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Bio-lubricant production from black liquor as a sustainable biorefinery strategy

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Abstract

The paper and pulp industry annually generates approximately 170 million tons of black liquor, yet research directly targeting its utilization remains scarce. Addressing this gap, our study tackles the challenge of revalorizing black liquor through innovative techniques. Concurrently, the lubricant industry's pursuit of eco-friendly alternatives necessitates effective thickeners for semi-solid lubricant formulations derived from vegetable oils. Our research focuses on revalorizing weak black liquor via supercritical water hydrolysis, presenting a novel avenue for semi-solid bio-lubricant production. We obtained and treated four lignin waste fractions, including original black liquor and depolymerized variants through supercritical water hydrolysis, followed by additional processes such as spray-drying, oven-drying, and ethyl acetate extraction. These lignin fractions were then incorporated into epoxy-modified vegetable oils to formulate sustainable lubricants. Evaluation of these formulations revealed promising rheological and tribological properties. The resulting castor oil-based bio-lubricants not only exhibited excellent stability and appearance but also demonstrated notable performance improvements in rheological and tribological tests, noticing a maximum wear scar size reduction of around 50%, while maintaining friction factor values. Our findings highlight the potential of depolymerization hydrolysis in enhancing the lubricating properties of castor oil-based formulations, thus advancing the revalorization of weak black liquor.

Keywords Biomass · Polyol · Lignin · Depolymerization · Rheology · Thickener

Abbreviations

BL	Black liquor
HBL	Hydrolyzed black liquor
SD	Spray dried
OD	Oven dried
EA	Ethyl acetate-extracted oven-dried material
ECO_BL	Epoxidized black liquor

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ECO_SD	Epoxidized spray dried
ECO_OD	Epoxidized oven dried
ECO_EA	Epoxidized ethyl acetate-extracted oven-dried
	material

1 Introduction

The pulp and paper industry remains the primary source of lignin, maintaining its stronghold despite the emergence of modern lignin-based biorefineries and start-ups. The kraft pulping process, in particular, retains its dominant position among various pulping techniques, accounting for over 90% of all chemical pulps produced globally [1]. The paper and pulp industry, as reported by the International Energy Agency (IEA), annually produces approximately 170 million tons of black liquor (dry basis), with an additional 50–70 million tons attributed to lignin [2]. Currently, much of this material is either burnt for energy recovery or utilized in kraft lignin production. The widespread and centralized availability of black liquor presents a compelling opportunity to explore cost-effective

valorization techniques aimed at generating valuable biobased products.

Despite the extensive body of research on lignin depolymerization and its applications, there remains a notable scarcity of studies directly utilizing black liquor for product manufacturing without having an intermediate step of producing kraft lignin [1]. Recognizing lignin as a valuable aromatic bio-polymer within black liquor holds significant potential for advancing both academic literature and industrial applications. The lignin fraction derived from black liquor represents a promising aromatic feedstock for the synthesis of various materials, including lubricants and polyurethanes [3-5]. Some studies also covered the use of lignin or modified lignin from hardwood or softwood and obtained a polyol-rich fraction that can be used to create different types of materials [6, 7]. The lignin used in these studies is generally a solid made from acidification of black liquor [8], modified lignin [9], or depolymerized [10, 11]. One approach to generate polyols from black liquor is the continuous hydrothermal depolymerization [12]. This technology offers several advantages like the use of inexpensive and safe solvents, and the direct use of black liquor as feedstock [13–15]. Hence, a custom-designed continuous hydrothermal depolymerization pilot plant was developed by the PressTech research team to carry out rapid reactions (<1 s) [16]. This specialized device enables precise control over reaction times, effectively mitigating side reactions that could otherwise result in repolymerization. Supercritical water (SCW) was chosen as the reaction medium due to its abundance, cost-effectiveness, and environmentally friendly properties [17]. Achieving rapid depolymerization of lignin is attributed to a combination of factors, including the unique properties of SCW, a process design featuring instantaneous heating and cooling, and enhanced reaction kinetics and mass transfer [18].

The use of polyols derived from biomass offers distinct advantages in producing bio-based compounds [19, 20]. These materials serve as alternatives to petroleum-derived substances in various applications including coatings, lubricants, emulsions, and bio-plastics [21-24]. A growing trend involves substituting mineral or synthetic oils with vegetable oils or their derivatives in lubricant production [25, 26]. However, achieving optimal lubricating performance with vegetable oils often requires additives or chemical modifications, especially when structuring oils to obtain semisolid lubricants [27]. For instance, sustainable lubricant formulations have been developed by promoting chemical crosslinking of vegetable oils and bio-polymers (as a source of polyols) [28, 29]. Utilizing epoxides that react with compounds containing active hydrogen atoms through nucleophilic attack has shown promise. Two approaches to epoxidation have demonstrated success in synthesizing eco-friendly lubricant compositions. The first involves epoxidizing hydroxyl groups found in lignocellulose with dior tri-functional epoxides, followed by reaction with castor oil [4]. The second approach entails epoxidizing the double bonds of vegetable oil glycerides followed by reaction with lignocellulose hydroxyl groups [30]. Despite both methods resulting in well-structured crosslinked networks, they exhibit different rheological properties. Among all the likely available vegetable oils, castor oil has excelled owing to its non-edible characteristics and superior viscosity values, what has been proven more appropriate for lubrication purposes [31]. Additionally, dispersion of epoxy-modified lignocellulosic material into castor oil typically leads to highly structured systems with gel-like responses [4]. Conversely, a wider range of rheological properties, from Newtonian to non-Newtonian viscoelastic liquids, can be achieved by controlling the degree of epoxidation when epoxidizing castor oil and subsequently dispersing lignocellulosic materials [30].

