure

Lignin samples from *Eucalyptus globulus* and *Pinus radiata* sawdust were obtained through an organosolv delignification treatment employing a 1.5 L stainless steel 5500 Parr reactor equipped with a 4848 Parr controller. After the delignification process, the resulting black liquors were treated by an ultrasonication process using a HD 3100 Sonoplus ultrasonic homogenizer. Finally, the black liquors were acidified to precipitate the lignin, obtaining an aqueous phase and a solid phase (lignin) which were separated by membrane filtration in a 2 L stainless steel holder employing a 0.22 μm pore diameter nylon filter. The reaction conditions for the organosolv and ultrasonication processes were defined in a previous study [31]. The molecular weight distribution of the resulting ultrasonicated organosolv lignin samples from *Eucalyptus globulus* and *Pinus radiata* (EUL and PUL respectively) are listed in Table 1 and were determined by gel permeation chromatography (details described in Section 2.4.2).

2.3. Synthesis of bio-polyols through microwave assisted liquefaction

Table 2 summarises the reaction conditions used to synthesise the bio-polyols. These reaction settings were established as optimal in a previous work [30].

The reaction was carried out employing a CEM Microwave Discover System Model with a temperature control instrument and an internal temperature sensor. The reactions were performed as follows: the solid liquid ratio was 1:6 in all cases and the reaction time was 5 min, under constant stirring. Previously established quantities of reagents were weighed into a quartz vessel and (4 g in total) introduced into the reactor. As soon as the reaction was completed, the vessel was cooled down to a safe temperature for handling. Acetone was employed to dilute the obtained product to facilitate filtration to separate the bio-polyol from the solids. Finally, a rotary evaporator was used to remove the acetone from the bio-polyol.

2.4. Transesterification of vegetable oil to obtain crude glycerol

CG was obtained by the transesterification reaction of used vegetable oil (sunflower oil for cooking) with methanol in a molar ratio of 6:1 (methanol:oil). The reaction was catalysed by KOH (1 % wt. of oil). Oleic acid with a molecular weight of 884 g/mol was assumed as the predominant triglyceride for the calculations. The reaction was performed as follows: firstly, the oil was filtered to remove the impurities; then it

Table 1
Molecular weight distribution of lignin samples.

Sample	M_w (g/mol)	M_n (g/mol)	PI
EUL	2837	888	3.196
PUL	2924	911	3.209

Table 2

Liquefaction reaction conditions (data pending publication).

Bio-polyol	Rigid bio-polyol		Elastic bio-polyol	
	EPR_{CG}	PPR_{CG}	EPE_{CG}	PPE_{CG}
Cat (% wt.)	0	0	5	3.86
Temperature (°C)	161	159	180	160
PEG/CG (% wt.)	3/1	3/1	7.57/1	7.34/1

was heated to 60 °C in a volumetric flask employing a heating plate with magnetic stirring (600 rpm). Once the temperature of 60 °C was reached, a previously prepared methanol/KOH mixture was added. The reaction was kept for 120 min under reflux to maximise the conversion. The reaction was considered finished as soon as a good phase separation of the mixture was observed, and it was left for 24 h in a separation funnel to separate the biodiesel and glycerol.

2.4.1. *Characterisation of crude glycerol*

Physical properties of CG, such as density, pH and viscosity were determined. The density was calculated by measuring the weight of a known volume of crude glycerol at room temperature. The pH of the CG was determined at room temperature employing a pH meter Crison basic 20 by dissolving 1.00 ± 0.1 g of CG in 50 mL of deionised water. Ash content was analysed following the ISO 2098-1972 Standard method, which consist in burning at 750 °C for 3 h 1 g of CG in a muffle furnace. The elemental analysis was carried out using a Leco TruSpec HCNS micro elemental analyser at 1050 °C. Both carrier gas (pure Helium 3×) and test gas (extra pure Oxygen 4×) were supplied by Nippon Gases. The calibration was performed using Leco Sulfamethazine (C = 51.78 %; H = 5.07 %; N = 20.1 %; O = 11.5 %; S = 11.5 %). Triplicate assays were performed using 2 mg samples. Oxygen was calculated by difference.

The chemical composition of CG was determined through GC–MS analysis. 0.2 g of CG were dissolved into 25 mL of methanol (HPLC grade), and the solution was injected in a GC (7890)-MS (5975C inert MSD with Triple-Axis Detector) Agilent equipped with a HP-5MS ((5 %-Phenyl)-methylpolysiloxane, 30 m × 0.25 mm) capillary column with Helium as carrier gas. The temperature program is as follows: the program started at 50 °C; then, it was raised to 120 °C at an 8 °C/min heat rate; this temperature was kept for 5 min; then, it was increased to 280 °C at 8 °C/min and held for 8 min; finally, the temperature was raised to 300 °C at 10 °C/min and held for 2 min.

FTIR analysis was performed to analyse and compare the chemical structure between CG and commercial glycerol. A PerkinElmer Spectrum Two FT-IR Spectrometer equipped with a Universal Attenuated Total Reflectance accessory provided with an internal reflection diamond crystal lens was employed. 20 scans in transmission mode were collected with a resolution of 4 cm^{-1} in the range of 4000–400 cm^{-1}.

2.4.2. *Characterisation of the obtained bio-polyols*

Bio-polyols that were obtained through the liquefaction of lignin employing PEG400 and CG were characterised to determine important parameters, such as molecular weight distribution (M_w, M_n and PI), I_{OH}, A_n, and *f*.

A gel permeation chromatography (GPC) analysis was used to determine the molecular weight distribution of the bio-polyols. To this end, a JASCO instrument equipped with an LC.Netll/ADC interface, two columns in series (PolarGel-M 300 mm × 7.5 mm) and a RI-2031Plus refractive index detector was used. *N*,*N*-dimethylformamide with 1 % lithium bromide was employed as mobile phase with a flow rate of 700 mm^3/min and a temperature of 40 °C was used. The calibration curve was made employing polystyrene standards with molecular weight from 266 to 70,000 g/mol (Sigma-Aldrich).

I_{OH} (mg KOH/g) was calculated following the ASTM D4274 standard, as follows: 0.5–1 g of bio-polyol was dissolved into 25 mL of the phtalation reagent consisting of 115 g of phthalic anhydride dissolved in 700 mL of pyridine. The reaction was carried out at 115 °C for 1 h under constant stirring. Afterwards, 50 mL of pure pyridine was added through the condenser. The resulting solution was back titrated employing a NaOH solution (0.5 M). The acid number (A_n) was determined according to ASTM D974 standard by dissolving 0.4 g of bio-polyol in 50 mL of a 4:1 (v/v) solution of 1,4-dioxane in water. Due to the dark colour of the resulting solution, it was not possible to perform a titration using phenolphthalein as indicator. Therefore, a potentiometric titration was done using an automatic titrator (888 Titrando Metrohm) through Tiamo 2.5 software.

The thermal degradation of bio-polyols was studied through a thermogravimetric analysis (TGA). 5 mg of bio-polyol were heated under inert atmosphere (N_2 10mL·min^{-1}) from 25 °C to 800 °C. The heat rate was 10 °C·min^{-1}. The equipment employed was a TGA/SDTA RSI analyser (Mettler Toledo).

The rheological behaviour of the biopolyols were analysed through both oscillatory and rotational tests. The former was carried out to determine the storage modulus (G′), while the latter was used to study the viscosity and shear stress as a function of the shear rate. A Haake Viscotester IQ (Thermo Fisher Scientific) rheometer was employed using a coaxial cylinders geometry (CC 25 DIN/Ti adapter) with a piston radius of 12.54 mm and a ring gap of 1.00 mm. The frequency sweep for the oscillatory test was from 0.1 to 100 rad·s^{-1} at a fixed strain of 10 %, while for the rotational test a shear rate sweep from 0.02 to 120 s^{-1} was used. The measurements were collected at room temperature.

