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# Lignin-enriched residues from bioethanol production: chemical characterization, isocyanate functionalization and oil structuring properties

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## Abstract

Lignin-enriched waste products from bioethanol production of agriculture residues were tested as structuring agents in castor oil once functionalized with hexamethylene diisocyanate. Cane bagasse, barley and wheat straw were processed through steam explosion, pre-saccharification and simultaneous saccharification and fermentation (PSSF). Alternatively, cane bagasse was submitted to steam explosion and enzymatic hydrolysis (EH). Several Nuclear Magnetic Resonance techniques were used to characterize both residues and NCO-functionalized counterparts. The β-O-4´/resinol/phenylcoumaran content and hydroxyphenyl/guaiacyl/syringyl distribution depend on biomass source, pretreatment, and enzymatic hydrolysis. Total hydroxyl content (from 1.23 for cane bagasse to 1.85 for wheat straw residues), aromatic/aliphatic hydroxyl ratio (0.78 for cane bagasse and 0.61 and 0.49 for barley and wheat straw residues, respectively) and S/G ratio (ranging from 0.25 to 0.86) influence the NCO-functionalization and oleogel response. Oleogels obtained with barley straw residues exhibited the highest values of the storage modulus; around $2x10^5$ Pa and $10^4$ Pa for 25% and 20% contents, respectively. PSSF process showed weaker modification, leading to softer viscoelastic response compared to EH. These oleogels exhibited rheological properties similar to lubricating greases of different NLGI grades. Therefore, we herein show an integrative protocol for the valorization of lignin-enriched residues from bioethanol production as potential thickeners of lubricating greases.

**Keywords:** Bioethanol residue, Lignin, Lubricating grease, NMR, Oleogel, Rheology

## Introduction

Nowadays, there is an increasing willingness to leverage waste materials and by-products to optimize industrial processes and, hence, mitigate the depletion of resources and expensive treatments for these non-valuable materials disposal [1]. This is the case of lignin, which is mainly produced in the paper industry where is considered a waste or low valuable by-product, and whose main use consists of direct incineration to recover some of the energy spent during the process [2]. However, as the second most abundant biopolymer on Earth, just preceded by cellulose, interest in lignin is growing fast and potential research is being carried out due to its distinctive and intriguing entangled aromatic structure and available functional groups (hydroxyl, carboxyl and carbonyl groups) [3].

Nonetheless, even for state-of-the-art bioethanol production research, lignin is still considered an undesirable product [4–6]. In addition, the conversion of lignin waste into value-added products processes will help to increase the sustainability and profitability of paper mills and bioethanol plants and, consequently will also contribute to the development of the circular bioeconomy, which aims to optimize the use and value of all raw materials, products and residues [7]. Thus, lignin has recently been used as a key component for hydrogels with drug release applications [8,9], as an additive in construction materials [10], as a nanostructured biosensor for glucose detection [11], to obtain valuable phenolic compounds [12], or to produce bio-based adhesives [13,14], among others.

On the other hand, new policies for lubricant industries are also focused on reducing non-renewable and harmful materials traditionally used in their processes and producing more environmentally friendly products. In this way, the replacement of the traditionally used mineral oils for vegetable oils has been widely investigated [15–18].

However, lubricating greases include other components, such as gelling agents, responsible for self-assembling and arranging the oil structure, as well as other minor additives, added to mould some of the required characteristics. These gelling agents, also called thickeners, are traditionally metallic soaps and polyureas [19]. Their replacement by some biomolecules, such as natural waxes [20–23], lignocellulose constituents (cellulose, lignin, and some chemical derivatives) or chitin and chitosan [24–27] has also received attention recently. However, the use of these natural sources may result in several inconveniences basically regarding physical and mechanical stability and temperature dependence, due to chemical incompatibilities derived from differences in polarity between oil and bio-thickeners [19]. In this sense, previous work has been performed aiming to reduce these negative effects by using hexamethylene diisocyanate (HDI) as a crosslinker, which plays a double role, branching of the biopolymer chain and chemical interaction between the edge-free NCO groups of the thickening agent and the vegetable oil [18,25], thus generating a chemical gel. To achieve this chemical interaction between thickener and oil, the use of castor oil is preferred as it is the only commercially available oil with hydroxyl groups in the fatty chains.

As previously reported [25], oleogel formation follows a two-step process, where the first step is the functionalization of the lignocellulosic by-product with HDI, and then the functionalized lignin-enriched residue (FL) is mixed with castor oil, where new urethane bonds are generated. However, once the process is ended, the final product is still not ready to use, as an internal curing process is experienced due to free NCO groups that are still available to react, resulting in significant changes in the rheological response [24,25]. Against this background, the present work deals with the use of diverse lignin-enriched waste products from bioethanol production to obtain suitable gelling agents, via the previous functionalization with HDI, for a castor oil medium. Several agricultural residues and different procedures for bioethanol production, i.e., barley straw, wheat straw and cane bagasse from pre-saccharification and simultaneous saccharification and fermentation (PSSF) and cane bagasse from enzymatic hydrolysis (EH), were explored and evaluated, and the resulting lignin-enriched fractions were comprehensively characterized. Barley straw, wheat straw and cane bagasse are known to be widely available, with productions of around 51, 472 & 1044 Mt per year, respectively, and average cellulose, hemicellulose and lignin contents of 37, 24 and 17% for barley straw, 39, 26 and 14% for wheat straw and 45, 29 and 24% for cane bagasse, respectively [28].

# 1. Experimental

## 1.1. Materials

Four different lignin-enriched residues from bioethanol production were tested, i.e., those from PSSF of barley straw, wheat straw and cane bagasse and that from the EH of cane bagasse (see codes for samples in Table 1). HDI, toluene and triethylamine used in the functionalization reaction were purchased from Merck (Germany). Castor oil (211 cSt at 40 °C) was obtained from Guinama (Spain). The main physical properties of this vegetable oil, as well as the fatty acid profile, can be found elsewhere [29]. Both Cellic CTec2 (cellulase) and Cellic HTec2 (xylanase) enzymatic complexes were kindly provided by Novozymes (Bagsværd, Denmark).