This study pioneers sustainable lubricant formulations by incorporating depolymerized fractions of black liquor (as a bio-polyol) into epoxidized vegetable oil. To our knowledge, this represents the inaugural application of black liquor depolymerization, fractionation, and upgrading to produce semi-solid bio-lubricants. Our work establishes a novel pathway for developing consumer-ready products, while also investigating the impact of black liquor depolymerization treatments on the rheological and tribological properties of the resulting bio-lubricants.

2 Materials and methods

2.1 Materials

Black liquor was procured from ENCE wood pulping factory (Pontevedra, Spain). Refined castor oil was supplied by Import-quimia, S.L. (Guipuzkoa, Spain). The main physico-chemical properties of castor oil and its fatty acid composition can be found in the supporting information. The reagents used for the epoxidation reaction of castor oil were hydrogen peroxide (30% w/w), glacial acetic acid (99.7% w/w), and phosphoric acid (\geq 85% w/w). The reagents and solvents were purchased at Merck Sigma-Aldrich (Darmstadt, Germany) and used without further modification.

2.2 Supercritical water hydrolysis unit

Black liquor was treated with SCW in continuous reactors at very short reaction times [32]. The device allows the operator to pump the feedstock suspended in water without any preheating, which prevents side reactions during the heating stage. Briefly, water is pumped through an in-line heater that increases the fluid temperature up to supercritical conditions. The hot water stream is then mixed with the cold feedstock in a T-junction, which is the beginning of the reactor. The reaction starts as soon as these two streams are mixed. The reactor is tubular, and it is made of stainless-steel (SS 316) and works as plug-flow type. The length of the reactor is 50 cm, and the inner diameter is 3.04 mm. The pressure of the reactor is controlled by using a needle valve manually actuated by the operator. The pressure drop in the system is around 250 bar before and after the valve. That sudden depressurization promotes the production of vapor, which provides instantaneous cooling of the product stream. The temperature and pressure suddenly decrease from SCW conditions to about 150 ± 10 °C, and 5 ± 2 bar at the reactor outlet. This temperature is low enough to prevent lignin side reactions. After that, the product stream is cooled down to room temperature by a chiller. The hydrothermal treatment of black liquor was done at 385 ± 1 °C and 260 ± 5 bar, whereas the reaction times were between 0.36 and 0.40 s. The system was operated continuously for 60 min to generate the samples. The black liquor slurry concentration in the biomass tank was 20 wt.% of total solids. The slurry and SCW flows were set to 7.5 kg/h and 15 kg/h, respectively. A simplified scheme of the device stages is shown in Fig. 1.

2.3 Refining of hydrothermal products

Four black liquor samples were created to assess their potential as oil structuring agents for lubricant applications. The black liquor (BL) sample was obtained directly from a traditional pulp and paper mill, and it was used in this research as feedstock for hydrothermal treatment. The spray dried (SD) sample was obtained from drying the acidified (pH=2) hydrolyzed black liquor (HBL) from the SCW hydrolysis. This fraction was spray dried without further treatment. Spray drying was carried out using a mobile minor spray dryer with rotary atomizer supplied by Gea Niro. The acidified HBL sample was pumped using a peristaltic pump (Watson-Marlow 520) with a flow rate of 1.5 kg/h. The inlet air temperature was 160 °C, and the product outlet temperature was approximately 85–90 °C. The pressure supply of compressed air to the dryer nozzle was 6 bar [33]. The ovendried (OD) sample was obtained similarly to the SD but changing the drying method (see Figures S1 and S2). The oven drying was carried out at 100 °C and the fraction was then ball milled to reduce particle size. The ethyl acetateextracted (EA) sample was obtained by subjecting the OD sample to extraction with ethyl acetate. After extraction, the ethyl acetate was evaporated, and the EA sample was ground. The reasons for selecting these products were to check the effects of inorganic matter and drying methods on the bio-lubricant properties.

2.4 Castor oil epoxidation

The characteristics of the castor oil that was used in this study can be found in Tables S1 and S2. The refined castor oil was chemically modified according to the procedure outlined in a previous study [30]. In brief, castor oil was initially brought into contact with glacial acetic and phosphoric acid in a round-bottom flask fitted with a thermometer, a reflux condenser, and a dropping funnel. Upon heating the reagents mixture to 70 °C, a specific amount of H_2O_2 was dropwise added, maintaining the molar ratio of C = C/acetic acid/ H_2O_2 of 1/0.77/24.4 (see mass proportions in Table 1). The epoxidation reaction was run for 4 h under agitation (700 rpm). After completion of the reaction procedure, the resulting solid product was filtered, washed with distilled water, and dried in a vacuum oven at 60 °C overnight. The epoxy index of the chemically modified castor oil was

 Table 1
 Mass proportions of reagents used in the castor oil epoxidation reaction

Epoxidized castor oil	Castor oil (g)	CH ₃ COOH (g)	$H_{3}PO_{4}\left(g\right)$	$H_{2}O_{2}\left(g\right)$	Epoxy index (mol/kg)
ECO	80.0	12.0	0.8	48.0	2.0



Fig. 1 SCW depolymerization and downstream separation basic flow diagram

evaluated in accordance with the International Standard ISO 3001:1999 (E), as detailed elsewhere [30].