3. Results and discussion

3.1. *Crude glycerol characterisation*

This section contains the physical properties and composition of CG. The pH of the obtained crude glycerol was 10.55 ± 0.02, which indicates the presence of residual KOH catalyst and potassium salts formed during the transesterification reaction. This value is in agreement with those obtained by other authors who characterised crude glycerol from the transesterification reaction of vegetable oils with NaOH or KOH as catalyst [32–34]. As it was expected, the density of CG (1.03 ± 0.07 g/cm^3) resulted lower than that of pure glycerol (1.259 g/cm^3) due to the presence of lighter impurities such as fatty acids, fatty acids methyl esters (FAMEs), water and methanol traces [33]. The water content in CG significantly varies depending on the manufacturing industry, from a 3.6 % in the case of the soap industry to a 55.3 % in CGs from Stearin production. CGs obtained from transesterification reaction present water contents from 8.16 % to 43.2 % [35], although a maximum of 12 % is recommended to reduce purification costs [36]. Therefore, the water content of the CG obtained in this work (11.64 ± 1.61 %) is within the specifications of a crude glycerol obtained through transesterification reaction. Such water, can hydrolyse the triglycerides to form free fatty acids (FFA) which results in soaps decreasing the reaction yield [35].

The elemental analysis of CG showed that the 46.00 ± 1.29 % of the organic matter corresponded to Carbon (C). This high value can be explained by the high presence of impurities, such as, soaps, FAMEs and glycerides, which have higher C content than glycerol. Hu et al. [33] reported similar C values for CG obtained from different soy and vegetable oil wastes. In addition, the obtained nitrogen (0.15 ± 0.01 %), hydrogen (8.17 ± 0.33 %) and oxygen (35.6 ± 1.58 %) percentages were in accordance with the values reported for different CG obtained from different vegetable oils [20,33,37]. Nevertheless, the measured sulphur concentration (1.33 ± 0.04) was higher than the values obtained in the mentioned studies, ranging from ppms to a maximum of 0.078 %. The chemical composition of CG was determined through GC–MS. In addition to glycerol (41.84 ± 0.17 %), CG was found to be rich in other compounds which include fatty acids (11.46 ± 6.01 %) and FAMEs (26.31 ± 7.68 %), among others (Fig. 1).

The chemical structure of the CG was determined through FTIR analysis and it was compared with a commercial glycerol sample

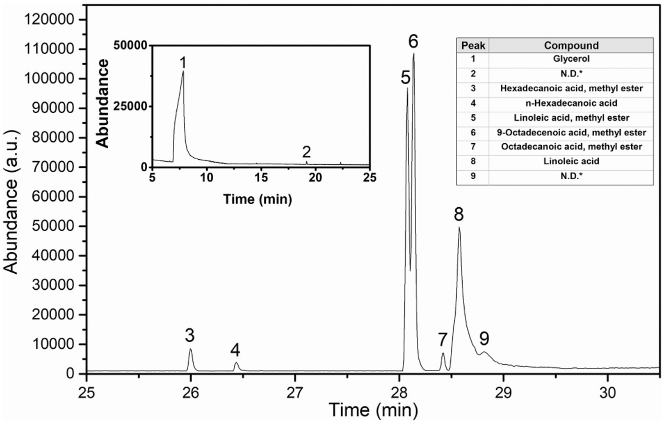


Fig. 1. GC–MS chromatogram of crude glycerol.

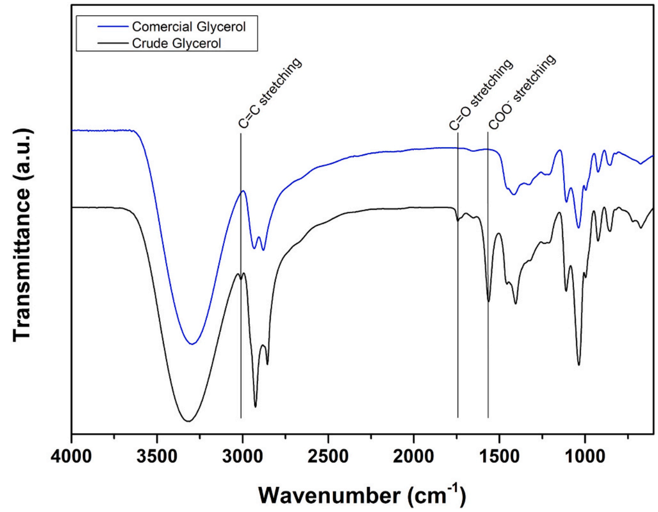


Fig. 2. FTIR spectra of commercial glycerol and crude glycerol.

(Fig. 2). CG showed the main functional groups of commercial grade glycerol: O—H stretching and bending (3300 cm^{-1} and 920 cm^{-1} respectively), C—H asymmetric and symmetric stretching (2920 cm^{-1} and 2851 cm^{-1} respectively), C—O stretching of primary alcohol (1456 cm^{-1}) and secondary alcohol (1110 cm^{-1}) as well as H_2O blending (1650 cm^{-1}) [32,38]. Moreover, characteristic peaks of CG were also observed. The first one, a small peak associated to C=C stretching (3015 cm^{-1}) related to unsaturated compounds [32]; the second one, associated with the presence of carbonyl groups (C=O) of esters or carboxylic acids of fatty acids (1745 cm^{-1}) [39]. Finally, a signal related to the presence of carboxylate ions COO^{-} was observed (1560 cm^{-1}), indicating the presence of soap in the CG sample [32,39].

3.2. *Characterisation of the bio-polyols*

Table 3 summarises the data obtained from the characterisation of the bio-polyols. An adequate M_w of polyols is essential to obtain PUs with the desired soft segment properties. Depending on the final application, the PUs' molecular weight should be between 300 and 1000 (g/mol) for rigid PU, and between 2000 and 10,000 (g/mol) for elastic PU [40].

As expected, the higher the acid concentration, the higher the M_w. Thus, bio-polyols for rigid PU (EPR_{CG}, PPR_{CG}) where no catalyst was used, showed lower M_w than the bio-polyols for elastic PU (EPE_{CG}, PPE_{CG}) (Fig. 3). This increase in the M_w is a consequence of the repolymerisation reactions which are favoured in the presence of an acid catalyst [41]. In addition, EPE_{CG} bio-polyol showed a significantly higher M_w than PPE_{CG} since, as the catalyst concentration increased above 3 %, the repolymerisation reactions also increase [18]. On the other hand, it has been documented that the polymerisation reactions between glycerol, FFA and FAMEs of CG can also increase the M_w of bio-polyols [42]. However, since the bio-polyols with higher CG content but without catalyst showed the lowest molecular weight, it could be concluded that these reactions were of lesser importance than the repolymerisation reactions caused by the acid catalyst. The polydispersity index is also crucial for the final application of the PU, as it is related to the chain length variation and, depending on the chain length of the polymer, the PU could show an undesired behaviour [43]. It was observed that the polydispersity index was also affected by repolymerisation reactions caused by an increase in catalyst concentration. Thus, the bio-polyol with the highest catalyst concentration (EPE_{CG}) exhibited the highest M_w and polydispersity index, followed by PPE_{CG}. As stated above, EPE_{CG} and PPE_{CG} bio-polyols' M_w values fitted in the range for the manufacture of elastic PUs. On the other hand, although the molecular weights of EPR_{CG} and PPR_{CG} bio-polyols were slightly higher than the required for the manufacture of rigid PUs, they could be considered suitable for the manufacture of this kind of PUs.