## 1.2. Steam explosion pretreatment

First of all, the different agricultural residues were submitted to a steam explosion pretreatment, which has been thoroughly described elsewhere [30]. This process opens up the fibres and makes the carbohydrates contained in the biomass more accessible for subsequent processes, i.e. PSSF or EH. Both temperature and residence time were adjusted thus the highest glucose recovery was obtained, i.e., 210ºC and 5 min for both wheat and barley straws (severity factor 3.93) and 190ºC and 12 min for cane bagasse (severity factor 3.72). After the steam explosion pretreatment, the materials were recovered, cooled, and filtered for solids and liquors recovery. The solid fractions were thoroughly washed obtaining the water-insoluble solid (WIS) fractions, highly enriched in lignin and cellulose. Contrary, the liquors were highly concentrated in hemicellulose, soluble lignin and sugar-degraded products (furfural, hydroxymethylfurfural, etc). The solid product was subsequently submitted to either EH or PSSF.

### 1.3. Enzymatic hydrolysis (EH)

The enzymatic hydrolysis of cane bagasse WIS fraction was accomplished by using Cellic Ctec2 and Cellic Htec2 enzymes in 90/10 ratio, 0.05 M sodium citrate buffer (pH 4.8) at 50°C, 30 FPU/g glucan, 15% (w/w) solid content and 72 h residence time. After that, the solid residue, enriched on lignin, was washed, freeze-dried and used as raw material for further functionalization. The solid content was selected taking into account that economically feasible lignocellulosic enzymatic conversion processes require high-solid contents, despite possible lower yields [31].

### 1.4. Pre-saccharification and simultaneous saccharification and fermentation (PSSF)

PSSF experiments involved a pre-hydrolysis (pre-saccharification) step of cane bagasse, wheat straw and barley straw WIS fractions using the enzyme mixture described above and an enzyme concentration, solid content and residence time which depend on the lignocellulosic feedstock, i.e., 30 FPU/g glucan, 15% (w/w) solid content and 48 h residence time for cane bagasse, 20 FPU/g glucan, 20% (w/w) and 24 h residence time for wheat straw and 25 FPU/g glucan, 25% (w/w) and 24 h residence time for barley straw. After that, the temperature was decreased to 35°C and the media was inoculated (1 g/L) with the yeast *Saccharomyces cerevisiae* Ethanol Red (Fermentis, France) [4].

Once PSSF was accomplished, the liquid fraction, enriched in bioethanol, was separated from the solid fraction, enriched on lignin. Then, the solid fraction was washed, freeze-dried and used as raw material for further functionalization.

### 1.5. Functionalization of lignin-enriched residues

The functionalization of lignin-enriched fractions followed an already-described protocol [19]. Briefly, 100 mL of toluene were added to a three-neck round-bottom flask and maintained under argon atmosphere for 30 min to eliminate all moisture. After that, lignin-enriched residues and diisocyanate (in 1/2 lignin/HDI w/w ratio) were added and stirred vigorously for 24 h, using triethylamine as a catalyst (1/1 HDI/catalyst w/w ratio). Residual toluene and triethylamine were eliminated through evaporation under vacuum using a rotatory evaporator. Afterwards, the isocyanate functionalized lignin-enriched residue was immediately used for oleogel formation and characterisation. The different functionalized lignins were named as FL followed by the lignin-enriched residue code (see Table 2).

### 1.6. Preparation of oleogels

The functionalized lignin-enriched fractions were poured into a 100 mL stainless-steel reactor containing the castor oil, at 20-25% w/w concentration, and stirred for 24 h using an anchor impeller coupled to a RW 20 (IKA, Germany) stirrer, at 70 rpm. Oleogels will be referred to as O followed by the lignin-enriched residue code and thickener concentration. For instance, OCEH25 means the oleogel containing functionalized CEH as thickener and 25% concentration.

### 1.7. Lignin-enriched residues composition

The compositional analysis of the diverse lignin-enriched residues studied was performed by following NREL standard methods, i.e., preparation of samples for compositional analysis (NREL/TP-510-42620), cellulose, hemicellulose and lignin content evaluation (NREL/TP-510-42618), and determination of ashes concentration (NREL/TP-510-42622).

### 1.8. Thermogravimetric analysis (TGA)

Lignin-enriched residues and the NCO-functionalized counterparts were analysed by TGA. Mass loss profile as a function of temperature was obtained using a Q-50 model (TA instrument Waters, USA). A constant rise of 10ºC/min from room temperature up to 600ºC was applied under $N_2$ atmosphere.

### 1.9. Fourier transform infrared spectroscopy (FTIR)

Lignin-enriched residues, the NCO-functionalized counterparts and resulting oleogels were subjected to FTIR analysis. FTIR spectra were obtained using a JASCO FT/IR 4200 (Jasco inc. Japan), measured within the wavenumber range of 400-4000 cm$^{-1}$ at 4 cm$^{-1}$ resolution. The spectra of lignin-enriched residues were acquired from lignin/KBr disks, with 1/10 w/w lignin/KBr content. On the contrary, functionalized lignins and oleogels were measured placing the sample between two KBr disks of 32 mm diameter and 3 mm thickness.

### 1.10. Nuclear magnetic resonance spectroscopy (NMR)

Lignin-enriched and resulting NCO-functionalized lignin-enriched residues were analysed by NMR spectroscopy. Acetylation of lignin-enriched residues was accomplished by following a protocol described elsewhere [32]. Briefly, 2 g of lignin samples were poured into a round bottom vessel with equal volumes of both pyridine and acetic anhydride (8 mL each) and stirred vigorously at room temperature. After 48 h, the acetylated lignin-enriched residue was precipitated by adding 1% HCl solution at 0ºC. The solid obtained was washed, filtered and dried overnight in an oven at 40ºC.

Both $^{1}H$ NMR & $^{13}C$ NMR and two-dimension (2D NMR) spectra were obtained using a Bruker Avance III 500 MHz. The solvent selected was DMSO-$d_6$. The operational conditions were described elsewhere [33].

### 1.11. Rheological characterization

Rheological characterization of oleogels was carried out in an ARES (Rheometric Scientific, U. K.) controlled-strain rheometer, equipped with a 25 mm rough plate-plate geometry and 1 mm gap. Small-amplitude oscillatory tests (SAOS) from 100 to 0.03 rad/s, in the linear viscoelastic regime, were performed. The linear viscoelastic regime was previously determined through strain amplitude sweeps. Viscous flow measurements were carried out by applying an increasing stepped shear rate ramp from 0.01 to 100 $s^{-1}$. The viscous flow curves obtained were fitted to the power-law model equation [34]:

$$\eta = K \cdot \dot{\gamma}^{n-1} \qquad (1)$$

where η and $\dot{\gamma}$ refer to the apparent viscosity and the shear rate applied, whilst $K$ and $n$ are the consistency and flow indexes, respectively. For all tests, a fresh sample was used and each measurement was replicated at least twice.

