

Functionalising lignin in crude glycerol to prepare polyols and polyurethane

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Abstract

In this work, crude glycerol liquefaction of lignins produced in the pulp and paper industry, as well as an organosolv lignin (sugarcane bagasse), was studied with the ultimate aim of preparing bio-based polyols for polyurethane (PU) preparation. This is a proposed strategy to valorise the by-products of biodiesel and lignocellulose biorefineries. Size-exclusion chromatography revealed that the lignins behave differently during liquefaction based on a ranging product molecular weight (MW). The MW of the liquefaction products was concluded to be related to the phenolic and aliphatic hydroxyl group content of the respective lignins, as well as the removal of glycerol and monoacylglycerol during liquefaction. Lignin was modified to yield mostly a solid-phase product. Fourier transform infrared spectroscopy suggests that crude glycerol constituents like glycerol and fatty acid esters are bound to lignin during liquefaction through formation of ether and ester bonds. Liquefaction yield further also varied with lignin type. The liquefaction products were effectively employed as bio-based polyols to prepare PU.

Keywords

Kraft lignin, lignosulphonate, organosolv, biorefinery

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Introduction

Lignin is currently a major by-product of the pulp and paper industry and production of fuels and chemicals from lignocellulose in biorefineries will form an additional source of lignin by-products.^{1,2} The modification of lignocellulose and lignin has been demonstrated to be effective means to prepare bio-based polyols for polyurethane (PU) preparation from renewable and sustainable resources.^{3,4} Reaction with propylene oxide as well as liquefaction in solvents such as polyethylene glycol (PEG), diethylene glycol, EG and glycerol are most often reported. Modification with the said compounds results in product structures with hydroxyl groups (OH) that are more accessible and therefore have higher reactivity.^{5,6} Recently, green liquefaction solvents like cyclic organic carbonates, butanediol and crude glycerol have been employed to further increase bio-based content.^{7–11} Other green modification strategies reported include esterification of lignin with a fatty acid followed by functionalisation¹² and depolymerisation of kraft lignin (KL) by hydrolysis with water to yield polyols.¹³

In the above-mentioned work, the molecular weight (MW) of lignin and reaction products were monitored by some as a means to study the liquefaction process.^{14,15} Decreases and increases in MW are indicators of depolymerisation of lignin and formation of higher MW products during reaction, respectively.^{16,17} The OH of lignin are important reactive sites,^{3,18} and comparing functional groups in lignin and liquefaction products also gives insight into the behaviour of the solvents and lignin or lignocellulose during modification.¹⁹ Lignin type has previously been shown to influence polyol preparation through oxypropylation due to differences in MW, OH content and structure.^{20,21}

Crude glycerol is a low value by-product of the biodiesel industry produced in high volume and is, therefore, seen as potential renewable feedstock for green products.²² It has only recently been employed as a lignin liquefaction solvent. Lee et al.²³ and Kim et al.²⁴ prepared polyols through crude glycerol liquefaction of saccharification residues of empty fruit bunches and sunflower stalks, respectively. The residues had high lignin contents. Muller et al. previously reported on the preparation of polyols through crude glycerol liquefaction of technical lignins from the pulp and paper industry, as well as an agricultural crop residue.²⁵

The products of lignin and lignocellulose liquefaction are characterised and employed for PU preparation in either an unprocessed form^{9,26–28} or it can be purified by removing solid-phase residues prior to further use.^{18,29–32} The residue yield is used to describe the extent of biomass liquefaction.³ In the present application, the aim is to maximise the use of lignin by-products from biorefineries and the liquefaction product is to be used without prior removal of residues, which represent lignin derivatives.³³ The inherent structure of lignin can be beneficial to the properties of polyurethane foam (PUF),^{5,34,35} supporting the use of the residues. The liquefaction product liquid and solid phases were, however, characterised separately in this work to establish the modifications which lignin and crude glycerol undergo to form the polyol product, ultimately determining the importance of using the solid and liquid phases in PU preparation, which is uncertain at present.

Three technical lignins (kraft, lignosulphonate (LS) and organosolv) and their respective products from liquefaction in crude glycerol were compared in terms of MW and structure by means of size-exclusion chromatography (SEC) and Fourier transform infrared (FTIR) spectroscopy. The results of the comparison present new information in this field of study. The possible formation of PU through reaction of the products with diisocyanate was finally evaluated. This would present a new PU product with high bio-based content that can act as a potential application for the low value by-products of biorefineries looking to maximise profits from biomass.