The I_{OH} required for the synthesis of rigid PUs ranges between 200 and 1000 mg KOH/g, while for elastic PUs it is between 28 and 160 mg KOH/g [44]. It is also well known that an elevated A_n can decrease the efficiency of the reaction, so a low A_n value is desired [45]. These two

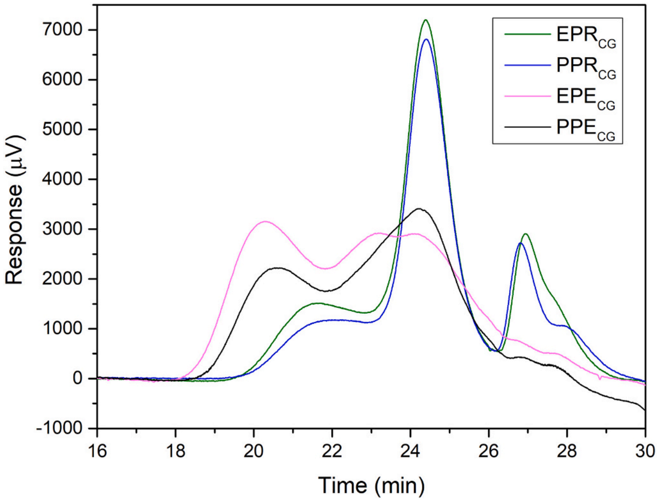


Fig. 3. Molecular weight distribution of the liquefied bio-polyols.

Table 3
Molecular weight distribution, I_{OH}, A_n, functionality (*f*), equivalent weight (EW) and yield of bio-polyols.

Sample	M_n (g/mol)	M_w (g/mol)	PDI	I_{OH} (mg KOH/g)	A_n (mg KOH/g)	*f*	EW	Yield (%)
EPR_{CG}	442 ± 34	1742 ± 275	4.25 ± 0.55	554 ± 4	1.91 ± 0.06	4.16 ± 0.10	101.20 ± 0.66	93.55 ± 3.00
EPE_{CG}	941 ± 30	8818 ± 127	9.38 ± 0.16	228 ± 36	20.94 ± 2.75	3.51 ± 0.68	248.98 ± 38.77	70.75 ± 0.47
PPR_{CG}	453 ± 24	1431 ± 362	3.14 ± 0.63	383 ± 8	4.21 ± 0.90	3.14 ± 0.16	146.68 ± 3.23	90.60 ± 0.56
PPE_{CG}	780 ± 20	5530 ± 131	7.10 ± 0.31	173 ± 16	25.09 ± 2.59	2.08 ± 0.27	325.36 ± 30.16	79.35 ± 0.83

parameters are closely related, since an increase of the acid number decreases the hydroxyl number of the polyol [46]. This correlation is observed for the obtained bio-polyols, where those with the highest I_{OH} index (EPR_{CG} and PPR_{CG}) presented the lowest A_n value. The higher A_n index observed in EPE_{CG} and PPE_{CG} compared to EPR_{CG} and PPR_{CG} resulted from the use of sulphuric acid as reaction catalyst. The highest I_{OH} values of EPR_{CG} and PPR_{CG} compared to EPE_{CG} and PPE_{CG} can be explained, firstly, by the absence of catalyst in the reaction, which decreased the I_{OH} index [47]. On the other hand, the higher amount of glycerol used in the formulation of EPR_{CG} and PPR_{CG} bio-polyols contributed to the increase of the I_{OH} index [48].

The synthesis of PUs requires different functionalities depending on the final application, as shown in Scheme 1. Thus, for the synthesis of rigid PUs, high functionalities between 3 and 8 are preferred to produce crosslinks that reinforce the structure, while for elastic PUs, such as flexible foams, elastomers or adhesives, among others, the desired functionalities are between 2 and 3. Such low functionalities result in materials with low crosslink density that allow the mobility of the polymer chains [40].

Consequently, the bio-polyols synthesised for rigid PU applications showed appropriate functionalities of 4.16 in the case of EPR_{CG} and 3.14 for PPR_{CG}. In the case of the bio-polyols for elastic PU applications, while PPE_{CG} had an adequate functionality of 2.08, EPE_{CG} was slightly above 3. However, considering its I_{OH} and M_w values, it could be considered suitable for the manufacture of elastic PUs. The chain derived from a hydroxyl group, or the equivalent weight of the polyol, is also a relevant parameter to be considered (Eq. (1)). A short chain implies a higher density of urethane bonds and therefore more cohesion between them, mainly through secondary hydrogen bonds. This, together with the high functionality, results in a rigid structure. On the other hand, a long chain decreases the concentration of urethane bonds, decreasing the cohesion between them, and together with a low functionality and high mobility of the main polyol chain, resulting is an elastic PU [49].

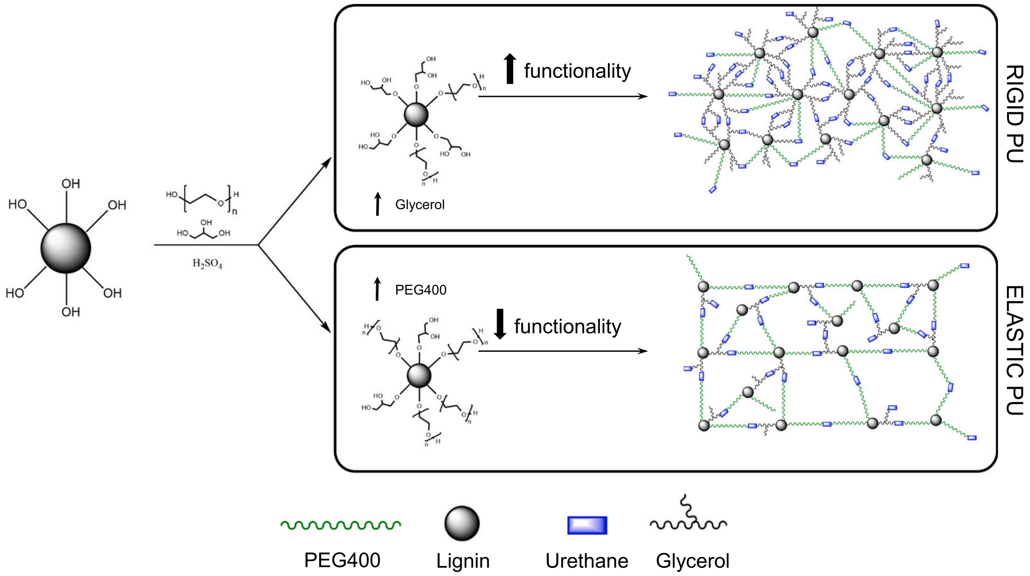
$$EW = \frac{56.1\cdot 100}{\text{Corrected } I_{OH}} \quad (1)$$

As expected, according to the data summarised in Table 3, the bio-polyols EPR_{CG} and PPR_{CG}, showed a low EW, which is adequate for the synthesis of rigid PUs, while bio-polyols with lower I_{OH} value, EPE_{CG} and PPE_{CG}, presented a higher EW more suitable for polyurethanes with a more flexible structure.