2.5 Dispersion of black liquor samples in epoxidized castor oil

Lignin dispersions in the epoxidized castor oil (ECO) were prepared according to the following two-step procedure. The black liquor and derived fractions were dispersed into ECO maintaining a selected lignin fraction:ECO weight ratio of 20:80 (see codes applied in Table 2). The materials were mixed using a controlled-rotational speed mixing device (RW 20, Ika, Germany) fitted with an anchor impeller (60–70 rpm) for 24 h at room conditions to promote the chemical interaction between the lignocellulosic fraction and ECO. Afterwards, the ensuing intermediate product was left for curing in a second stage for 2 h in a convection oven under static conditions and subsequently homogenized with the aid of an Ultra-Turrax turbine (Ika T-25, Germany) at a rate of 10,000 rpm for 60 s. Resulting gel-like dispersions were stored at room temperatures and further characterized, at least, 1 month after preparation to ensure complete sample curing.

2.6 Analytical techniques

2.6.1 Compositional characterization

The content of carbohydrates, acid soluble and insoluble lignin, moisture, and ash were determined using the National Renewable Energy Laboratory (NREL) Laboratory Analytical Procedure (LAP) [34–37]. Briefly, the 0.3 g of sample was placed in pressure tubes and first treated with 72% sulfuric acid at 30 °C. Upon completion of 60-min digestion, the mixture was diluted so the acid reached a 4% concentration by adding deionized water, and tubes were then placed for 1 h at 120 °C. Afterward, the hydrolysis product was cooled at room temperature and filtered through previously measured ashless filter paper. The solid phase on filter paper was washed several times with deionized water and placed in the oven at 40 °C overnight for drying while the liquid phase was neutralized with calcium carbonate up to pH 6 to

 Table 2
 Proportions used in lignin-structured epoxidized castor oil formulations

Bio-lubricant nomenclature	ECO content (wt. %)	Lignin fraction	Content of lignin fraction (wt. %)
ECO_BL	80	BL	20
ECO_SD	80	SD	20
ECO_OD	80	OD	20
ECO_EA	80	EA	20

prepare samples for HPLC sugar analysis. The carbohydrates and their derivatives were analyzed by high pressure liquid chromatography (HPLC). A Shodex SH-1011 column was used with 0.01 N sulfuric acid as the mobile phase. The flow rate was 0.8 mL·min⁻¹ and the column temperature was 60 °C. A Waters 2414 refractive index detector was used component detection. Samples for carbohydrate analysis were prepared according to the NREL protocol.

2.6.2 Characterization of bio-aromatics and bio-polyols

A fractionation method was applied to characterize low molecular weight compounds, such as aromatic monomers, bio-polyols, and oligomers (mainly dimers and trimers) for *BL* and *HBL* (see Figure S1). Sulfuric acid was added to HBL sample to lower the pH to 2 and precipitate larger lignin molecules. That material was centrifuged, and 2 fractions were obtained: dissolved solids (DS) and suspended solids (SS). The suspended solids fraction was further washed with pH 2 water to ensure that all DS was extracted from SS. The DS and SS fractions were then extracted separately with ethyl acetate. The ethyl acetate was recovered by evaporation in rotavapor. The ethyl acetate-extracted fractions were labelled as DS-EA and SS-EA. GC–MS characterization was applied to the DS-EA fraction to identify aromatic components.

Gas chromatography analyses were performed using an Agilent 7820 GC-MS with quadrupole mass spectrometer detector. A low bleed, non-polar capillary HP-5MS (Agilent, USA) column, 30 m \times 0.250 mm \times 0.25 µm was used for the analyses. Helium was used as the carrier gas. Bio-polyol including monomers and oligomers were analyzed by using a derivatization method. Briefly, 10 mg \cdot mL⁻¹ lignin oil (LO) was dissolved in acetone, and then 10:1:2 (v:v:v) of the LO:pyridine:BSTFA mixture was heated at 45 °C for 20 min before injection, using BSTFA (N,O-Bis(trimethylsilyl)trifluoroacetamide with 1% trimethylchlorosilane) as the silylating agent. The oven was started at 150 °C, and increased at a rate of 4 °C·min⁻¹ until 300 °C, and held for 18 min. Trimethylsilyl (TMS)-derivatized monomers determination was carried out with a 10:1 split ratio, solvent delay of 4 min, and an oven start temperature of 80 °C, while the determination of TMS-derivatized oligomers was carried out with a 2.5:1 split ratio and a solvent delay of 15 min to avoid overloading the detectors with the monomers.

2.6.3 Elemental analysis

Elemental analysis of the black liquor and its depolymerized products was performed using a Leco CS-225 instrument. Carbon, hydrogen, nitrogen, and sulfur contents were determined by this analysis. The ash analysis was also used in calculations to estimate the amount of oxygen by difference. The oxygen content was estimated as the difference between 100% and the sum of carbon, hydrogen, nitrogen, sulfur, and ash content.

2.6.4 Thermogravimetric analysis

Thermogravimetric analysis was conducted using a Mettler Toledo TGA/SDTA RSI analyzer. Approximately 5 mg of the sample was heated at a rate of 10 °C/min under a nitrogen atmosphere with a flow of 50 mL/min. The temperature started at 30 °C and increased to 900 °C. The temperature was held constant at 900 °C under a nitrogen flow for 10 min with the same flow rate.

2.6.5 Hydroxyl groups analysis

The aliphatic hydroxyl groups were analyzed according to ASTM D4274 technique [38]. Following the literature, method B of this standard was followed. Each sample was subjected to a phthalation process in a pyridine:phthalic anhydride medium. The mixture was heated to 98 ± 2 °C. After heating, a specific amount of pyridine was added, and the mixture was back-titrated with 1 N NaOH solution. Due to the dark color of the samples, the change in potential was read and recorded using a pH meter. In accordance with the test method, the OH number was determined as mg KOH/g sample and converted to mmol OH/g sample.