Experimental

Materials

Crude glycerol was prepared through potassium hydroxide (KOH) catalysed transesterification of sunflower oil with ethanol (see Supplementary Material). The composition of the crude glycerol is presented in Supplementary Material, Table S1. Organosolv lignin (OL) was extracted from sugarcane bagasse (Tsb Sugar RSA, Malelane, South Africa) according to Xu et al.,³⁶ employing a mixture of acetic acid, formic acid and water with hydrochloric acid as a catalyst (see Supplementary Material). Hardwood calcium LS was donated by Sappi's Saiccor mill (Umkomaas, South Africa). Softwood KL (Product 471003), dimethyl sulphoxide (DMSO; Chromasolv Plus, 99.7%), tetrahydrofuran (99.9%, containing 250 ppm BHT), lithium bromide (LiBr; 99%), monoolein (analytical standard) and acetyl bromide (99%) were obtained from Sigma-Aldrich (Kempton Park, South Africa). Glycerol (99%), D-glucose (99.5%), acetic acid (98.5%) and sulphuric acid (H_2SO_4 ; 98%) were obtained from Associated Chemical Enterprises (Johannesburg, South Africa). Ethanol (99.9%) was obtained from Rochelle (South Hills, South Africa). Desmodur 44V20 L (diphenylmethane-4,4'-diisocyanate) was donated by Bayer Material Science (Isando, South Africa). Air Products (Kempton Park, South Africa) donated PU catalysts and surfactants. Chemicals were used as received. The lignins were previously characterised by proton nuclear magnetic resonance (^1H NMR) and phosphorus-31 nuclear magnetic resonance (^{31}P NMR) and elemental analysis (Supplementary Material, Table S2).²⁵

Liquefaction

Liquefaction was conducted as previously described²⁵; H_2SO_4 as a catalyst was added to crude glycerol to obtain pH 8. The mixture was heated to 160°C in a glass reactor open to atmosphere on a temperature controlled hotplate. The specific lignin was added (crude glycerol: lignin at 9:1, wt/wt) and the liquefaction conducted for 90 min under stirring, where after the product mixture was immediately cooled to room temperature. The liquid- and solid-phase product fractions were separated by addition of ethanol (15 mL g^{-1} product) under stirring, followed by centrifugation (4000 r min^{-1} for 10 min). The precipitate was washed with ethanol and dried at 40°C to give a solid-phase product. Ethanol was removed from the supernatant liquid in a rotary evaporator at 30°C to yield a liquid-phase product. The hydroxyl numbers of the unfractionated products were determined according to the standard method, ASTM D4274-11 method D.³⁷

Size-exclusion chromatography

The MWs of the lignins and liquefaction products were determined on a Perkin-Elmer Flexar system (Shelton, Connecticut, USA), consisting of a degasser, isocratic LC pump, autosampler, column oven and refractive index detector (RI). The system was operated through TotalChrom version 6.3.2 software. The column set consisted of two Agilent PolarGel L columns ($7.5 \times 300\text{ mm}$, $8\text{ }\mu\text{m}$ particle size). The eluent used was DMSO/water (9:1, v/v) containing 0.05 mol dm^{-3} LiBr³⁸ and was chosen because it is reported to be a solvent which enables the analysis of underivatized lignins. The flow rate was 0.4 mL min^{-1} , oven temperature 55°C , injection volume $100\text{ }\mu\text{L}$ and sample concentration 8 mg mL^{-1} . Samples were stirred 24 h and filtered through $0.45\text{ }\mu\text{m}$ syringe filters (PALL Acrodisc, Gx/GHP) before injection. The system was calibrated with Pullulan standards (Sigma-Aldrich, batch BCBR0400 V) of $M_{\text{Peak max}}$ (g mol^{-1})

Table 1. Lignin and liquefaction solid-phase product MW.

	$\bar{M}_W^a$ (g mol ⁻¹)	$\bar{M}_n^b$ (g mol ⁻¹)	Dispersity ($\bar{M}_W/\bar{M}_n$)
KL	13176	2102	6.3
OL	3566	787	4.5
LS	3688	688	5.4
KL solid product	5088	2316	2.2
OL solid product	7867	1615	4.9
LS solid product	7384	2434	3.3

MW: molecular weight; KL: kraft lignin; OL: organosolv lignin; LS: lignosulphonate.

^aWeight-average MW.