While all the studied properties are relevant to obtain bio-polyols with the appropriate characteristics for PU production, the yield constitutes another key factor and is equally important to make the process industrially feasible. In the lignin liquefaction process, the catalyst has a significant impact on the reaction yield, since in the presence of an acid catalyst the lignin repolymerisation reactions are increased, generating a higher amount of solid residue, and therefore reducing the yield [18]. The presence of water in the reaction can promote the fragmentation of lignin into smaller and more reactive molecules through hydrolysis increasing the reaction yield [25]. This water can be formed as a by-product of the condensation of glycerol into polyglycerol during the liquefaction reaction, therefore, the more glycerol in the medium, the more water and the higher the yield [50]. According to the results obtained and summarised in Table 3, EPR_{CG} and PPR_{CG} bio-polyols with a higher amount of crude glycerol and without catalyst showed higher yield than EPE_{CG} and PPE_{CG} bio-polyols where catalyst and lower concentration of glycerol were used. The use of CG in liquefaction reactions can reduce the yield of such reactions. This is due to the presence of impurities such as FA and FAMEs and a lower amount of glycerol in the reaction medium [45]. However, the presence of acid catalyst in the medium showed more influence on the reduction of the liquefaction yield. Thus, EPE_{CG} and PPE_{CG} with a lesser CG content showed a substantially lower yield than EPR_{CG} and PPR_{CG}, which can only be explained by the greater influence of the acid catalyst. Furthermore, it was also observed that with a very similar PEG/CG ratio, but with a higher catalyst concentration, EPE_{CG} showed lower yield than PPE_{CG}.

Thermogravimetric analysis of the resulting bio-polyols was performed to determine the relationship between chemical structure and degradation. The TGA thermograms and their corresponding derivative thermogravimetric curves (DTG) are shown in Fig. 4. Based on the DTG curves, it was concluded that EPE_{CG} and PPE_{CG} bio-polyols showed four degradation zones, while only three degradation zones were observed in EPR_{CG} and PPR_{CG} bio-polyols. In addition, EPE_{CG}, PPE_{CG} and PPR_{CG} showed an unidentified degradation zone which was not observed in EPR_{CG} sample. This degradation stages are summarised in Table 4.

The first one, between 30 and 110 °C, is associated with moisture or the presence of solvent in the sample. It could be observed a weight loss in all cases in this degradation zone. However, it was clearly visible a higher weight loss in PPR_{CG} and PPE_{CG} samples, which could be due to the presence of the acetone employed in the process. The second degradation region (115–270 °C) corresponds to the degradation of glycerol [51]. The third degradation region takes place between 275 and



Scheme 1. Hypothetical crosslinking in lignin-based rigid and elastic polyurethanes.

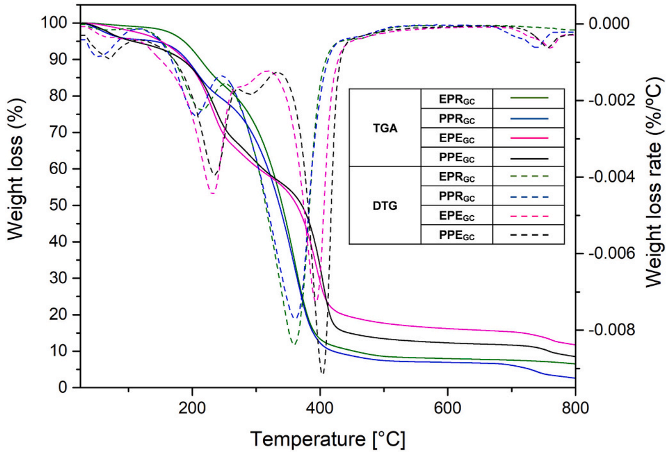


Fig. 4. TGA thermograms and DTG curves of liquefied bio-polyols.

335 °C for EPE_{CG} and PPE_{CG} and it is related to the degradation of PEG [51]. It should be noted that the degradation of the β—O—4 and C—C bonds of lignin occurs between 250 and 400 °C. Nevertheless, depending on the M_w and the repolymerisation degree of the lignin molecule, this degradation could happen at different temperatures [52]. Thus, in the case of EPE_{CG} and PPE_{CG}, with higher M_w, lignin degradation (4th degradation area) was observed between 315 and 440 °C, whereas in bio-polyols with lower M_w (EPR_{CG} and PPR_{CG}), this degradation takes place at lower temperatures. This can be caused because, in the latter, the degradation zone of PEG and lignin overlap, showing a single degradation zone, i.e. the third degradation region for these bio-polyols. Finally, between 690 and 775 °C, a small weight loss was observed, possibly due to the presence of inorganic impurities in the samples. However, the origin of this peak could not be clearly determined.

Finally, to determine the viscoelastic properties and the fluid behaviour of the bio-polyols, a rheological study of the samples was performed. To study the viscoelastic behaviour, an oscillatory test was carried out comparing the storage module (G′) with the loss module (G″). Based on the analysis of this test, illustrated in Fig. 5, it was concluded that the bio-polyols exhibited a liquid behaviour, since in all cases the G″ was higher than the G′ over the whole frequency range. Furthermore, as expected, the value of the modules increased with increasing molecular weights, EPE_{CG} and PPE_{CG} showed higher modules than EPR_{CG} and PPR_{CG} [53].

The fluid behaviour of bio-polyols, as well as their viscosity, was studied through a rotational test analysing the relation between the viscosity (η), shear stress (τ) and shear rate ($\dot{\gamma}$). These parameters were fitted to the Ostwald-de Waele power-law equation (Eq. (2)), where the fitting parameters (n and k) are dependent on the nature of the fluid and the measurement conditions.

$$\tau = k \cdot \dot{\gamma}^n \tag{2}$$

Thus, the fluid can be Newtonian, pseudo plastic or dilatant when the flow index parameter (n) is $n = 1$, $n < 1$ and $n > 1$, respectively. The value of the parameter k, known as the consistency index, which is associated with the apparent viscosity of the fluid at a shear rate of 1 s^{-1}, increases with increasing viscosity. A summary of the data provided by the software is presented in Table 5, and the obtained flow curves are shown in Fig. 6a and b.

R^2 values >0.99 were obtained in all cases, indicating that the rheograms were well adjusted, and, therefore, the selected model to evaluate the rheological behaviour was adequate. In all cases, since the flow index (n) values were equal or very close to unity, it was concluded that the bio-polyols were Newtonian-type. This behaviour was observed in Fig. 6a, where the viscosity remained constant regardless the applied shear rate ($\dot{\gamma}$) and was confirmed by studying the behaviour between the shear stress (τ) and shear rate ($\dot{\gamma}$) (Fig. 6b). It was observed that, in all cases, the graphical representation of these parameters resulted in a straight line which passed through the origin and whose slopes were equal to the k value of each bio-polyol. Furthermore, as expected, the viscosity of the bio-polyols with higher M_w were higher than those with lower molecular weights [54]. Thus, the viscosity of each bio-polyol was in concordance to its consistency index (k) value [55], being 1.4299 Pa·s for EPE_{CG}, 0.7290 Pa·s for EPR_{CG}, and 0.9352 Pa·s and 0.7927 Pa·s for PPE_{CG} and PPR_{CG}. Therefore, as these values were lower than 300 Pa·s, the bio-polyols were suitable for PU production.

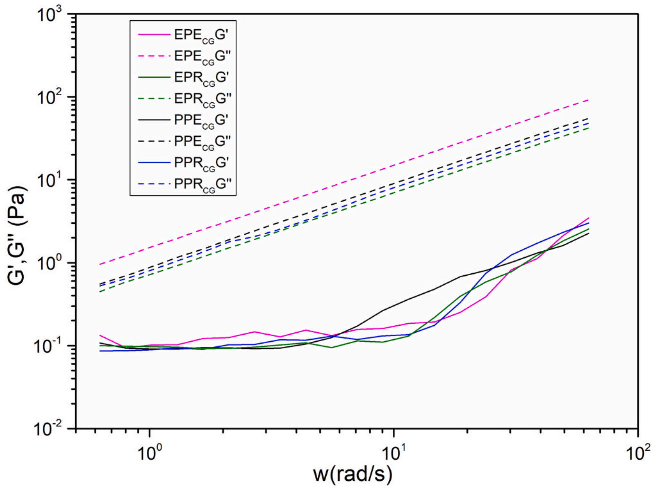


Fig. 5. Storage module (G′) and loss module (G″) (Pa) as function of ω (rad/s) of bio-polyols.