## 2. Results and discussion

### 2.1. Chemical characterization of non-modified and isocyanate-functionalized lignin-enriched residues

### 2.1.1. *Lignin-enriched residues composition*

The composition of lignin-enriched residues, obtained from both PSSF and EH processes, is included in Table 1. During the steam explosion, water at high temperature and pressure cause an autocatalyzed cleavage of glycosidic bonds in hemicelluloses and lignin-hemicellulose linkages [35]. This, along with the production of acetic acid from acetyl groups, facilitates the removal of hemicelluloses from the plant cell wall, making cellulose more accessible to hydrolytic enzymes [35]. Nevertheless, depending on the biomass source, the severity factor of the steam explosion pretreatment, the solid content and the different enzyme dosages, i.e., cellulase (Cellic CTec2) and xylanase (Cellic HTec2) used for the subsequent enzymatic hydrolysis and PSSF, different carbohydrates content remaining in the lignin-enriched residues could be observed. Then, cellulose was still broadly present, varying from 11.0 to 25.8 % w/w content, while almost complete elimination of the whole hemicellulose was achieved. These results also demonstrated EH to be able to digest lignocellulosic biomass at a superior level for cane bagasse, leading to both lower hemicellulose and cellulose content than the PSSF process. The presence of carbohydrates in the lignin-enriched residues may be beneficial in the functionalization reaction with HDI as an additional source of hydroxyl groups, as well as in oleogel formation [27,33].

### 2.1.2. *Thermogravimetric analysis (TGA)*

Fig. 1 shows TGA curves for the lignin-enriched residues and the NCO-functionalized counterparts. For a better comparison, each thermal event was described according to the temperature at the beginning of each thermal degradation event ($T_{onset}$), temperature related to maximum derivative weight loss ($T_{max}$), final temperature ($T_{final}$) and weight loss ($\Delta W$). These parameters as well as the final residue content at the end of the test are included in Table 2.

As can be observed in Fig. 1a, all lignin-enriched residues exhibited similar characteristics, i.e., an initial moisture loss (around 3-4 wt.%), a weak hydroxyl group dehydration starting at 165ºC and the main weight-loss centred at 345-366ºC, as a consequence of several linkages breakage [36]. The main weight loss was slightly influenced by the lignin source. While lignin-enriched residues from wheat and barley straws presented very similar weight loss values, lignin-enriched residues from cane bagasse showed higher values. Furthermore, lignin-enriched residues from EH of steam-exploded cane bagasse again demonstrated a stronger modification, achieving higher weight loss in the main degradation event and therefore lower final residue value.

The different NCO-functionalized lignin-enriched residues, according to their different origin, exhibited completely different thermal behaviour too, as shown in Fig. 1b. The first thermal event assigned to unreacted diisocyanate content takes place around 120-150ºC. FLCEH showed the highest weight loss of isocyanate (37%), followed by FLWF (36%), FLCF (28%) and finally FLBF (23%). The higher concentration of free diisocyanate in functionalized cane bagasse residue from enzymatic hydrolysis may be due to the lower hydroxyl content and a higher proportion of syringyl units, as described below, thus hindering the reaction because of the steric impedance consequence of methoxyl groups at both sides of the hydroxyl moiety. However, this fact could be only observed in FLCEH, demonstrating FLCF an intermediate behaviour. The four functionalized lignin-enriched fractions also present an additional degradation event at around 250ºC, which may be a consequence of thermally unstable urethane linkages [37–39], being both straws the ones with the lowest weight losses in this. Peaks appearing at around 309-336ºC represent the degradation of the main lignin structure observed in non-functionalized samples, while the last peak at around 450ºC is a consequence of the hard segments resulting from the crosslinking reaction, as has been reported in previous work [24,25], confirming that appropriate reaction has been carried out. As a result, those samples with higher free-diisocyanate content after functionalization reaction also presented a lower degree of crosslinking, i.e., lower weight loss in the last event [40]. The differences shown between FLCF and FLBF may be a consequence of even more stable structures generated by a higher crosslinking degree at upper temperatures in the case of FLBF, which is also supported by the higher final residue value.

### *2.1.3. Fourier-transform infrared spectroscopy (FTIR)*

The different non-modified and functionalized lignin-enriched residues and derived oleogels FTIR spectra were very similar among them, as similar functional groups and structures are present (data not shown). As with other lignin fractions from non-woody plants, lignin FTIR spectra from these agriculture residues contain the typical bands centred at around 1330-1320 cm$^{-1}$, 1263-1271 cm$^{-1}$ and 833 cm$^{-1}$, assigned to syringil (S), guaiacyl (G) and H units, respectively [41,42]. Nonetheless, the FTIR technique also let us confirm the successful formation of urethane linkages after functionalization and the subsequent formation of the chemical oleogel, which was demonstrated by the appearance of several absorption peaks (see Fig. S1 in the Supporting information). As well-known, absorption bands centred at around 3400 and 3330 cm$^{-1}$ are due to O–H and N–H stretching vibrations, respectively. As expected, no N–H absorption peak was observed for the lignocellulosic residues, only showing a clear wide O–H absorption peak. However, once functionalization was achieved, and further, after oleogel formation, an important reduction in the O–H absorption intensity, in detriment of N–H formation, was clearly observed. A second peak confirming urethane formation is that observed at 1570 cm$^{-1}$, a consequence of the in-plane N–H bending vibration, which was observed in both functionalized samples and oleogels. A third one was related to free isocyanates, depicted at around 2270 $cm^{-1}$. As can be seen, functionalization provides the lignin-enriched residues with significant amounts of free isocyanate moieties. However, after the curing process, oleogels do not show any significant absorption band corresponding to free isocyanate, indicating the crosslinking reaction has taken place completely. Finally, C=O groups generate two observable absorption bands at around 1740 and 1710-1635 $cm^{-1}$ for unconjugated and conjugated bonds respectively, the last ones related to urethane and urea formation and consequent H-bonding [43]. The potential increase in conjugated bonds appearing after lignin functionalization demonstrated once again the urethane and urea formation. This peak was also observed in oleogels, however, unconjugated bonds were significantly higher, as a consequence of the remaining non-crosslinked C=O groups of castor oil.