^bNumber-average MW.

as follows: 107000, 47100, 21100, 9600, 6100, 1080 and 342, as well as glucose (180.16 g mol⁻¹). Standards of monoacylglycerol (MAG) and glycerol were injected to determine their elution volumes. The data were processed according to Gavrilov and Monteiro³⁹ and Shortt.⁴⁰ Averages are based on at least three samples. The SEC MALLS system that used tetrahydrofuran (THF) as eluent is described in the Supplementary Material.

FTIR

Diffuse reflectance spectra were recorded on a Shimadzu (Kyoto, Japan) IRAffinity-1 FTIR spectrometer fitted with a PIKE Technologies (Madison, Wisconsin, USA) EasiDiff accessory. Samples of the lignin, solid-phase products and PU were analysed in a potassium bromide matrix. Spectra were recorded between 4000 cm⁻¹ and 400 cm⁻¹, at 4 cm⁻¹ resolution with 45 scans. Intensities were aligned at the C=C aromatic band around 1600 cm⁻¹.⁴¹ The crude glycerol and liquid-phase products were analysed by attenuated total reflectance FTIR spectroscopy, employing the PIKE Technologies HATR accessory with a zinc selenide crystal plate. Spectra were recorded between 4000 cm⁻¹ and 800 cm⁻¹ as above. A three-point baseline correction was applied.

PU preparation

PU were prepared from the three respective lignin liquefaction products (unfractionated). The liquefaction product was first added to a beaker followed by addition of a gelling catalyst (Polycat 8), blowing catalyst (Polycat 5), surfactant (DC5357) and water and then stirred at 6000 r min⁻¹ for 10–15 s. Diisocyanate was then added to obtain an isocyanate index of 1.05 (see Supplementary Material, Table S3). Again the mixture was stirred for 10–15 s, and left to rise and cure.

Results and discussion

Size-exclusion chromatography

The KL was found to have higher MW (Table 1) than the LS and OL, which in turn did not differ significantly from each other. Table 2 shows values reported for lignins either extracted by similar methods, from similar sources, or analysed on similar SEC systems.

The aforementioned factors are known to influence the measurement of lignin MW.⁵² Values of lignin MW vary in literature, but there are some agreement between values for the respective lignin

Table 2. Literature MW data of technical lignins.

Lignin isolation	Source	$\bar{M}_w$ (g mol ⁻¹)	$\bar{M}_n$ (g mol ⁻¹)	Dispersity	Eluent	Detector/Standards	Authors
Kraft	Birch	19,650	7523	2.69	Aqueous	RI	Chen and Li ⁴²
Kraft	Softwood/ hardwood	10,844–15,195	4530–8071	1.8–2.4	LiBr, DMSO	RI, Pullulan	Zhu et al. ⁴³
Indulin (Kraft)	Softwood	3060	1900	1.6	THF/H ₂ O	Diode array, polystyrene/ PMMA	Andrianova et al. ⁴⁴
Formic acid/acetic acid/H ₂ O ^a	Wheat straw	4170	2660	1.57	Aqueous	RI, Pullulan.	Xu et al. ³⁶
'Organosolv'	'Wheat straw'	5000	860	5	THF, acetobromination ^b	'RI and diode array detector, Polystyrene'	Lange et al. ⁴⁵
NaOH and H ₂ O ₂		13600	750	18	THF, acetylation ^b		
Organosolv	Sugarcane bagasse	2180	1460	1.49	0.02 M NaCl, aqueous	Pullulan	Sun et al. ⁴⁶
	Wheat straw	8420	480	17.54	'0.5% LiBr, DMSO'	'RI and UV, polystyrene sulphonate'	Sulaeva et al. ⁴⁷
Indulin (Kraft)	Softwood	2887	375	7.71			
LS	Spent sulphite liquor	8302	842	9.86			
LS	Hardwood	3833	2041		0.5 M NaOH, aqueous	UV, polystyrene sulphonate	Baumberger et al. ⁴⁸
LS	Hardwood	6600	1200	5.5	'0.05 M LiBr, DMSO/H ₂ O'	'Multiple, ^c Pullulan'	Ringena et al. ³⁸
Curan (kraft)	Softwood	9900	1300	7.6			
Soda lignin	Bagasse	3600	1100	3.3			
Curan (kraft)	Softwood	11,000	2000	5.5	0.11 M LiCl, DMAc	Multiple, ^c PEG/oxide	
Formic acid/H ₂ O ^a	M. × giganteus	2679	1564	1.7	THF	UV, polystyrene	Wang et al. ⁴⁹
Acetic acid or formic acid/H ₂ O ^a	M. × giganteus	6024/6656	1444/2122	4.17/3.14	THF, acetylation ^b	UV	Villaverde et al. ⁵⁰
Formic acid/acetic acid/H ₂ O ^a	Alfa grass	3230	1300	2.48	THF	RI, polystyrene	Abdelkafi et al. ⁵¹

MW: molecular weight; LiBr: lithium bromide; DMSO: dimethyl sulphoxide; THF: tetrahydrofuran; H₂O: water; RI: refractive index; NaCl: sodium chloride; NaOH: sodium hydroxide; LiCl: lithium chloride; UV: PEG: polyethylene glycol; DMAc: dimethylacetamide; PMMA: poly(methyl methacrylate).