Table 5
Power-Law linear functions based on the rheological data obtained from the studied bio-polyols.

Sample	Function	k (Pa·s^n)	n	R^2
EPE_{CG}	$\tau = 1.4299 \cdot \dot{\gamma}^{1.0176}$	1.4299	1.0176	0.9985
EPR_{CG}	$\tau = 0.7290 \cdot \dot{\gamma}^{0.9911}$	0.7290	0.9911	0.9995
PPE_{CG}	$\tau = 0.9352 \cdot \dot{\gamma}^{0.9978}$	0.9352	0.9978	0.9988
PPR_{CG}	$\tau = 0.7927 \cdot \dot{\gamma}^{1.0011}$	0.7927	1.0011	0.9939

Table 4
Degradation stages on of the TGA-DTG curves of the analysed bio-polyols.

Sample	1st		2nd		3rd		4th		5th	
	Tint	Tm	Tint	Tm	Tint	Tm	Tint	Tm	Tint	Tm
EPE_{CG}	30–100	72	115–270	233	270–315	283	315–440	391	705–775	758
EPR_{CG}	30–110	70	125–255	214	214–513	360	–	–	–	–
PPE_{CG}	30–110	70	120–270	235	270–335	291	335–450	403	705–775	758
PPR_{CG}	30–110	56	120–250	205	250–512	361	–	–	690–770	740

Tint: Temperature interval; Tm: Maximum degradation temperature.

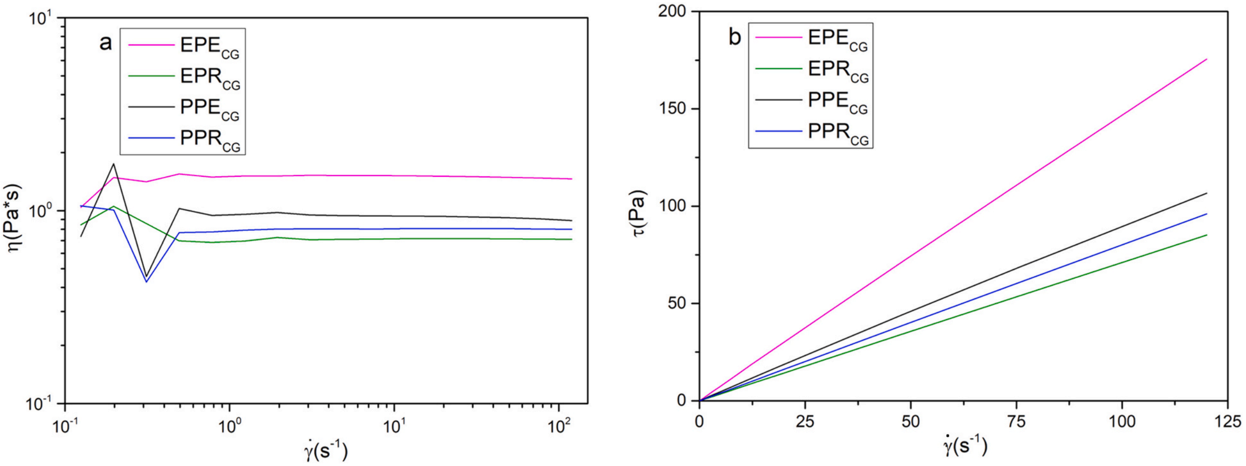


Fig. 6. (a) Viscosity (η) as a function of shear rate ($\dot{\gamma}$); (b) shear stress (τ) as a function of shear rate ($\dot{\gamma}$).

3.3. *Effect of crude glycerol in bio-polyols parameters*

The results obtained by other authors by liquefying lignocellulosic biomass employing, among others, glycerol and CG as solvents are summarised in Table 6. Nonetheless, since the reaction conditions employed in this study were the optimal conditions established in our previous work, the results obtained in this work (Table 3) were first compared with the results obtained in our previous work (Table 6) [30].

The reaction yields employing CG and technical grade glycerol were very similar, however a decrease was observed when CG was used due to the presence of impurities and lower glycerol content, which decreased the reaction efficiency [45]. In addition, the lower amount of glycerol molecules in crude glycerol and the consumption of hydroxyl groups due to competitive reactions caused by impurities are responsible for the decrease of the I_{OH} index in bio-polyols comparing to those obtained when commercial glycerol was employed [23]. The A_n exhibited the same behaviour as that observed in our previous study, i.e., the higher the catalyst concentration, the higher the number of acids. Nonetheless, using crude glycerol as solvent, the A_n values were slightly lower since organic impurities in the crude glycerol could lead to the consumption of acidic compounds [23]. Comparing the molecular weight obtained in this work with those obtained in our previous work, where a technical

Table 6
Different studies of lignocellulosic biomass and lignin liquefaction employing commercial or crude glycerol.

Raw material	Solvent	Yield (%)	I_{OH}	A_n	Mw	PI	*f*	Catalyst H_2SO_4	USE	Ref.
Eucalyptus globulus organosolv lignin	PEG + G	98.63 ± 0.71	595.15 ± 33.92	2.74 ± 0.00	1394 ± 12	3.69 ± 0.08	4.03 ± 0.15	–	Rigid PU	[30]
		71.98 ± 1.41	253.84 ± 60.59	33.01 ± 0.00	4895 ± 325	9.37 ± 1.12	2.36 ± 0.44	5 %	Elastic PU	
Pinus radiata organosolv lignin		98.93 ± 0.14	514.28 ± 42.70	5.63 ± 0.23	1383 ± 43	3.58 ± 0.08	3.55 ± 0.26	–	Rigid PU	
		87.56 ± 3.30	209.67 ± 3.70	30.56 ± 0.15	5408 ± 765	6.95 ± 0.91	2.91 ± 0.08	3.86 %	Elastic PU	
Eucalyptus globulus Kraft lignin	PEG + G	95.27	537.95	–	1775	3.51	–	3 %	–	[54]
Olive tree pruning organosolv lignin	PEG + G	99.07	811.8	–	–	–	–	1 %	–	[57]
Eucalyptus globulus kraft lignin	PEG + G	>86	100–660.08	0.8–10.70	1459–1990	–	–	3, 6, 9 (organic acids)	–	[58]
Enzymatic hydrolysis lignin of cornstalk	PEG + G	>90	191–409	–	–	–	–	15 %	–	[47]
Alkaline corncob lignin	PEG + G	97.47	484.03	–	525	1.13	–	1.5 %	PU foam	[59]
Kraft lignin (softwood)	CG	>0.61 (g/g CG)	412		5088	2.2	–	–	PU foam	[27]
Organosolv lignin (sugarcane bagasse)			224		7867	4.9	–			
Lignosulphonate (hardwood)			592		7384	3.3	–			
Acetone soluble lignin	CG + 1,4-BDO	72.64	≈1100	≈4	–	–	–	–	PU foam	[29]
Kraft pine lignin	CG + 1,4-BDO	93	670	–	–	–	–	–	PU foam	[25]
Rapeseed cake	PEG + G	84	586	–	–	–	–	80:20:3 (PEG: G: H_2SO_4)	–	[51]
Data seeds		96	395	–	–	–	–			
Olive stone		92	496	–	–	–	–			
Corncob		91	504	–	–	–	–			
Apple pomace		97	428	–	–	–	–			
Wheat straw		–	350	28	1270	1.22		–	PU foam	[48]
Taiwan acacia	PEG + G	95.2	310	25.6	–	–	–	3:1:0.09 (solvent: biomass: H_2SO_4)	Adhesives	[60]
China fir		98.4	287	38.0	–	–	–			
Norway spruce	EG	99.7	825–623	48.2–47.8	–	–	–	4.5 g	Adhesives	[61]