### *2.1.4. Nuclear magnetic resonance analysis*

The $^{1}H$ NMR technique was used to identify the relative content of the monolignol units in analysed lignin-enriched residues (see Fig. S2 in the Supporting Information). The diverse aromatic protons signals, which were found within the range of 8-7.43 for *p*-hydroxyphenyl (H), 7.43-6.70 for guaiacyl (G) and 6.70-6.28 for syringyl (S) units [44], let quantitative relationships among these three units to be assessed. The S/G ratios obtained by using this technique demonstrated S units to be much more concentrated on cane bagasse lignin samples than both straw lignin samples, confirming what was mentioned above (see Table 1). Moreover, always a low content of H units was obtained, as expected (data not shown).

On the other hand, regarding acetylated lignin-enriched residues, both hydroxyl content and aromatic/aliphatic OH ratio have been determined and displayed in Table 1. Aliphatic and aromatic hydroxyl groups are known to be directly correlated to acetyl groups formed, leading to signals appearing between 1.5-2.1 and 2.1-2.4 ppm, respectively [45]. To obtain the total hydroxyl content, the whole quantity of both aliphatic and aromatic hydroxyl groups was relativized to C9 units [45]. As can be seen, total hydroxyl content was higher for both lignin-enriched residue straws, while similar hydroxyl content was obtained regardless of the treatment for cane bagasse.

$^1$H NMR spectra were also conducted to functionalized lignins (see Fig. 2). Along with the low signals previously identified for monolignols, new incipient peaks were also found, centred around 7.26-7.13 ppm. Wheat straw peaks were displaced to 7.39-7.32 ppm. These peaks are a consequence of the diverse lignin units bearing a urethane group [33,46]. The following peaks, observed between 5.76-4.03 ppm, were attributed to branching and linear chains where urethane groups were present [46], but also to urea protons, which can be a consequence of the air present within the vessel and long storage time, generally centred around 5.08, 4.96, 4.20 and 4.04 ppm, but with displacements due to the complex interactions [47].

In the same way as crude lignin-enriched residue, methoxyl groups along with aliphatic hydrogens were present. Nonetheless, between these two regions where previously no peaks had been observed, now several signals were detected, probably because of the H-bonds and other secondary interactions of urethane and urea groups with linear chains, thus increasing the chemical shifts usually observed by those aliphatic hydrogen atoms, as already seen in other polyurethane-based systems [47,48]. Moreover, the aliphatic hydrogens were able to reach extremely high values, up to 3 ppm even in some cases, probably because of the small hexamethylene chain which can be highly influenced.

$^{13}$C NMR technique is a powerful tool to discern the strongest C units within the lignin structure, as shown in Figs. S3 & S4 (Supporting Information). Different regions can be normally distinguished, carboxyl and carbonyl carbon atoms from 200 to 160 ppm, quaternary and aromatic ones from 160 to 100 ppm and the third region of aliphatic carbons, divided into two smaller ranges, from 100 to 55 ppm, corresponding to carbons joined to oxygen atoms and from 55 to 10 ppm, related to non-oxygenated saturated carbons [49]. The first of the regions did not include any visible peak, due to the low concentration of those groups [49]. On the other hand, the second region did show several important signals. Two peaks concerning $C_3/C_5$ of syringyl moieties were observed at 152.7 and 147.9 ppm [50], the last one also coincident with $C_3/C_4$ of guaiacyl units [51]. Really weak signals regarding $C_1$ and $C_4$ of etherified syringyl and $C_1$ of guaiacyl moieties were shown at 135.0 ppm [51,52]. $C_2/C_6$ in esterified *p*-coumaric acid are weakly present at 130.2 ppm but for BF [52], whilst $C_3/C_5$ of the same unit together with $C_5$ units of guaiacyl can be found at 115.4 ppm [50–52], again much weaker for BF, demonstrating *p*-coumaric acid to be low concentrated or non-existent for this straw kind. On the other hand, at 104.1 ppm, another significant peak consequence of $C_2/C_6$ in syringyl units is shown [51,53]. Within the last region, a prominent peak at 55.91 ppm due to $OCH_3$ in syringyl and guaiacyl units appears. Finally, at 28.97 ppm, β-methylene units of n-propyl side chains are observed [52,53].

Functionalized lignin-enriched residue samples were also characterized by this technique, where several important facts were observed. The first of them is that only one new clear peak centred around 128.77 ppm appeared in the new spectra (data not shown) because of the low solubility, regardless of the sample. This peak was related to $C_4$ atoms linked to urethane groups [54]. Nonetheless, the remaining peaks for $^{13}C$ NMR spectra considering both lignin and lignin-based polyurethane were generally maintained as demonstrated in the literature [49].

With the techniques previously mentioned, the main monolignols of analysed lignins have been elucidated and even some relationships have been obtained. However, there is still a lot of information missed, as how these monolignols are bonded or other possible structures are still unknown. For that reason, 2D NMR is addressed as it represents an excellent tool for untangling the complex lignin structure [55]. The 2D HSQC spectra of lignin-enriched residues include three diverse regions according to aliphatic (between $\delta_C/\delta_H$ 0–50/0–4.5 ppm), oxygenated aliphatic (around $\delta_C/\delta_H$ 50–95/2.6–5.6 ppm) and aromatic (around $\delta_C/\delta_H$ 95–150/5.6–9.0 ppm) units. The 2D-spectra of BF, WF, CF and CEH raw lignin-enriched residues can be seen in Fig. 3.

Within the aliphatic region, several bands around $\delta_H$ 0.8-1.45 appeared, as a consequence of extractives, principally lipids, which may be chemically linked to the lignin structure. Together with those signals, other bands between $\delta_H$ 1.9-2.8 and $\delta_C$ 20.6-44.1, due to aliphatic groups next to alkenes and oxygen-containing moieties such as ethers, carbonyls and alcohols, originated from degraded lignin products, were present [55,56].

For the oxygenated aliphatic and aromatic regions, Table 3 summarises the main bands observed according to those previously detailed in the literature [55,57,58]. The main substructures elucidated are displayed in Fig. 4 [55,59].