^aMixture of solvents.

^bSample derivatisation.

^cRI, UV, viscosimetric, LALLS.

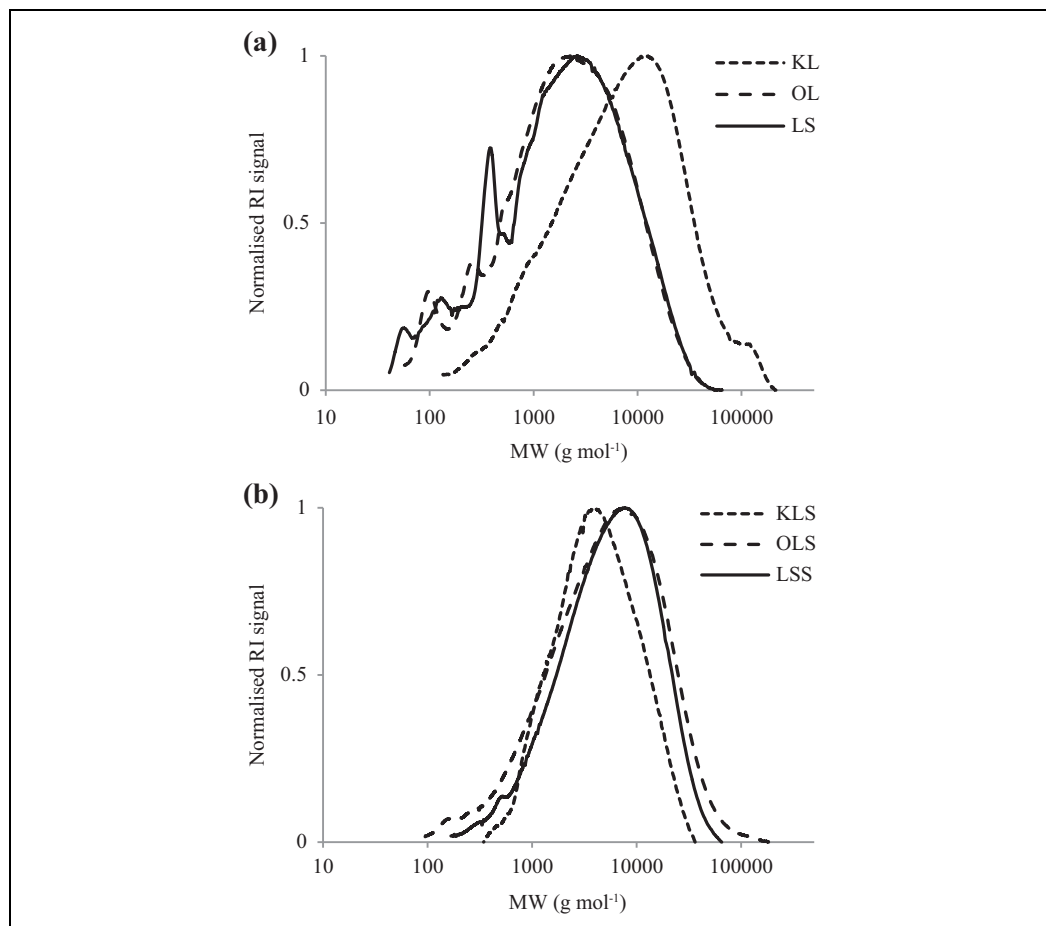


Figure 1. MW distributions of the lignins (a) and solid-phase products (b). KLS, OLS and LSS refer to the KL, OL and LS solid products, respectively. MW: molecular weight; KL: kraft lignin; OL: organosolv lignin; LS: liginosulphonate.

types in Tables 1 and 2. Figure 1(a) shows an overlay of the lignin MW distributions. The OL and LS show more peaks in the low MW region, representing lower MW lignin fractions and impurities.^{38,53} The higher MW of the KL is concluded to be a result of condensation reactions during isolation.⁵⁴ Previous characterisation by ³¹P NMR spectroscopy of the same lignins²⁵ revealed that the KL had a higher content of condensed phenolic OH than the OL and LS (1.56 vs. 0.27 and 0.48 mmol g⁻¹, respectively). In the same study, KL was also found to have the lowest hydrogen content, an indication of condensation.