1,4-Butanediol (1,4-BDO), glycerol (G), crude glycerol (CG), ethylene glycol (EG).

grade glycerol was used for the liquefaction process, it is worth noting that there was an increase on the molecular weight in all cases, particularly in EPE_{CG} bio-polyol. This can be explained by the polymerisation reactions between glycerol, FFA and FAMEs [56]. Consequently, the polydispersity indexes of the CG synthesised bio-polyols were higher than those obtained with technical grade glycerol. This increase in the M_w and PI was in agreement with that reported by Hu et al. [45]. It could also be concluded that the functionalities were also similar in all cases and appropriate to the class of PUs for which they were synthesised. However, in the case of EPE_{CG}, the functionality was slightly above the limit value for the synthesis of elastic PU. As for the viscosities, it should be noted that, as expected, with the increase in the molecular weight of the samples obtained with crude glycerol, the viscosities also increased or remained practically equal, as in the case of PPE_{CG}.

EPR_{CG} and PPR_{CG} bio-polyols yields were within the typical values obtained for the liquefaction of lignocellulosic biomass or lignin, despite using CG instead of technical grade glycerol (Table 6). However, the yields obtained by Tran et al. [29] liquefying soluble acetone lignin using CG and 1,4-BDO in the presence of sulphuric acid were very similar to those obtained for EPE_{CG} and PPE_{CG}. It is noteworthy that, in most of the studies that are summarised in Table 6, polyols were used for the manufacture of foams. In such studies, the I_{OH} varied between 100 mg KOH/g and 811.8 mg KOH/g. Therefore, the I_{OH} values obtained for EPR_{CG} and PPR_{CG} bio-polyols, which are intended for rigid PUs, were found to be in good concordance with the values of the literature. Few of the studies summarised in Table 6 indicated the PI of polyols, and those that did so, referred to polyols for the synthesis of PU foams. The PI obtained for EPR_{CG} and PPR_{CG} in this work are in line with those reported by other authors in such studies.

Lee et al. [60] liquefied Taiwan acacia and China fir employing PEG and glycerol with sulphuric acid as catalyst to produce polyols. Such polyols, which showed a I_{OH} of 310 and 287 (mg KOH/g), were used to synthesise PU adhesives. EPE_{CG} and PPE_{CG} bio-polyols, synthesised to be used in the elaboration of elastic PUs, showed a very similar I_{OH} to those obtained in that study. Similarly, Jiang et al. [61] synthesised PU adhesives employing polyols from liquefied lignocellulosic biomass (Norway spruce). However, in this case the I_{OH} was significantly higher (825 and 623 mg KOH/g). As for PI, unfortunately, to the best of our knowledge, no studies were found indicating the PI value for polyols obtained through the liquefaction of lignin for PU adhesive synthesis. Likewise, no papers were found indicating the functionality of polyols obtained through this process. Finally, the A_n value was, in all cases, within the usual range (0–40 mg KOH/g) for this type of process.

4. Conclusions

In this paper, bio-polyols suitable for the manufacture of rigid and elastic PUs were successfully prepared through the liquefaction of organosolv lignin from *Eucalyptus globulus* and *Pinus radiata*. The liquefaction reaction was carried out employing a microwave reactor using the optimal reaction conditions established in a previous study. Polyethylene glycol and crude glycerol, which was obtained from used vegetable oil, were utilised as solvents for this process. The effect of crude glycerol is obvious when comparing the results obtained with those obtained in our previous work. The liquefaction yields decreased in all cases due to the lower amount of glycerol in the mixture. Thus, the yields obtained for bio-polyols produced for rigid PUs where no catalyst was employed were higher than 90 %, whereas for bio-polyols intended for elastic PUs, where sulphuric acid was used as catalyst, the yields were significantly lower, between 70 and 80 %. The I_{OH} of bio-polyols were also affected by the lower glycerol content when crude glycerol was used. The I_{OH} values obtained in this study were 554 and 383 (mg KOH/g) for EPR_{CG} and PPR_{CG} bio-polyols respectively and 228 and 173 (mg KOH/g) for EPE_{CG} and PPE_{CG}. The A_n value of the samples was in the expected range for this type of polyols. Regarding the functionalities, although in the case of EPE_{CG} the obtained value was slightly above the desired one, it could be said that the functionalities were adequate for the manufacture of the type of PU for which they were intended. This assumption was confirmed by taking into account these results together with the rest of the parameters that were studied. Overall, even though the results of some parameters have worsened, it can be said that crude glycerol recovered from used oil is suitable for the manufacture of bio-polyols to produce elastic and rigid PUs.

CRediT authorship contribution statement

Fabio Hernández-Ramos: Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Validation, Writing – original draft, Writing – review & editing. **María González Alriols:** Supervision, Validation, Data curation, Visualization. **M. Mirari Antxustegi:** Supervision, Validation, Data curation, Visualization. **Jalel Labidi:** Validation, Formal analysis, Resources, Supervision. **Xabier Erdocia:** Methodology, Investigation, Formal analysis, Data curation, Validation, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Fabio Hernandez-Ramos reports financial support was provided by Gipuzkoa Provincial Council.

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References

[1] P.J. Crutzen, Geology of mankind - Crutzen - nature, Nature 415 (2002) 2002.
[2] T.A.P. Hai, M. Tessman, N. Neelakantan, A.A. Samoylov, Y. Ito, B.S. Rajput, N. Pourahmady, M.D. Burkart, Renewable polyurethanes from sustainable biological precursors, Biomacromolecules. 22 (2021) 1770–1794, https://doi.org/10.1021/acs.biomac.0c01610.
[3] P. Stachak, I. Łukaszewska, E. Hebda, K. Pielichowski, Recent advances in fabrication of non-isocyanate polyurethane-based composite materials, Materials (Basel) 14 (2021), https://doi.org/10.3390/ma14133497.
[4] S. Magina, N. Gama, L. Carvalho, A. Barros-Timmons, D.V. Evtuguin, Lignosulfonate-based polyurethane adhesives, Materials (Basel) 14 (2021) 1–18, https://doi.org/10.3390/ma14227072.
[5] M. Ghasemlou, F. Daver, E.P. Ivanova, B. Adhikari, Bio-based routes to synthesize cyclic carbonates and polyamines precursors of non-isocyanate polyurethanes: a review, Eur. Polym. J. 118 (2019) 668–684, https://doi.org/10.1016/j.eurpolymj.2019.06.032.
[6] J. Perez-Arce, A. Centeno-Pedrazo, J. Labidi, J.R. Ochoa-Gómez, E.J. Garcia-Suarez, A novel and efficient approach to obtain lignin-based polyols with potential industrial applications, Polym. Chem. 11 (2020) 7362–7369, https://doi.org/10.1039/d0py01142h.
[7] O. Gómez-Jiménez-Aberasturi, J.R. Ochoa-Gómez, New approaches to producing polyols from biomass, J. Chem. Technol. Biotechnol. 92 (2017) 705–711, https://doi.org/10.1002/jctb.5149.
[8] A. Saravanan, P. Senthil Kumar, S. Jeevanantham, S. Karishma, D.-V.N. Vo, Recent advances and sustainable development of biofuels production from lignocellulosic biomass, Bioresour. Technol. (2022), https://doi.org/10.1016/j.biortech.2021.126203.
[9] G. Velvizhi, C. Goswami, N.P. Shetti, E. Ahmad, K. Kishore Pant, T.M. Aminabhavi, Valorisation of lignocellulosic biomass to value-added products: paving the pathway towards low-carbon footprint, Fuel. 313 (2022), 122678, https://doi.org/10.1016/j.fuel.2021.122678.
[10] S. Tanpichai, A. Boonmahitthisud, N. Soykeabkaew, L. Ongthip, Review of the recent developments in all-cellulose nanocomposites: properties and applications, Carbohydr. Polym. 286 (2022), 119192, https://doi.org/10.1016/j.carbpol.2022.119192.
[11] H. Wang, H. Xie, H. Du, X. Wang, W. Liu, Y. Duan, X. Zhang, L. Sun, X. Zhang, C. Si, Highly efficient preparation of functional and thermostable cellulose nanocrystals via H2SO4 intensified acetic acid hydrolysis, Carbohydr. Polym. 239 (2020), 116233, https://doi.org/10.1016/j.carbpol.2020.116233.