Phenolic hydroxyl groups were analyzed by the Folin-Ciocalteu method. For this analysis, the samples were dissolved in 0.01N NaOH medium. The method used to determine the phenolic content is a UV–Vis spectrophotometric method in which the absorbance at 765 nm is recorded by means of the blue color developed by the samples after incubation with the reagents for 2 h at room temperature. The concentrations are calculated from a phenol calibration line.

2.6.6 Molecular weight distribution

Four samples were prepared for gel permeation chromatography to check the molecular weight distribution of the products. The samples were dried overnight in an oven at 50 °C to remove moisture prior to preparation. THF was used to dissolve the dried samples at 1 mg/mL concentrations. A Phenomenex Phenogel 5 μ m GPC column with the dimensions of 300×7.8 mm was used for the analysis. A Hewlett Packard 1100 series autosampler injected 25- μ L injection volumes from each sample. The column temperature was kept constant at 26 °C. THF was used as the carrier solvent at a flow rate of 1 mL·min⁻¹. UV diode array detector at a wavelength of 220 nm with a reference wavelength of 360 nm and a slit width of 4 nm was used to analyze the samples. A calibration curve was established between molecular weight and the retention time using PSS low molecular polystyrene ReadyCal set M(p) 266–66000 (see Figure S4). The UV response and retention time data were correlated with the calibration curve, and used to calculate M_w , M_n , and M_z .

2.6.7 Rheological characterization

Dispersions of black liquor and derived fractions in ECO were subjected to rheological characterization at 25 °C in a controlled-stress rheoscope (Thermo Haake, Germany) rheometer. Grooved 20-mm-diameter parallel plates geometry (1-mm gap) was selected to prevent wall slip phenomena. Steady-state viscous flow tests were carried out in the shear rate range from 0.01 up to 100 s^{-1} . In addition, small-amplitude oscillatory shear (SAOS) tests were also conducted in the frequency range from 0.03 to $100 \text{ rad} \cdot \text{s}^{-1}$ within the linear viscoelastic region, previously determined in stress sweep experiments performed at 1 Hz. All rheological results are reported as the average of at least two replicates.

2.6.8 Tribological characterization

Aiming to test the different dispersions of black liquor fractions in ECO as potential bio-lubricants, tribological experiments were carried out at 25 °C using a tribological cell coupled to a Physica MCR 501 controlled-stress rheometer (Anton Paar, Graz, Austria) fitted with a ball-on-three-plates friction pair. As detailed elsewhere [39], this experimental arrangement comprises a lower geometry holding three 45°-inclined steel plates (1.4301 AISI 304) and an upper measuring tool coupled with a 12.7-mm diameter polished bearing ball (1.4401 grade 100 AISI 316). The ball was fixed to the upper geometry to prevent likely rolling and slides in the tribological contact. This configuration enabled the evaluation of the friction coefficient (μ), defined as the ratio between the applied normal force (F_N) and monitored friction force (F_F) . All the samples were submitted to sliding speed sweep tests from 0 to 1000 rpm by applying 20 N normal force to obtain the characteristic Stribeck diagrams and thus identify the different lubrication regimes. Afterward, transient friction measurements were conducted at 20 N and 10 rpm for approximately 10 min, at a given rotational speed within the mixed friction lubrication regime. The friction coefficient was obtained as the mean value once reached the steady state, i.e., almost constant values over time. Each tribological measurement was replicated at least six times on fresh samples. After performing the transient friction tests, at constant rotational speed, the area of the ensuing wear tracks located on the plates were examined by using an Olympus System Microscope BX52 (Japan) coupled with a digital camera C5050Z (4×and 10×magnification objectives). Reported areas are the average of three replicates.

3 Results and discussion

The reaction of black liquor in supercritical water provided 77% w/w bio-oil yield in 0.4 s These results are described more in detail elsewhere [40]. The coming section will review the sample fractionation and use in lubricants applications. The samples produced in during the experimental work and their code nomenclature are shown in Table 3.

3.1 Extraction and characterization of lignin fractions

The chemical compositions of the black liquor and hydrolyzed black liquor can be seen in Table 4. The ash content of the black liquor is 49 wt.% on a dry basis. According to the procedures that were described in Sect. 2.3, OD and SD samples include the acid added during the precipitation. For this reason, the ash contents of OD and SD are higher than BL. On the contrary, EA sample had a low amount of ash (viz. 2.3 wt.%), and a higher total lignin content since it is the fraction that was extracted by ethyl acetate. The carbohydrate content of the samples was less than 1% by weight in all cases.

The results of the elemental analysis can be found in Table S3. The atomic ratios of hydrogen to carbon and oxygen to carbon were calculated and presented in a Van Krevelen diagram in Fig. 2. Black liquor shows a higher H:C ratio compared to the hydrolyzed products of SCW. The difference between BL and HBL products indicates that demethylation occurred during the SCW hydrolysis and subsequent refining processes. Although there is a decrease in the H:C ratio, which normally indicates the presence of dehydration reactions [15], the increase in the O:C ratio suggests demethylation overall. SD has a higher O:C ratio than OD, and EA has the highest O:C ratio. This is an indication of increased aromaticity after the SCW process of BL. Gaseous products were possibly formed during the acidification of HBL. CO₂,

 Table 4
 Composition in weight percentage (%) of the different lignin fractions

Designation	Acid insoluble lignin	Acid solu- ble lignin	Total lignin	Ash	Carbs
BL	21.0	12.3	33.3	49.0	<1
SD	18.3	9.8	28.1	60.7	<1
OD	23.5	6.2	29.7	59.8	<1
EA	50.9	18.8	69.7	2.3	<1

 H_2S , and methanethiol are known to occur during the acidification of black liquor [41]. It is therefore probable that these gases played a role in the decrease of the H:C ratio and an increase in the O:C ratio.