In the oxygenated aliphatic region, correlation signals from methoxyl groups and side chains in β-O-4′ substructures (A) were the commonly observed signals in all lignin spectra, being the methoxyl group signal observed at $\delta_C/\delta_H$ 55.4/3.72 the most prominent one. β-O-4′ substructures included correlations of $C_\alpha$–$H_\alpha$ for β-O-4´ G and S lignin units ($A_\alpha$) in all lignin spectra; $C_\beta$–$H_\beta$ for β-*O*-4´ G and S units ($A_\beta$) in lignin spectra from barley straw and wheat straw; and $C_\gamma$–$H_\gamma$ ($A_\gamma$) in all lignin spectra together with a signal tentatively assigned to $C_\gamma$–$H_\gamma$ of γ-acylated β-O-4´ ($A'_\gamma$) (arising from *p*-coumarates acylating the γ-position of the lignin side chain) [57] in lignin spectra from wheat straw and cane bagasse (both EH and PSSF). Signals for resinol (β-β´), comprising correlations of $C_\alpha$–$H_\alpha$ ($B_\alpha$), $C_\beta$–$H_\beta$ ($B_\beta$) and the double $C_\gamma$–$H_\gamma$ ($B_\gamma$) were observed in lignin spectra from barley straw and wheat straw. Meanwhile, phenylcoumaran signals including correlations of $C_\alpha$–$H_\alpha$ ($C_\alpha$), $C_\beta$–$H_\beta$ ($C_\beta$) and $C_\gamma$–$H_\gamma$ ($C_\gamma$) were also found in lignin spectra from barley straw and wheat straw and in a lesser extent in the lignin spectrum of cane baggase (PSSF).

Signals for sugars were also observed in the oxygenated aliphatic region of all lignin-enriched residues spectra, according to the carbohydrates content previously described. These signals included mainly correlations of xylan chain for $C_2$–$H_2$ ($X_2$), $C_3$–$H_3$ ($X_3$), $C_4$–$H_4$ ($X_4$), and $C_5$–$H_5$ ($X_5$). Moreover, the C-1 cross peak for (1-4) β-D-xylopyranosyl of xylan was observed in wheat straw and cane baggase (EH) lignins, the C-1 cross peak for (1-4), β-D-Glcp from cellulose was found in wheat straw and barley straw lignins, and the reducing end of (1-4) α-D-Xylp was showed in wheat straw and barley straw lignin-enriched residue.

In the aromatic region of the all lignin-enriched residue spectra, the main correlation signals correspond to aromatic rings of the syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) lignin units, respectively, according to FTIR, $^1$H NMR and $^{13}$C NMR experiments. The S lignin units showed correlations of $C_{2,6}$–$H_{2,6}$ ($S_{2/6}$) and $C_{2,6}$–$H_{2,6}$ in S units bearing a ketone group in $C_\alpha$ ($S'_{2/6}$). On the other hand, the G lignin units exhibited different correlations for $C_2$–$H_2$ ($G_2$), $C_5$–$H_5$ ($G_5$), and $C_6$–$H_6$ ($G_6$). Finally, the H lignin units displayed correlations of $C_{3,5}$–$H_{3,5}$ ($H_{3/5}$) and $C_{2,6}$–$H_{2,6}$ ($H_{2/6}$). Prominent signals corresponding to *p*-coumarate (PCA) and ferulate (FA) substructures were also found in all lignin spectra, typical of non-woody plants [55,57,58,60]. Cross signals of the *p*-coumarates corresponding to the $C_{2,6}$–$H_{2,6}$ and $C_{3,5}$–$H_{3,5}$ of the aromatic ring and signals for the correlations of the unsaturated $C_\alpha$–$H_\alpha$ and $C_\beta$–$H_\beta$ were observed. Signals corresponding to the $C_2$−$H_2$ and $C_6$−$H_6$ correlations of ferulate substructures were also elucidated, especially in wheat and barley straw lignin-enriched residues. Regarding the correlations corresponding to the unsaturated $C_\alpha$–$H_\alpha$ and $C_\beta$–$H_\beta$ of ferulates overlapped with those of the *p*-coumarates, *p*-coumarates are esterified to the lignin side chain [57], as it is shown in the oxygenated aliphatic region of wheat straw and cane bagasse spectra, with a signal corresponding to the correlations of γ-acylated β-O-4′ substructures with *p*-coumarates. On the other hand, ferulates are mostly linked to lignin by ether bonds, mainly at the α- and β-carbons contributing to lignin-carbohydrate bridges [55]. Finally, the wheat straw lignin-enriched residue spectrum showed cross signals corresponding to tricin (T, 5,7,4′-trihydroxy-3′,5′-dimethoxyflavone). Tricin is widely distributed in grasses linked to a phenylpropanoid moiety through a β-O-4′ bond, which may be incorporated into the lignification of plants, acting as lignin monomers [60].

Table 4 shows the abundance of lignin substructures (per 100 aromatic units) and aromatic units (molar percentage), as well as S, G & H relative content of the lignin-enriched residues studied, obtained from the volumetric integration of the different $^1$H-$^{13}$C contours [55,61]. In addition to the hemicellulose removal produced during steam explosion pretreatment, it is well known that under this treatment conditions, β-O-4′ bonds of lignin are also cleaved by the organic acids formed from the acetylated lignocellulose components [35,62,63]. Even the subsequent enzymatic hydrolysis of the steam pretreated material again cleaves acetates [63], which can again act on lignin. Despite β-O-4′ bond degradation during the steam explosion and subsequent enzymatic hydrolysis reported in the literature, the semi-quantitative HSQC spectra results still showed a content of β-O-4´ substructures for wheat straw lignin (29.1 linkages per 100 aromatic units), barley straw lignin (16.2 linkages per 100 aromatic units), cane bagasse lignin from PSSF (12.8 linkages per 100 aromatic units) and cane bagasse lignin from EH (10.6 linkages per 100 aromatic units). Regarding other substructures, barley and wheat straw lignins still showed significant resinol and phenylcoumaran contents (Table 4), while cane bagasse lignin from PSSF only exhibited 4.3 linkages per 100 aromatic units of phenylcoumaran.

In agreement with the above $^1$H NMR experiments, HSQC quantification confirmed the higher S/G ratios for cane bagasse lignins (also included in Table 1) (1.7 from enzymatic hydrolysis and 1.5 from PSSF) compared to wheat straw lignin (1.0) and barley straw lignin (0.9). In addition, higher content of H units was also observed for cane bagasse lignins (18.6% and 17.9% for cane bagasse lignins from HE and PSSF, respectively) compared to wheat straw lignin (4.9%) and barley straw lignin (2.1%). Different changes in the *p*-hydroxyphenyl/guaiacyl/syringyl distribution during the bioethanol production have also been described by several authors. Yelle et al. [63] have suggested that no transformation of lignin aromatics of agriculture residues is produced during bioethanol production, while Heikkinen et al. [64] have reported a substantial decrease in the S/G ratio. Thus, the variability of the content of β-O-4´, resinol and phenylcoumaran substructures as well as hydroxyphenyl/guaiacyl/syringyl distribution depend on the biomass source, the severity of steam explosion pretreatment conditions, and subsequent enzymatic hydrolysis alone or integrated into a PSSF process.