Figure 1(b) shows an MW distribution overlay for the solid-phase liquefaction products. In the case of OL and LS, the respective solid-phase products have increased $\bar{M}_w$ and $\bar{M}_n$, while the KL product $\bar{M}_w$ decreased (Table 1). The OH contents of the lignins were previously determined to be as follows: aliphatic OH were 4.1, 2.5 and 4.5 mmol g⁻¹ and phenolic OH were 2.1, 4.0 and 1.9 mmol g⁻¹ for the OL, KL and LS, respectively.²⁵ The similar aliphatic OH contents of the OL

Table 3. Lignin and corresponding lignin-derived polyol MW reported.

Lignin type	Lignin MW (g mol ⁻¹)	Polyol MW (g mol ⁻¹)	OH number (mg KOH g ⁻¹)	Liquefaction	Reference
Olive tree pruning, OL	4209/3.77 ^a	2117/3.54	176–821	PEG/glycerol, H ₂ SO ₄ ^b	Sequeiros Echeverria ⁵⁶
Empty fruit bunch, KL	1564/2.62	16730/13.94	–	PEG/glycerol, H ₂ SO ₄	Faris et al. ³¹
Alkaline lignin	2726	1079	462	PEG/glycerol, H ₂ SO ₄	Li et al. ²⁸
LS	19000/1.1	2226/1.6	321–494	Glycerol/DEG, PTSA ^c	Gao et al. ⁵⁷
Corncob, alkaline lignin	2792/3.07	1108/2.43	–	PEG/glycerol, H ₂ SO ₄	Xue et al. ²⁷
Birch, ethanol/water lignin	2560/1.67	4990/1.08	4.4 (mmol g ⁻¹)	PEG/glycerol, H ₂ SO ₄	Xue et al. ¹⁵
Beech, milled wood lignin	5800/1.9	2950/2–5500/8	–	EG, PTSA	Jasiukaitytė- Grojzdek et al. ⁵⁵

MW: molecular weight; OH: hydroxyl groups; PEG: polyethylene glycol; DEG: diethylene glycol; KOH: potassium hydroxide; H₂SO₄: sulphuric acid.

^aDispersity.

^bCatalyst.

^c*p*-Toluene sulphononic acid monohydrate.

and LS could have resulted in their similar MW changes, opposed to that of the KL with the higher phenolic OH content.^{33,55} Dispersity of the solid-phase product relative to that of lignin is reduced significantly for KL and LS but increases for OL. Formation of polyols through liquefaction of lignin is reported to occur through fragmentation of lignin and polymerisation or binding among lignin fragments and liquefaction solvents such as EG, PEG and glycerol.^{33,55} The KL seems to be fragmented more extensively during the liquefaction. The KL solid-phase product $\bar{M}_n$, however, remains stable, indicating that larger MW fractions are preferentially fragmented, reducing $\bar{M}_w$.

In the case of LS, the $\bar{M}_w$ and $\bar{M}_n$ increased in the product. The same was seen for the OL, but $\bar{M}_n$ increased less, relative to $\bar{M}_w$, indicating a greater degree of modification among larger MW fragments. The crude glycerol constituent contents were previously found to undergo differing changes during liquefaction of each of the three lignins (see Supplementary Material, Figure S1).²⁵ The most significant change with regard to the aforementioned SEC results firstly appears to be the 16.8 mol% decrease in MAG during LS liquefaction compared to 34.8 and 54.6 mol% increases for OL and KL, respectively. The MAG might have reacted with low MW LS fractions to a greater extent, affecting the increase in $\bar{M}_n$. Secondly, the glycerol content decreased 49.6 wt% during liquefaction of OL compared to 43.8 wt% for LS, and greater incorporation of glycerol might have led to a greater change in $\bar{M}_w$ of the OL solid-phase product. ¹H NMR did indicate that the aliphatic content was higher in the LS product than in the OL product, supporting the respective reaction of MAG (or fatty acid ethyl esters (FAEEs)) and glycerol.

Table 3 gives literature values found by others during polyol preparation from lignin through liquefaction. No clear trend is observed when comparing the lignin and corresponding polyol MW, with both increases and decreases reported. It can also be seen that liquefaction of lignin in PEG/glycerol might produce higher MW polyols than crude glycerol liquefaction.