The chemical composition of bio-polyols including monomers and oligomers was determined using GC-MS. The chromatograms are shown in Figs. 3 and 4. The chromatograms were observed by applying two different methods. Figure 3 shows the monomer focused GC-MS method results, while Fig. 4 demonstrates the output of the oligomer focused GC-MS method as it was mentioned in Sect. 2.6. In Fig. 3, the compounds detected up to first 15 min of the retention time (RT) were mainly responsible for the carbohydrate-derived compounds (Region 1). Compared to the HBL sample, BL has larger intensity and area, which means that simple carbohydrate-derived compounds were consumed during SCW treatment. This indicates that decarboxylation occurs during the process. A recent study also emphasizes the presence of decarboxylation reactions during rapid SCW process [32]. On the other hand, monomeric compounds of lignin can be seen between the retention times of 15-40 min (Region 2) (Fig. 3). In comparison to the BL sample, HBL sample has much higher intensity and area. This region includes common identified monomers for both BL and HBL samples such as, guaiacol, catechol, syringol, vanillin, acetovanillone, syringaldehyde, and acetosyringone. These monomeric compounds were also observed in other studies [14,

Table 3 Sample obtained from the experimental work and analysis

Abbreviation	Terminology	Comments
BL	Black liquor	Sample—raw material
SD	Spray dried	Sample-hydrolysed black liquor (HBL) followed by spray drying
OD	Oven dried	Sample—hydrolysed black liquor followed by oven drying
EA	Ethyl acetate extracted	Sample-oven dried followed by ethyl acetate extraction
DS	Dissolved solids	GC analysis
SS	Suspended solids	GC analysis
DSEA	Dissolved solids ethyl acetate extracted	GC analysis: monomer and oligomer including fraction
SSEA	Suspended solids ethyl acetate extracted	GC analysis
LO	Lignin oil	GC analysis: refers to DSEA fraction itself. Used as LO to indi- cate it is an oil fraction

1.80





Fig. 3 GC-MS chromatograms of dissolved solids ethyl acetate-extracted fraction by using a derivatization method, obtained by using monomer focused method

15]. The total area of peaks in this region, was found 75% higher than BL. GC–MS analysis showed that this region includes aldehyde and ketone groups like the structures of ArOH, ArOR, ArCHO, ArCOR, and particularly the presence of methoxy and hydroxyl groups. The aromatic monomers and some of the main peaks are summarized in Table 5. Increased abundance of these substructures in HBL products after depolymerization process proves the raise of the methoxy and hydroxyl group compounds. The molecular weight of this region was found to be in the range ~ 120–300 Da. It

is possible that some of these compounds were formed by the compounds detected after 40 min of the retention time.

It was hard to identify the exact composition of the compounds after 40 min of the retention time. However, as the resolution was very low in monomer-focused method, this region better examined using oligomer-focused method bypassing the detector overload with the monomers. Figure 4 chromatograms consisted of polyphenols, stilbenoids, terpenes, flavonoids, hydroxy naphtoquinones, resinols, and plant hormones (phytoestrogen, phytoandrogen, phytosterol,



Fig. 4 GC-MS chromatograms of dissolved solids ethyl acetate-extracted fraction by using a derivatization method, obtained by using oligomer focused method

Table 5 Some of the major structures identified and corresponding area percentages	Region	Peak no	Avg. retention time (min)	Compound name	Area % in BL	Area % in HBL
in black liquor and hydrolyzed	Region_1	1	12.05	Lactic acid	6.47	3.30
black liquor using monomer	-	2	14.45	2-hydroxybutyric acid	13.87	6.08
can be found in Fig. 3	Region_2	3	17.55	Guaiacol	0.82	0.98
		4	20.72	Catechol	2.40	2.61
		5	23.36	Syringol	3.70	16.00
		6	27.43	Vanillin	1.31	1.86
		7	29.91	Acetovanillone	1.24	2.38
		8	32.25	Syringaldehyde	4.11	6.03
		9	33.95	Vanillic acid	2.09	0.31
		10	34.15	Acetosyringone	6.72	10.28
		11	35.71	Homovanillic acid	n.d	1.68
		12	37.47	Syringic acid	6.09	0.96
		13	43.33	Gallic acid	6.55	2.03
	Region_3	14	60.10	Tocopherol (β-carotene) derivative	1.82	n.d
		15	67.46	Medioresinol	2.58	n.d
		16	68.06	Phytosterol derivative	4.47	n.d
		17	69.01	Syringaresinol	2.84	0.37

etc.) which can be generalized as oligomers and have typical molecular weight of more than 250-350 Da. Although, some of the familiar structures that can be found in lignin, (e.g., resinol (β - β), phenylcoumaran (β -5), dibenzodioxocin (5–5), and spirodienone $(\beta$ -1)) were tracked, determining the exact compositions require deeper analysis like NMR [42]. The total area calculated for HBL sample in this region was about 3.5 times less than the BL sample, which states the existence of the depolymerization reactions took place. The chromatography area comparison should be analyzed carefully, then all analyses were performed on the same day in sequence, with the same tune settings. Reference samples

were run after each sample set of triplicates to monitor for any deviations. To summarize, GC–MS analysis demonstrated the occurrence of decarboxylation, increment of methoxy and hydroxyl groups, and depolymerization reactions. However, even though these happened in a smaller scale, in the big picture elemental analysis verifies the demethylation took place. The major compounds (mainly > 1% of total area) identified using GC–MS were summarized in Tables S5 and S6.