[12] A. Morales, F. Hernández-Ramos, L. Sillero, R. Fernández-Marín, I. Dávila, P. Gullón, X. Erdocia, J. Labidi, Multiproduct biorefinery based on almond shells: impact of the delignification stage on the manufacture of valuable products, Bioresour. Technol. 315 (2020), https://doi.org/10.1016/j.biortech.2020.123896.

[13] A. Morales, J. Labidi, P. Gullón, Impact of the lignin type and source on the characteristics of physical lignin hydrogels, Sustain. Mater. Technol. 31 (2022), https://doi.org/10.1016/j.susmat.2021.e00369.

[14] W. Zhao, Z. Liang, Z. Feng, B. Xue, C. Xiong, C. Duan, Y. Ni, New kind of lignin/polyhydroxyurethane composite: green synthesis, smart properties, promising applications, and good reprocessability and recyclability, ACS Appl. Mater. Interfaces 13 (2021) 28938–28948, https://doi.org/10.1021/acsami.1c06822.

[15] M. Alinejad, C. Henry, S. Nikafshar, A. Gondaliya, S. Bagheri, N. Chen, S.K. Singh, D.B. Hodge, M. Nejad, Lignin-based polyurethanes: opportunities for bio-based foams, elastomers, coatings and adhesives, Polymers (Basel) (2019), https://doi.org/10.3390/polym11071202.

[16] B.M. Upton, A.M. Kasko, Strategies for the conversion of lignin to high-value polymeric materials: review and perspective, Chem. Rev. 116 (2016) 2275–2306, https://doi.org/10.1021/acs.chemrev.5b00345.

[17] S. Laurichesse, L. Avérous, Chemical modification of lignins: towards biobased polymers, Prog. Polym. Sci. 39 (2014) 1266–1290, https://doi.org/10.1016/j.progpolymsci.2013.11.004.

[18] S. Hu, X. Luo, Y. Li, Polyols and polyurethanes from the liquefaction of lignocellulosic biomass, ChemSusChem. 7 (2014) 66–72, https://doi.org/10.1002/cssc.201300760.

[19] D.B. Nde, M. Barekati-Goudarzi, P.D. Muley, L. Khachatryan, D. Boldor, Microwave-assisted lignin liquefaction in hydrazine and ethylene glycol: reaction pathways via response surface methodology, Sustain. Mater. Technol. 27 (2021), e00245, https://doi.org/10.1016/j.susmat.2020.e00245.

[20] J.C. Thompson, B.B. He, Characterization of crude glycerol from biodiesel production from multiple feedstocks, Appl. Eng. Agric. 22 (2006) 261–265, https://doi.org/10.13031/2013.20272.

[21] L.R. Kumar, R. Kaur, R.D. Tyagi, P. Drogui, Identifying economical route for crude glycerol valorization: biodiesel versus polyhydroxy-butyrate (PHB), Bioresour. Technol. 323 (2021), 124565, https://doi.org/10.1016/j.biortech.2020.124565.

[22] P. Koranian, Q. Huang, A.K. Dalai, R. Sammynaiken, Chemicals production from glycerol through heterogeneous catalysis: a review, Catalysts 12 (2022), https://doi.org/10.3390/catal12080897.

[23] S. Hu, C. Wan, Y. Li, Production and characterization of biopolyols and polyurethane foams from crude glycerol based liquefaction of soybean straw, Bioresour. Technol. 103 (2012) 227–233, https://doi.org/10.1016/j.biortech.2011.09.125.

[24] S. Hu, Y. Li, Two-step sequential liquefaction of lignocellulosic biomass by crude glycerol for the production of polyols and polyurethane foams, Bioresour. Technol. 161 (2014) 410–415, https://doi.org/10.1016/j.biortech.2014.03.072.

[25] K. Gosz, P. Kosmela, A. Hejna, G. Gajowiec, Ł. Piszczyk, Biopolyols obtained via microwave-assisted liquefaction of lignin: structure, rheological, physical and thermal properties, Wood Sci. Technol. 52 (2018) 599–617, https://doi.org/10.1007/s00226-018-0991-4.

[26] L.C. Muller, S. Marx, H.C.M. Vosloo, E. Fosso-Kankeu, I. Chiyanzu, Rigid polyurethane foams from unrefined crude glycerol and technical lignins, Polym. Renew. Resour. 9 (2018) 111–132, https://doi.org/10.1177/2041247918803187.

[27] L.C. Muller, S. Marx, H.C.M. Vosloo, I. Chiyanzu, Functionalising lignin in crude glycerol to prepare polyols and polyurethane, Polym. Renew. Resour. 10 (2019) 3–18, https://doi.org/10.1177/2041247919830833.

[28] L.C. Muller, S. Marx, H.C.M. Vosloo, Polyol preparation by liquefaction of technical lignins in crude glycerol, J. Renew. Mater. 5 (2017) 67–80, https://doi.org/10.7569/JRM.2016.634130.

[29] M.H. Tran, J.H. Yu, E.Y. Lee, Microwave-assisted two-step liquefaction of acetone-soluble lignin of silvergrass saccharification residue for production of biopolyol and biopolyurethane, Polymers (Basel) 13 (2021), https://doi.org/10.3390/polym13091491.

[30] F. Hernández-Ramos, V. Novi, M.G. Alriols, J. Labidi, X. Erdocia, Optimisation of lignin liquefaction with polyethylene glycol/glycerol through response surface methodology modelling, Ind. Crop. Prod. 198 (2023), https://doi.org/10.1016/j.indcrop.2023.116729.

[31] F. Hernández-Ramos, M.G. Alriols, T. Calvo-Correas, J. Labidi, X. Erdocia, Renewable biopolyols from residual aqueous phase resulting after lignin precipitation, ACS Sustain. Chem. Eng. (2021), https://doi.org/10.1021/acssuschemeng.0c09357.

[32] S. Kongjao, S. Damronglerd, M. Hunsom, Purification of crude glycerol derived from waste used-oil methyl ester plant, Korean J. Chem. Eng. 27 (2010) 944–949, https://doi.org/10.1007/s11814-010-0148-0.

[33] S. Hu, X. Luo, C. Wan, Y. Li, Characterization of crude glycerol from biodiesel plants, J. Agric. Food Chem. 60 (2012) 5915–5921, https://doi.org/10.1021/jf3008629.

[34] C.V. Rodrigues, K.O. Santana, M.G. Nespeca, J. Eduardo de Oliveira, S. I. Maintinguer, Crude glycerol by transesterification process from used cooking oils: characterization and potentialities on hydrogen bioproduction, Int. J. Hydrog. Energy 41 (2016) 14641–14651, https://doi.org/10.1016/j.ijhydene.2016.06.209.