Figure 2(a) shows an overlay of the crude glycerol and liquid-phase liquefaction product chromatograms. MAG elutes at close to 16.5 mL and glycerol at 17.0 mL in each of the samples.

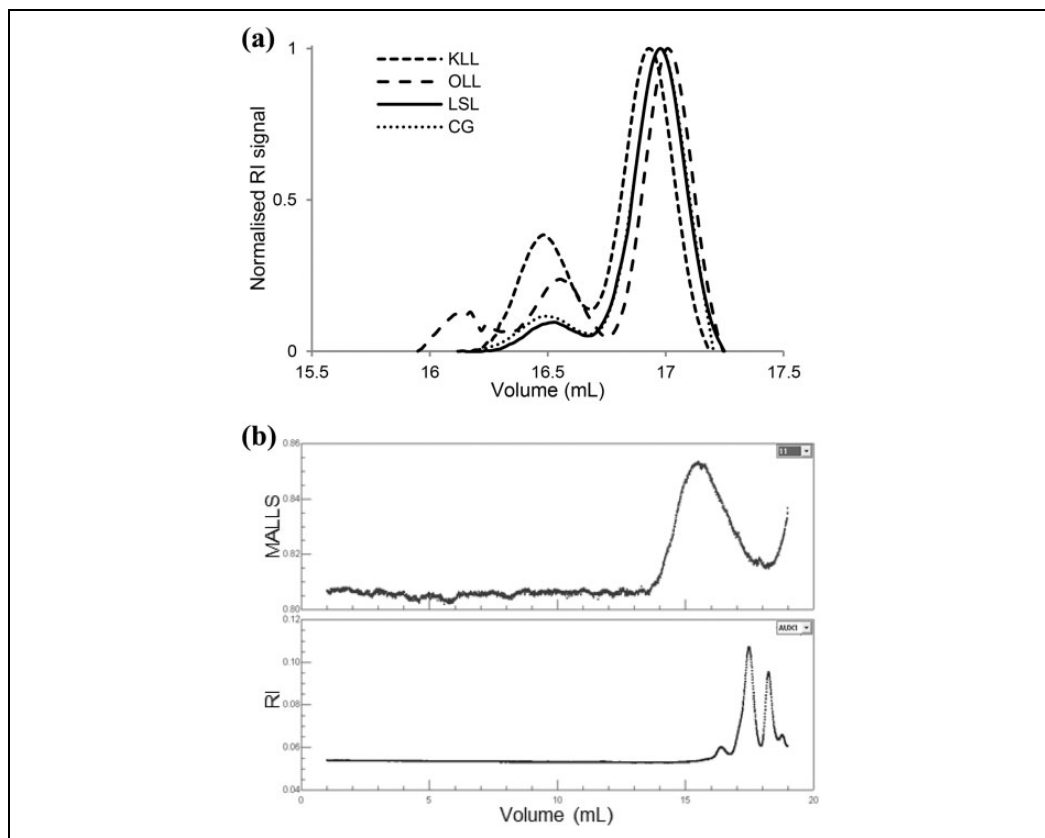


Figure 2. Liquid-phase product SEC elution profiles: (a) DMSO/H₂O system (KLL, OLL, LSL and CG refer to KL, OL, LS liquid product and crude glycerol, respectively). (b) OL liquid product analysed on the THF system (peaks from 18 mL onwards are due to solvent effects, not attributable to the samples). SEC: size-exclusion chromatography; DMSO: dimethyl sulphoxide; CG: crude glycerol; THF: tetrahydrofuran; H₂O: water.

The OL liquid product shows an additional peak at 16.1 mL. This should represent lignin derivatives formed during liquefaction.^{14,55} Sunflower oil (triacylglycerol), diacylglycerol and FAEEs were found to be insoluble in the mobile phase (DMSO/H₂O). The liquid-phase products exhibited similar chromatograms when analysed with THF as the mobile phase (Figure 2(b) and Supplementary Material, Figure S2). The OL liquid product did not show an additional peak on the RI response, but the MALLS detector did show a low intensity peak that seemed to correspond with the peak at 16.1 mL in the DMSO/H₂O system. The presence of OL derivatives in the liquid product is supported by the ¹H NMR spectroscopy results reported earlier,²⁵ which indicated that the OL liquid product had increased lignin-derived aromatic content compared to the KL and LS liquid products (Supplementary Material, Figure S3). The SEC results reveal that lignin was modified in a manner to yield mostly a solid-phase product during liquefaction, with only a minor fraction converted to the liquid phase. Crude glycerol components made up most of the liquid-phase product.