Due to the presence of polyphenols and high M_w biopolyols which are not possible to identify by GC–MS, gel permeation chromatography and hydroxyl groups determination were carried out to have a better understanding of the characteristics of these molecules. The molecular weight distribution of the bio-polyol-containing samples was analyzed to determine the number average molecular weight (M_n) , weight average molecular weight (M_w) , z-average molecular weight (M_z) , and polydispersity index (PDI). The corresponding values can be seen in Table 6.

Table 6 Peak maxima (min), M_n (g/mol), M_w (g/mol), M_z (g/mol), and PDI values of the black liquor and its depolymerized products

Sample	Peak maxima (min)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI
BL	10.690	1461	2002	2547	1.371
SD	11.227	1004	1485	1997	1.478
OD	11.181	1069	1598	2162	1.495
EA	11.129	1207	1522	2262	1.261

Fig. 5 Molecular weight distribution of the black liquor and its depolymerized products

The BL had the highest average molecular weight (2002 g/mol), and this value is in the range of the kraft lignin $M_{\rm w}$ in different types of black liquor according to the previous reports [43–45]. The observed peak height sequence was SD > OD > EA > BL. In contrast, the average molecular weight sequence was BL > OD > EA > SD. Although sample EA was expected to have the lowest molecular weight (1522 g/mol), sample SD had a slightly lower molecular weight (1485 g/mol). TGA data of these samples were given in Figure S3 and Table S4. Thermogravimetric analysis (TGA) data indicated that sample EA underwent the most significant degradation of the samples in the temperature range of 120-550 °C, where lignin degradation usually ends [46]. This would normally represent a lower molecular weight for sample EA. However, as it can be seen in Fig. 5, sample EA exhibited three times greater intensity at the higher molecular weight peak compared to the other samples. This behavior can be explained by the fact that sample EA was obtained following the ethyl acetate extraction of sample OD, resulting in the transfer of the entire organic fraction from sample OD to sample EA, culminating in an approximate molecular weight of 1522 g/mol for sample EA. Sample SD, subjected to milder spray drying conditions, should theoretically contain a slightly higher amount of low molecular weight short chain aromatic compounds, resulting in an average molecular weight of 1485 g/mol. As expected, the molecular weight of sample OD was slightly higher at 1598 g/mol compared to the other two samples.

As it can be seen in Table 6, the polydispersity index values of all samples were similar. Sample EA had the lowest PDI at 1.261, while sample OD had the highest at 1.495. The PDI for sample BL was recorded as 1.371, reflecting



Residence Time (min)

a smaller difference between its high and low molecular weight regions compared to samples OD and SD. The low molecular weight region for sample BL produced a signal at 11.7 min (~937 g/mol) with an intensity about half of the main peak. On the other hand, the samples SD and OD had a much lower intensity at low molecular weight region (~432 g/mol) than their respective main peaks. Overall, the PDI values suggest a homogeneous molecular weight distribution, close to that of industrial polyether and polyesters, which typically have PDIs of 1.05 and 1.3 respectively [47]. The molecular weights corresponding to the retention times of the signals at 937 g/mol (at 11.7 min) and 432 g/mol (at 12.5 min) imply that, in this region, samples SD and OD consist mainly of dimers and trimers, whereas sample BL consists mainly of trimers and larger oligomers. In summary, the molecular weights of all samples are in the range of 150-6500 g/mol, suitable for lubricant or polyurethane production [48]. Another notable point is the decrease in molecular weight of the depolymerized samples compared to BL. The GPC results support the previous discussion about oligomers depolymerization observed with the GC-MS results.

As it can be seen in Table 7, the content of aliphatic hydroxyl groups was quantified, and the following order was obtained SD > EA > OD > BL. Conversely, the aromatic hydroxyl group content was found to be in the order EA > OD > SD \approx BL. These results differ significantly from those reported in the literature where bio-polyols have been produced by liquefaction of lignin. For example, Briones et al. used agro-industrial residues and polyhydric alcohols, obtaining a range of ~7.04–10.45 mmol OH/g across different feedstocks [49]. Similarly, da Silva et al. used polyhydric alcohols and organic acids with kraft lignin and reported ~11.76 mmol OH/g [50].

To the best of our knowledge, there is a void of hydrothermal treatment studies where bio-polyol fractions have been obtained directly from the processing of alkali black liquor, which restricts direct comparison with the existing literature. The closest parallel is the study by Hernandez-Ramos et al. where they extracted bio-polyols from organosolv black liquor using ultrasonication [6]. Though their

 Table 7
 Aliphatic and aromatic hydroxyl groups of the black liquor and its depolymerized products

	mmol OH/g	mmol OH/g	mmol OH/g
Sample	Aliphatic OH groups	Aromatic OH groups	Total OH groups
BL	0.00	1.08	1.08
SD	4.83	1.08	5.91
OD	0.93	1.56	2.49
EA	1.59	2.36	3.95

monomer fraction lacked certain bio-polyols, they isolated dimers, trimers, and oligomers rich in hydroxyl groups fractions from eucalyptus black liquor (~10.46 mmol OH/g) and pine organosolv black liquor (~11.02 mmol OH/g). To compare, the hydroxyl group content observed in this study is lower than that reported in the literature. However, it is important to note that the samples BL, OD, and SD contain significant amounts of inorganic matter which contribute to the observed reduction in hydroxyl numbers.