[35] L.R. Kumar, S.K. Yellapu, R.D. Tyagi, X. Zhang, A review on variation in crude glycerol composition, bio-valorization of crude and purified glycerol as carbon source for lipid production, Bioresour. Technol. 293 (2019), 122155, https://doi.org/10.1016/j.biortech.2019.122155.

[36] C.A.G. Quispe, C.J.R. Coronado, J.A. Carvalho, Glycerol: production, consumption, prices, characterization and new trends in combustion, Renew. Sust. Energ. Rev. 27 (2013) 475–493, https://doi.org/10.1016/j.rser.2013.06.017.

[37] M.D. Bohon, B.A. Metzger, W.P. Linak, C.J. King, W.L. Roberts, Glycerol combustion and emissions, Proc. Combust. Inst. 33 (2011) 2717–2724, https://doi.org/10.1016/j.proci.2010.06.154.

[38] A. Hejna, P. Kosmela, M. Klein, K. Formela, M. Kopczyńska, J. Haponiuk, Ł. Piszczyk, Two-step conversion of crude glycerol generated by biodiesel production into biopolyols: synthesis, structural and physical chemical characterization, J. Polym. Environ. 26 (2018) 3334–3344, https://doi.org/10.1007/s10924-018-1217-4.

[39] M. Nanda, Z. Yuan, W. Qin, Purification of crude glycerol using acidification: effects of acid types and product characterization, Austin J. Chem. Eng. 1 (2014) 1–7. http://flash.lakeheadu.ca/~wqin/websitepapersnov14/2014MalayaAustinJournalPaper.pdf.

[40] M. Ionescu, Polyols, in: De Gruyter (Ed.), Polyols for Polyrethanes, Boston, Berlin, 2019, pp. 1–10, https://doi.org/10.1515/9783110644104-001.

[41] Y. Lee, E.Y. Lee, Liquefaction of red pine wood, *Pinus densiflora*, biomass using Peg-400-blended crude glycerol for biopolyol and biopolyurethane production, J. Wood Chem. Technol. 36 (2016) 353–364, https://doi.org/10.1080/02773813.2016.1156132.

[42] X. Luo, S. Hu, X. Zhang, Y. Li, Thermochemical conversion of crude glycerol to biopolyols for the production of polyurethane foams, Bioresour. Technol. 139 (2013) 323–329, https://doi.org/10.1016/j.biortech.2013.04.011.

[43] J. D'Souza, R. Camargo, N. Yan, Biomass liquefaction and alkoxylation: a review of structural characterization methods for bio-based polyols, Polym. Rev. 57 (2017) 668–694, https://doi.org/10.1080/15583724.2017.1283328.

[44] Y.Y. Li, X. Luo, S. Hu, Introduction to bio-based polyols and polyurethanes, in: Bio-based Polyols and Polyurethanes, 2015, pp. 1–79, https://doi.org/10.1007/978-3-319-21539-6.

[45] S. Hu, Y. Li, Polyols and polyurethane foams from base-catalyzed liquefaction of lignocellulosic biomass by crude glycerol: effects of crude glycerol impurities, Ind. Crop. Prod. 57 (2014) 188–194, https://doi.org/10.1016/j.indcrop.2014.03.032.

[46] S.H. Lee, M. Yoshioka, N. Shiraishi, Liquefaction of corn bran (CB) in the presence of alcohols and preparation of polyurethane foam from its liquefied polyol, J. Appl. Polym. Sci. 78 (2000) 319–325, https://doi.org/10.1002/1097-4628(20001010)78:2<319::AID-APP120>3.0.CO;2-Z.

[47] Y. Jin, X. Ruan, X. Cheng, Q. Lü, Liquefaction of lignin by polyethyleneglycol and glycerol, Bioresour. Technol. 102 (2011) 3581–3583, https://doi.org/10.1016/j.biortech.2010.10.050.

[48] F. Chen, Z. Lu, Liquefaction of wheat straw and preparation of rigid polyurethane foam from the liquefaction products, J. Appl. Polym. Sci. 111 (2009) 508–516, https://doi.org/10.1002/app.29107.

[49] M. Ionescu, Relationships between the oligo-polyol structure and polyurethane properties, in: De Gruyter (Ed.), Polyols for Polyurethanes, Boston, Berlin, 2019, pp. 307–320, https://doi.org/10.1515/9783110644128-011.

[50] M. Ionescu, Z.S. Petrović, On the mechanism of base-catalyzed glycerol polymerization and copolymerization, Eur. J. Lipid Sci. Technol. 120 (2018) 1–9, https://doi.org/10.1002/ejlt.201800004.

[51] R. Briones, L. Serrano, J. Labidi, Valorization of some lignocellulosic agro-industrial residues to obtain biopolyols, J. Chem. Technol. Biotechnol. 87 (2012) 244–249, https://doi.org/10.1002/jctb.2706.

[52] A. Morales, B. Gullón, I. Dávila, G. Eibes, J. Labidi, P. Gullón, Optimization of alkaline pretreatment for the co-production of biopolymer lignin and bioethanol from chestnut shells following a biorefinery approach, Ind. Crop. Prod. 124 (2018) 582–592, https://doi.org/10.1016/j.indcrop.2018.08.032.

[53] K. Behera, Y.H. Chang, F.C. Chiu, J.C. Yang, Characterization of poly(lactic acid)s with reduced molecular weight fabricated through an autoclave process, Polym. Test. 60 (2017) 132–139, https://doi.org/10.1016/j.polymertesting.2017.03.015.

[54] S.H.F. da Silva, P.S.B. dos Santos, D. Thomas da Silva, R. Briones, D.A. Gatto, J. Labidi, Kraft lignin-based polyols by microwave: optimizing reaction conditions, J. Wood Chem. Technol. 37 (2017) 343–358, https://doi.org/10.1080/02773813.2017.1303513.

[55] P. Parcheta, J. Datta, Structure-rheology relationship of fully bio-based linear polyester polyols for polyurethanes - synthesis and investigation, Polym. Test. 67 (2018) 110–121, https://doi.org/10.1016/j.polymertesting.2018.02.022.

[56] X. Luo, S. Hu, X. Zhang, Y. Li, Thermochemical conversion of crude glycerol to biopolyols for the production of polyurethane foams, Bioresour. Technol. 139 (2013) 323–329, https://doi.org/10.1016/j.biortech.2013.04.011.

[57] A. Sequeiros, L. Serrano, R. Briones, J. Labidi, Lignin liquefaction under microwave heating, J. Appl. Polym. Sci. 130 (2013) 3292–3298, https://doi.org/10.1002/app.39577.

[58] S.H.F. da Silva, I. Egüés, J. Labidi, Liquefaction of Kraft lignin using polyhydric alcohols and organic acids as catalysts for sustainable polyols production, Ind. Crop. Prod. 137 (2019) 687–693, https://doi.org/10.1016/j.indcrop.2019.05.075.

[59] B.L. Xue, J.L. Wen, R.C. Sun, Producing lignin-based polyols through microwave-assisted liquefaction for rigid polyurethane foam production, Materials (Basel) 8 (2015) 586–599, https://doi.org/10.3390/ma8020586.

[60] W.-J. Lee, M.-S. Lin, Preparation and applicaction of polyurethane adhesives made from polyhydric alcohol liquefied Taiwan Acacia and China fir, J. Appl. Polym. Sci. 109 (2008) 23–31, https://doi.org/10.1002/app.28007.

[61] W. Jiang, R. Hosseinpourpia, V. Biziks, S.A. Ahmed, H. Militz, S. Adamopoulos, Preparation of polyurethane adhesives from crude and purified liquefied wood sawdust, Polymers (Basel) 13 (2021) 1–18, https://doi.org/10.3390/polym13193267.