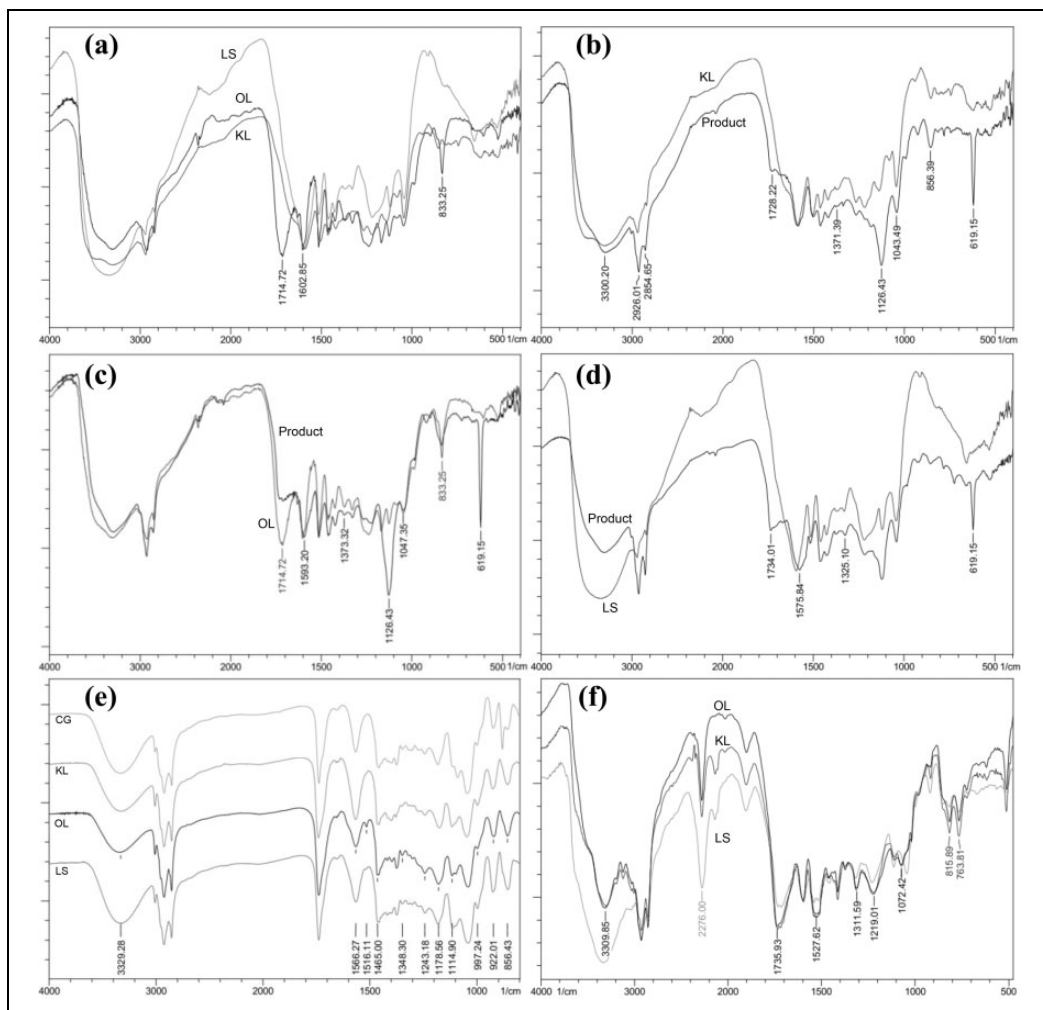


Figure 3. FTIR spectra: (a) lignin, (b) KL and solid product, (c) OL and solid product, (d) LS and solid product, (e) crude glycerol and liquid products, and (f) PUs (Figure S4). KL: kraft lignin; OL: organosolv lignin; LS: lignosulphonate; FTIR: Fourier transform infrared; PU: polyurethane.