The ASTM D4274 method is the most effective for samples with a higher proportion of aliphatic hydroxyl groups. Due to the significant aromatic components detected by GC-MS analysis, the total phenol content was also evaluated to estimate the amount of aromatic hydroxyl groups. According to the data presented in Table 7, the total hydroxyl group content is in decreasing order SD > EA > OD > BL. These values help to clarify the presence of increased number of OH reactive groups in each sample compared to sample BL. Even though the analysis of aromatic hydroxyl groups does not provide a direct measure of the abundance of OH reactive groups, it does provide a close approximation. Hence, by correlating molecular weight analysis with hydroxyl group data, we infer that all samples underwent rapid depolymerization under SCW conditions, fragmenting into smaller, more reactive components.

3.2 Dispersions of black liquor and derived fractions in ECO

As detailed in the experimental section, upon epoxidation, castor oil was structured by dispersing 20% w/w of the different lignin-rich fractions studied. In general terms, all lignin-structured ECO formulations exhibited long-term physical stability and showed a homogeneous appearance, which has been previously related to the chemical interaction between the epoxidized oil and lignin [30]. The viscous flow curves of the resulting dispersions are shown in Fig. 6 in comparison with the lignin-free ECO sample. All lignin dispersions in ECO showed a shear-thinning behavior where the apparent viscosity decreased with the shear rate until reaching a high-shear rate-limiting viscosity. This rheological behavior has been previously found in traditional lithium soap-thickened lubricating greases modified with polymers [51], and can be suitably described by the Sisko model [52]:

$$\eta = \eta_{\infty} + K \cdot \dot{\gamma}^{n-1}$$

where η is the apparent viscosity, η_{∞} the high-shear ratelimiting viscosity, and *K* and *n* are the consistency and flow indexes, respectively. The lignin-free ECO sample also showed a shear-thinning flow characteristics in the whole shear rate range studied, although the tendency to reach a



Fig. 6 Evolution of the apparent viscosity with shear rate for the dispersions of lignin fractions in epoxidized castor oil

 Table 8
 Sisko model fitting parameters for the dispersions of lignin fractions in epoxidized castor oil

System	$K(\operatorname{Pa} \cdot \operatorname{s}^n)$	n	η_{∞} (Pa·s)	R^2
ECO (lignin-free)	46.5	0.692	-	0.996
ECO_BL	1502.4	0.020	22.0	0.977
ECO_SD	912.2	0.075	30.4	0.998
ECO_OD	490.9	0.047	31.0	0.993
ECO_EA	63.7	0.285	18.0	0.995

high-shear rate-limiting viscosity, h_{∞} , was not observed in this case. Table 8 collects the values of the fitting parameters.

In principle, the highest viscosity modification should be expected when adding the most lignin-enriched fraction, i.e., EA, or those with a higher amount of available –OH groups, i.e., EA and SD (see Table 7), due to the more extensive chemical crosslinking that occurs between lignin hydroxyl groups and the generated epoxy rings in ECO. However, in the light of experimental data shown in Fig. 6, ash content may exert an important effect on the ensuing flow properties acting as fillers. Therefore, the dispersion of BL, OD, and SD fractions, whose ash content ranges from 49.0 to 60.7% (see Table 4), into ECO-yielded bio-lubricants with higher apparent viscosity values. Additionally, the lower average molecular weight in OD, SD, and EA products because of SCW hydrolysis compared to BL (see Table 6), gave rise to ECO_BL having the higher viscosity, with a *K* value more than 30-fold higher than that of ECO.

On the other hand, ECO_OD and ECO_SD lignin dispersions exhibited higher values of the high shear rate-limiting viscosity values (η_{∞}), while extremely low values of the flow index were obtained in the three more structured samples, which were also typically found in traditional lubricating greases [53, 54], and it is indicative of their characteristic yielding behavior [55].

As stated in previous lines, there must be a synergistic thickening effect of different variables such as the ash content, the molecular weight (M_w) , the PDI, and the total amount of available hydroxyl groups. These parameters would contribute differently to the enhancement of the apparent viscosity with respect to ECO in this order: ECO_ $BL > ECO_SD > ECO_OD$ (Fig. 6), depending on the composition of the different residual lignin fractions. To better understand the effect of these different individual parameters on the viscous flow behavior of lignin dispersions, an analysis based on the correlation between the normalized values of the consistency index and a power function of these variables (also normalized respecting the maximum values) was made (see Table S7), and the predicted K values were plotted against the experimental K values, as shown in Figure S5. According to the obtained regression coefficient, $R^2 = 0.992$, a proper correlation among the experimental and predicted K values was achieved (see Figure S5), with different weights of each variable reflected in the exponents of the power series. As reflected by the power exponents, all these variables exert a positive influence over the K values, except for the PDI, which showed an inverse relationship (see Table S8), being PDI and the molecular weight the most influencing parameters and the amount of available hydroxyl groups the least influential.