Functionalized lignin-enriched residue HSQC spectra generate poor signals (data not shown), however, some remarkable facts can be observed. Two new areas, centred around 128.12/7.25 and 128.8/7.18 ppm appeared consequence of the functionalization, attributed to guaiacyl units close to urethane bonds [33]. Moreover, bands due to branched and linear chains close to urethane bonds, but in the oxygenated area, were faintly observed too, including methoxy units. More clearly and stronger, aliphatic moieties were observed between 60-0/3.5-0 ppm. First and second methyl units after ether linkage of urethane bonds were found to be present around 61.60/4.14 and 23.76/1.51 ppm, respectively, only for FLWF and FLCEH. For the same functionalized lignins, methyl units joined to carboxyl groups were slightly depicted around 62.30/3.34 ppm [65]. Apart from those peaks, several others concerning aliphatic moieties were also present.

### 2.2. Rheological characterization of functionalized lignin-enriched residues-based oleogels.

Fig. 5 displays the mechanical spectra obtained from SAOS measurements inside the linear viscoelastic range (a, b, c) and the viscous flow curves (d, e, f), for oleogels containing functionalized lignin-enriched residues as a function of the treatment applied to cane bagasse and the origin of the lignin-enriched residue treated with PSSF, i.e. barley straw, wheat straw and cane bagasse. As can be seen, the linear viscoelastic response is qualitatively similar for all the oleogels studied. The values of the storage modulus, G’, are higher than those found for the loss modulus, G”, in the whole frequency range studied, with a relatively low slope of the G’ versus frequency plot and a tendency to reach a crossover between both SAOS functions at high frequencies, especially for a 20% w/w concentration of the lignin fraction. Stronger gel response was obtained when using 25% w/w concentration, with even lower slopes of G’ and G” vs frequency plots. This behaviour is concordant with the definition given by Almdal et al. [66] for solid-like gels and has already been reported for gel-like systems using commercial lignin as a precursor and varying HDI and castor oil content [36], or also by modifying the precursor [24].

Oleogels obtained using cane bagasse-derived functionalized lignin-enriched residues from PSSF and EH processes were rheologically compared by SAOS tests (see Fig. 5a). Thus, oleogels containing 20% functionalized lignin-enriched residues (OCH20 and OCF20) exhibited almost no difference, whereas at 25% concentration the oleogel containing the lignin fraction from EH presented higher viscoelastic functions (increments of around 0.1-0.4x$10^4$ Pa). This result was unexpected, as cellulose content in CF was higher, which would have been responsible for increasing viscoelastic moduli, as seen in previous studies [67,68]. Nonetheless, in such similar residues, where both the hydroxyl content and the aromatic/aliphatic ratio are identical, these results must be attributed to the higher relative content of $\beta$-*O*-4´ substructures in the CEH lignin fraction (100%), as no resinols or phenylcoumarans are traceable by NMR in this sample (see Table 4). These structures, without hydroxyl groups (see Fig. 4), are not present in significant quantity, favouring the homogeneity and the crosslinking extent when reacting with HDI. Besides, viscoelastic response achieved for oleogels with 25% (w/w) is very similar to that obtained for NLGI 1-2 grade commercial lubricating greases, typically showing G’ values of $10^4$–$10^5$ Pa, and G’’ around one order of magnitude lower. Instead, the values of SAOS functions obtained with 20% lignin, correspond to softer lubricating greases of NLGI 0-1 grade. As well known, the NLGI grade of traditional lubricating greases is modulated by modifying the thickener concentration [69]. Thus, a wide range of different lubricating grease products could be simply covered by the selection of different resources or processing protocols for bioethanol production.

Regarding the viscous flow properties shown in Fig. 5d, oleogels again demonstrated the typical response of lubricating greases, as a well-marked shear-thinning behaviour was always depicted. However, the stronger oleogels led to sample ejection at relatively low shear rates. For all the oleogels, the values of the power-law model fitting parameters were included as an inset in Fig. 5. Higher *K* values indicate more viscous systems whereas lower *n* values imply more shear-thinning characteristics. As shown in Fig. 5d, regardless of the thickening agent concentration, CEH-based gels exhibited higher *K* values extremely low values of *n*.

On the other hand, Figs. 5b and 5c display the SAOS tests for oleogels formulated with 20 and 25% w/w, respectively, of the three different functionalized lignin-rich residues i.e., barley straw, wheat straw and cane bagasse, obtained from the PSSF treatment. As can be appreciated, noticeable differences among them were found. Independently of the thickener concentration, OBF samples always displayed the highest viscoelastic moduli, whereas OCFs showed the lowest ones, with OWFs showing an intermediate behaviour. These differences can be explained attending to several structural parameters: i) the higher values of the total hydroxyl content, immediate responsible for the crosslinking, ii) the lower S/G ratio, as G provides less steric impediments for reacting compared to S. In this sense, Antonino et al. [70] have recently studied the reactivity of lignin hydroxyl groups towards diisocyanates, either aliphatic hydroxyl groups or aromatic ones present in syringyl and guaiacyl units. They observed a complete reaction of aliphatic hydroxyl groups together with a higher reactivity of aromatic hydroxyl groups from guaiacyl units compared to those from syringyl units. This trend of lignin phenolic hydroxyl groups is related to steric hindrance effects [71], showing a more pronounced steric hindrance effect the two methoxy groups adjacent to phenolic groups of syringyl units compared to the one methoxy group adjacent to phenolic groups of guaiacyl units. And finally, iii) the higher aromatic/aliphatic ratio of cane bagasse, which may lead to lower reactivity, as aliphatic hydroxyl groups are known to be more reactive to diisocyanates [70]. Moreover, the number of unstable urethane bonds was much higher in FLCF, as well as the lower final residue value, indicating a lower level of crosslinking. Between both straws, the difference may lie in the total hydroxyl content, higher for barley straw, and lower S/G ratio, which favoured urethane formation and a higher entangled system to be created despite the lower relative β-*O*-4´ linkages (see Table 4). Therefore, as reported for other lignin-based products [8,10,34], the importance of the structure-property relationship is particularly relevant.