The viscoelastic properties of the dispersions of black liquor and derived hydrolyzed fractions in ECO were also investigated through SAOS experiments performed inside the linear viscoelastic regime, and the corresponding mechanical spectra are shown in Fig. 7. As can be seen from the evolution of both the storage (G') and loss (G") moduli with frequency (Fig. 7a), ECO and the ECO_EA lignin dispersion exhibited a predominant viscous response over an extended frequency range. Moreover, similarly to what was found in the viscous flow measurements, the values of both viscoelastic functions for the ECO EA sample are only slightly higher than those obtained for ECO. Similar liquid-like rheological response was previously found when dispersing lignocellulosic sugarcane bagasse waste in epoxidized vegetable oil [30]. This behavior was attributed to a high level of compatibilization due to the extensive crosslinking achieved. On the contrary, much higher values of the SAOS functions were obtained for the rest of dispersions, more specifically differences of more than two decades with respect to ECO values, as well as an extended plateau region, with values of G' significantly higher than those found for G" in a wide frequency range, characteristic of gel-like dispersions such as traditional lubricating greases [55, 56]. The relative elasticity of the different samples can also be inferred from the loss tangent vs. frequency plots (Fig. 7b). This solid-like behavior can be mainly attributed to the ash content acting as fillers in the matrix. However, in agreement with the values of the consistency index, dispersions of SD and BL fractions displayed the highest values of SAOS moduli within the whole frequency range studied, because of the already mentioned balance among the relevant characteristics of the different lignin fractions, i.e., ash content, M_W , OH, and PDI. From the comparison of SD and OD fractions with very similar total lignin and ash contents (see Table 4), the higher OH groups content in the former, as corroborated by the enhanced O:C ratio reported in the elemental analysis (Fig. 2), proves to play a significant role





in the establishment of chemical crosslinking, thus affecting their ensuing rheological behavior to some extent.

Finally, bearing in mind the potential application of these formulations as semi-solid bio-lubricants, a tribological characterization was carried out. Table 9 shows the stationary friction coefficient values within the mixed lubrication regime (20 N normal load and 10 rpm rotational speed, after 10 min) obtained when using the lignin-structured ECO formulations as lubricants in a tribological contact, in comparison with the neat epoxidized oil (ECO). As can be deduced

 Table 9
 Values of the stationary friction coefficient and wear scar areas obtained on the steel plates when using the different lignin dispersions studied as lubricants in a ball-on-plates tribological contact

Sample designation	μ(-)	Wear scar area (mm ²)
ECO	0.070 ± 0.005	0.41 ± 0.11
ECO_BL	0.089 ± 0.006	0.24 ± 0.04
ECO_SD	0.083 ± 0.006	0.34 ± 0.18
ECO_OD	0.080 ± 0.006	0.23 ± 0.02
ECO_EA	0.079 ± 0.005	0.19 ± 0.08

the data collected in Table 9, similar and suitable friction coefficient values were obtained for all the formulations, displaying values only slightly higher than those shown by neat epoxidized castor oil (ECO), due to the incorporation of lignin particles into the contact which provides a larger interface for friction. A slight increase in the friction coefficient respecting the (lignin-free) ECO is an expected result in the mixed lubrication regime since the penetration of any thickener particles into the contact may also contribute to friction, as for instance previously reported for epoxidized lignin or cellulose acetate butyrate nanofibers dispersed in castor oil [22, 57].

However, the main advantage of using these dispersions of lignin fractions as lubricants lies in a significant reduction of wear produced on the steel materials in contact. Thus, when analyzing wear scar dimensions on plates, as can be seen in Fig. 8, a noticeable reduction in the wear scar size was observed, from 313 μ m average diameter when using ECO as lubricants to, for instance, 160 μ m in the case of ECO_EA samples. Although all lignin dispersions provide a significant improvement of wear, ECO_EA sample yielded the optimum results, probably due to the softer rheological



Fig. 8 Microscopy images of wear scars obtained in the steel plates when using the lignin dispersions studied as lubricants in comparison to that generated by the neat epoxidized castor oil. Values of the average wear scar diameters are also inserted

characteristics that allow this sample to easily penetrate the contact area. These results may be explained on the basis of not only the reduced viscoelastic moduli and superior relative viscous character, but also taking into consideration the minimum ash content of only 2.3% (see Table 4), which may act as abrasive foreign particles [58, 59], thus slightly increasing the ultimate wear scars, as depicted in Fig. 8. Therefore, although the incorporation of lignin residues to structure epoxidized oils may slightly increase the friction in tribological contact, their use led to a significant wear reduction, which may help to extend the service life of lubricated surfaces in tools and machinery.

4 Conclusions

Supercritical water hydrolysis of weak black liquor yielded a series of depolymerized lignin fractions (spray-dried, ovendried, and ethyl acetate extracted). Fast SCW hydrolysis prevents lignin repolymerization while promoting the depolymerization of lignin and the production of bio-polyols. These lignin fractions, as well as the non-treated waste black liquor, have been successfully tested as feasible thickening agents for castor oil by implementing a chemical crosslinking route via epoxidation. The ensuing castor oil-based formulations exhibit noteworthy physical stability, suitable appearance, characteristic shear-thinning and viscoelastic behaviors, and adequate tribological response to be proposed as potential eco-friendly semi-solid lubricants.

The viscous response of these semi-solid lubricant formulations is the result of a delicate compromise among the filling effect of the ash content, average molecular weight and polydispersity index, and the likely chemical crosslinking ability of the lignin fractions, inherently related to the available OH groups content, among which molecular weight and PDI displayed the most significant contribution.

Furthermore, despite the expected slight increase in the friction coefficient, the addition of the lignin fractions to epoxidized castor oil significantly prevent wear in the contact elements as compared to the epoxidized castor oil. In particular, the ECO_EA system, with lower viscosity, may easily favor the replenishment of the tribological contact and, combined with its minimum abrasive ash content, provides the highest wear protection.

In summary, this research not only highlights the feasibility of the SCW hydrolysis to treat pulp and paper biorefinery residues but also the tunability of the obtained lignin fractions to thicken castor oil to different extents and impart lubricating performance, depending on the depolymerization treatment and the subsequent separation stages.

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Declarations

Competing interests The authors declare no competing interests.

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