Regarding thickener concentration, it is well apparent that oleogels containing 20% w/w thickener exhibited a weaker gel-like behaviour. *K* values obtained from the viscous flow curves correlate with the G’ and G” values, whereas *n* values are almost identical for all the lignin fractions and decreased by increasing the thickener concentration. Moreover, the influence of the lignocellulosic raw material was again much more evident when comparing 25% oleogels (see Fig. 5f). Sample ejection due to fracture at moderate shear rates was also noticeable for 25% oleogels. However, expelling took place at higher shear rates for both straws-derived thickeners as compared to the cane bagasse-derived lignin.

## 3. Conclusions

Different lignin sidestreams from bioethanol production were successfully functionalized with HDI and applied as thickening agents in a castor oil medium aiming to produce chemical oleogels for lubricant applications. The different lignin-enriched fractions evaluated were obtained from cane bagasse, barley and wheat straw processed through pre-saccharification and simultaneous saccharification and fermentation (PSSF) and, alternatively, from cane bagasse submitted to enzymatic hydrolysis (EH). Several parameters obtained from a comprehensive chemical characterization of the lignin-enriched fractions, including total hydroxyl content (1.23 for cane bagasse, 1.85 for barley straw and 1.72 for wheat straw residues), aromatic/aliphatic hydroxyl ratio (0.78 for cane bagasse, 0.61 for barley straw and 0.49 for wheat straw residues) and S/G ratio (0.86 for cane bagasse treated by EH, 0.76 for cane bagasse treated by PSSF, 0.25 for barley straw and 0.53 for wheat straw residues) demonstrated to influence the oleogel rheological response. Therefore, a variety of rheological behaviours could be covered by modifying the biosource and the concentration of the resulting isocyanate-functionalized thickening agent, achieving similar rheological properties to those found in commercial lubricating greases, for instance G' values of around $10^4$-$10^5$ Pa within the frequency range studied. The higher hydroxyl content and lower S/G ratio in barley straw led to the highest viscoelastic functions (G' values around $2x10^5$ Pa and $10^4$ Pa for oleogels with 25 and 20% NCO-functionalized residue content, respectively). On the other hand, lignin fractions obtained from both straws also yielded higher viscoelastic moduli than those obtained from cane bagasse, as a consequence of the lower S/G ratio, higher hydroxyl content and lower aromatic/aliphatic ratio, which resulted in the generation of highly-crosslinked units. When comparing the two different treatments for the production of bioethanol from cane bagasse, it was observed that EH was able to deeply degrade the lignin obtained, as deduced from the only traceable presence of β-*O*-4´ linkages, despite the similar hydroxyl content and aromatic/aliphatic hydroxyl ratio. This more severe process enhanced the strength of the resulting oleogel, mainly at 25% thickener concentration, yielding G' increments of around $0.4$-$0.8x10^4$ Pa. Overall, this study shows a comprenhensive characterization of lignin-enriched residues which allows to elucidate the slight differences observed in NCO-functionalization and subsequent oleogel formation, as well as the resulting rheological behaviour. These novel lignin-based oleogel formulations show the appropriate rheological properties to be proposed as alternative eco-friendly lubricating greases for different applications depending on the achieved consistency, thus showcasing a valorisation pathway for lignin-enriched waste from bioethanol production as a potential thickener for lubricants.

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## Tables

**Table 1.** Composition of lignin-enriched residues, S/G ratio, aromatic/aliphatic hydroxyl ratio and total hydroxyl content obtained from NMR.

| Biomass | Cellulose (%) | Hemicellulose (%) | Lignin (%) | Ashes (%) | S/G ($^1$H NMR) | S/G (2D NMR) | $OH_φ/OH_{al}$ ($^1$H NMR) | Total hydroxyl content |
|---|---|---|---|---|---|---|---|---|
| Enzymatic Hydrolysis Cane Bagasse (CEH) | 14.0±0.4 | 1.0±0.2 | 68.0±0.3 | 14.0±0.1 | 0.86 | 1.7 | 0.78 | 1.23 |
| Fermented Cane Bagasse (CF) | 25.8±0.3 | 3.6±0.9 | 56.3±1.1 | 11.4±0.2 | 0.76 | 1.5 | 0.78 | 1.23 |
| Fermented Barley Straw (BF) | 17.2±0.6 | 0.9±0.1 | 69.6±0.4 | 9.2±0.2 | 0.25 | 0.9 | 0.61 | 1.85 |
| Fermented Wheat Straw (WF) | 11.0±0.2 | 6.7±0.2 | 61.9±1.4 | 8.2±0.1 | 0.53 | 1.0 | 0.49 | 1.72 |

**Table 2.** TGA parameters for raw materials and functionalized lignin-enriched residues.

| Sample | $T_{onset}$ (ºC) | $T_{max}$ (ºC) | $T_{final}$ (ºC) | ΔW (%) | Residue (%) |
|---|---|---|---|---|---|
| CEH | 27/310/542 | 28/366/564 | 58/380/577 | 3/72/4 | 21 |
| CF | 26/285 | 28/360 | 63/375 | 4/60 | 36 |
| BF | 26/271 | 35/345 | 60/368 | 4/54 | 42 |
| WF | 30/266 | 37/351 | 53/370 | 3/52 | 45 |
| FLCEH | 129/221/309/355/427 | 157/244/327/369/447 | 175/260/334/386/480 | 37/15/15/14/9 | 10 |
| FLCF | 134/231/315/424 | 161/245/336/449 | 183/263/362/480 | 28/17/27/15 | 14 |
| FLBF | 92/214/283/406 | 120/248/309/438 | 132/255/332/475 | 23/9/32/14 | 22 |
| FLWF | 99/211/290/409 | 135/241/313/439 | 150/250/335/475 | 36/9/27/11 | 17 |

**Table 3.** Main structures found within the oxygenated aliphatic and aromatic regions of 2D HSQC for the lignin-enriched residues studied.

| $\delta_C/\delta_H$ (ppm) | Assignment | $\delta_C/\delta_H$ (ppm) | Assignment |
|---|---|---|---|
| 53.5/3.47 | $C_\beta$ –$H_\beta$ in phenylcoumaran substructures (C) | 104.3/6.70 | $C_{2,6}$–$H_{2,6}$ in S units (S) |
| 54.0/3.07 | $C_\beta$ –$H_\beta$ in resinol substructures (B) | 104.5/7.34 | $C_{2´}$–$H_{2´}$ and $C_{6´}$–$H_{6´}$ in tricin (T) |
| 56.3/3.75 | C-H in methoxyls (MeO) | 107.1/7.21 | $C_{2,6}$–$H_{2,6}$ in oxidized (Cα=O) S units (S´) |
| 60.1/3.78-3.36 | $C_\gamma$–$H_\gamma$ in β-O-4´ substructures (A) | 111.2/6.95 | $C_2$–$H_2$ in G units (G) |
| 61.6/4.1 | $C_\gamma$–$H_\gamma$ in cinnamyl alcohol end groups (I) | 111.4/7.31 | $C_2$–$H_2$ in ferulate (FA) |
| 63.7/4.34 | $C_\gamma$–$H_\gamma$ in β-O-4´ substructures (A´) | 114.2/6.26 | $C_\beta$–$H_\beta$ in p-coumarate (PCA) and ferulate (FA) |
| 72.4/4.85 | $C_\alpha$–$H_\alpha$ in β-O-4´ linked to a S type unit (A) | 115.7/6.62 | $C_{3,5}$–$H_{3,5}$ in p-hydroxybenzoate (PB) |
| 71.5/3.77-4.18 | $C_\gamma$–$H_\gamma$ in resinol substructures (B) | 115.9/6.6-6.8 | $C_5$–$H_5$ in G units (G), $C_{3,5}$–$H_{3,5}$ in p-hydroxyphenyl (H) & $C_3$–$H_3$ and $C_5$–$H_5$ in p-coumarate (PCA) |
| 72.0/4.75 | $C_\alpha$–$H_\alpha$ in β-O-4´ linked to a G type unit (A) | 119.3/6.77 | $C_6$–$H_6$ in G units (G) |
| 84.1/4.32 | $C_\beta$ –$H_\beta$ in β-O-4´ linked to a G type unit (A) | 123.7/7.13 | $C_6$–$H_6$ in ferulate (FA) |
| 85.6/4.63 | $C_\alpha$–$H_\alpha$ in resinol substructures (B) | 129.3/7.16 | $C_{2,6}$–$H_{2,6}$ in p-hydroxyphenyl (H) |
| 86.5/4.18 | $C_\beta$ –$H_\beta$ in β-O-4´ linked to a S type unit (A) | 130.6/7.51 | $C_2$–$H_2$ and $C_6$–$H_6$ in p-coumarate (PCA) |
| 87.7/5.45 | $C_\alpha$–$H_\alpha$ in phenylcoumaran substructures (C) | 145.2/7.51 | $C_\alpha$–$H_\alpha$ in p-coumarate (PCA) and ferulate (FA) |
| 92.6/4.92 | (1→4)-linked α-D-xylopyranosyl units | 72.5/3.16 | X2 |
| 97.4/4.28 | (1→4)-linked β-D-xylopyranosyl units | 74.4/3.31 | X3 |
| 98.9/6.23 | $C_6$–$H_6$ in tricin (T) | 75.7/3.66 | X4 |
| 103.0/4.44 | (1→4)-linked β-D-xylopyranosyl units | 63.2/3.26-3.95 | X5 |
|  |  | 94.6/6.56 | Tricin 8 (T) |

**Table 4.** Abundance of lignin substructures expressed as linkage per 100 aromatic units (as relative percentage of the total linkages considered) and aromatic units (molar percentage) from integration of $^{13}C$–$^{1}H$ correlation peaks in the HSQC spectra of lignins.

| Internal linkages | CEH | CF | BF | WF |
|---|---|---|---|---|
| β-O-4´ (A/A´) | 10.6 (100%) | 12.8 (74.9%) | 16.2 (70.9%) | 29.1 (75.1%) |
| Resinols (B) | 0 | 0 | 2.9 (12.6%) | 2.5 (6.5%) |
| Phenylcoumarans (C) | 0 | 4.3 (25.1%) | 3.8 (16.5%) | 7.1 (18.3%) |
| | | | | |
| H | 18.6% | 17.9% | 2.4% | 4.9% |
| S | 50.9% | 49.1% | 45.1% | 46.6% |
| G | 30.4% | 33.0% | 50.4% | 48.5% |

Abundance of β-*O*-4´, resinols and phenylcoumarans substructures was estimated by 2D-NMR from $C_\alpha$–$H_\alpha$ correlations. $C_{2,6}$–$H_{2,6}$ correlations from S units; and $C_2$–$H_2$ correlations from G units.

## Figure captions

**Fig. 1.** TGA curves for a) lignin-enriched residues and b) FLs studied. Dashed lines represent the derivative weight losses.

**Fig. 2.** $^1$H NMR spectra of the functionalized lignin-enriched residues studied.

**Fig. 3.** 2D HSQC results of BF, WF, CF and CEH lignin-enriched residues.

**Fig. 4.** Main lignin structures identified by NMR. (R indicates both aliphatic and aromatic chains). (A) β-O-4´ alkyl-aryl ethers; (A') β-O-4´ alkyl-aryl ethers with acylated γ’-OH with p-coumaric acid; (B) resinols; (I) p-hydroxycinnamyl alcohol end-groups; (C) phenylcoumarans; (PCA) p-coumarates; (FA) ferulates; (T) tricin incorporation into the lignin polymer through a G-type β-O-4´ linkage; (X) xylopyranose; (H) p-hydroxyphenyl unit; (G) guaiacyl unit; (S) syringyl unit; (S´) oxidized syringyl units with a Cα ketone.

**Fig. 5.** Evolution of viscoelastic functions and viscous flow curves of oleogels obtained from functionalized CF and CEH samples at 20 and 25% (Figs. 5a and 5d), CF, BF & WF samples at 20% (Figs 5b and 5e) and samples CF, BF & WF at 25% ( Figs 5c and f). Inset: values of consistency (K) and flow (n) indexes of the power-law model.

**Author statement file**

A.M. Borrero-López. Responsible of conceptualization, investigation, methodology, data curation, writing -original draft, review & editing.

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**Highlights**

- Valorization of lignin-enriched residues from different bioethanol processes.
- Diisocyanate functionalization to thicken castor oil, producing chemical oleogels.
- Bioethanol production protocol and raw material affected oleogel properties.
- Lignin aromatic/aliphatic OH ratio, total OH content and S/G ratio tune gel response.
- Rheological properties obtained mimic those of traditional lubricating greases.