FTIR spectroscopy

Lignin. The spectra (Figure 3(a)) of the three lignins resemble those reported in literature.^{36,58} There are differences at 1715 cm^{-1} where the OL has a band assigned to $\text{C}=\text{O}$ in carbonyl or carboxyl, formed through oxidation during isolation.³⁶ The lignins also differ in terms of syringyl (S), guaiacyl (G) and *p*-hydroxyphenyl (H) unit content due to their various origins.⁵⁹ The OL has a broad signal at 833 cm^{-1} assigned to S, G and H units of a grass-type lignin.⁴⁶ This band is absent in the KL and LS. The KL has a band at 855 cm^{-1} indicative of G units,⁵⁹ while bands in this area of the LS are difficult to distinguish. A higher ratio of band intensities between 1505 cm^{-1} and 1595 cm^{-1} is related to a higher level of condensation or cross-linking in lignin by some,^{60,61} also

indicative of a higher G relative to S unit content.^{62,63} Based on the intensities in the said bands of the lignin spectra, the LS clearly has a lower relative G unit content which can lower lignin reactivity, since steric hindrance is higher in S units.^{5,62}

Solid-phase products. In the FTIR overlay (Figure 3(b) to (d)) of the KL and the solid-phase product, the intensity of the OH absorbance band^{31,54,64} between 3600 cm^{-1} and 3100 cm^{-1} differed, indicating a change in the OH contents during liquefaction. There was a decrease in the intensity of the LS product in this band, while OL intensities also changed, but to a lesser extent. At 2926 and 2855 cm^{-1} , the KL product showed increased intensities, attributed to stretching vibrations of methyl and methylene groups.¹⁹ The same was observed in the case of the OL and LS, indicating introduction of aliphatic chains.³³ A new band became visible around 1728 cm^{-1} of the KL product spectra, assigned to the C=O stretch of aliphatic ester bonds.¹⁹ The OL showed a band at 1714 cm^{-1} assigned to C=O stretching in carboxyl or carbonyl groups of lignin,³⁶ which was reduced in the product along with the introduction of a shoulder at 1732 cm^{-1} , as in the KL product. The LS and its product spectra exhibited similar changes than the KL in this area. A band formed at 1126 cm^{-1} in the product spectra of all three lignins. This band is assigned to ether C–O–C stretching.^{33,65} Similarly, a band formed at about 619 cm^{-1} in the spectra of the solid products, which was absent in the starting lignin spectra. S–O stretching bands are assigned in this area.^{64,66}

To summarise, changes in the OH content of the lignins during liquefaction were observed. Aliphatic methyl and methylene absorbance increased in the products, likely indicating the introduction of fatty acid chains from MAG and FAEE.⁶⁷ This is supported by the appearance of aliphatic ester bond signals. The ester bonds absorb in the band assigned to aliphatic groups,⁶⁸ which might indicate that aliphatic lignin OH was preferentially esterified. There was clear formation of a signal assigned to aliphatic ether bonds in all the product spectra. The bonds were likely formed between lignin and glycerol or MAG OH.⁵⁵ Since signals of aliphatic OH (1040 cm^{-1}) and phenolic OH^{19,69,70} (1370 cm^{-1}) were still present in the solid product spectra, the lignin OH were only partially consumed. The introduction of glycerol OH was also expected to cause absorbance around 1040 cm^{-1} .⁷¹

Crude glycerol and liquid-phase products. Absorbance decreased in the OH band around 3329 cm^{-1} for the OL and KL liquid products compared to the crude glycerol (Figure 3(e) and Supplementary Material, Figure S4). Around 1566 cm^{-1} absorbance intensified for the KL product. This band is assigned to soap COO^- in crude glycerol.⁷² A small band in the OL and LS liquid products at 1516 cm^{-1} was assigned to aromatic C=C stretching in lignin (G-unit).⁶³ The products showed somewhat increased intensities around 1465 cm^{-1} . The band was assigned to C–O–H bending in crude glycerol⁷² and C–H deformation of lignin methoxyl.⁶³ Intensities were higher in the product spectra range 1350 – 1115 cm^{-1} , most noticeably at 1243 , 1179 and 1115 cm^{-1} . Absorbance in the aforementioned bands has been assigned to aromatic C–O, ester C–O³⁶ and aromatic C–H in S units^{63,70} of lignin, respectively. As discussed above, absorbance in the band around 1115 cm^{-1} is also assigned to ether bonds in polyols. Finally, the products showed increased absorbance at 997 , 922 and 856 cm^{-1} , while a band in the crude glycerol at 880 cm^{-1} is absent in the products. The first two bands may represent O–H bending and the third both =CH bending in crude glycerol^{72,73} and C–H deformation of G units in lignin.⁵⁹ Ethanol⁷¹ exhibits a band at 881 cm^{-1} and removal through evaporation during liquefaction was expected. In summary, the spectra showed that OH content was lowered in the OL and KL liquefaction products. It is unclear why the LS product

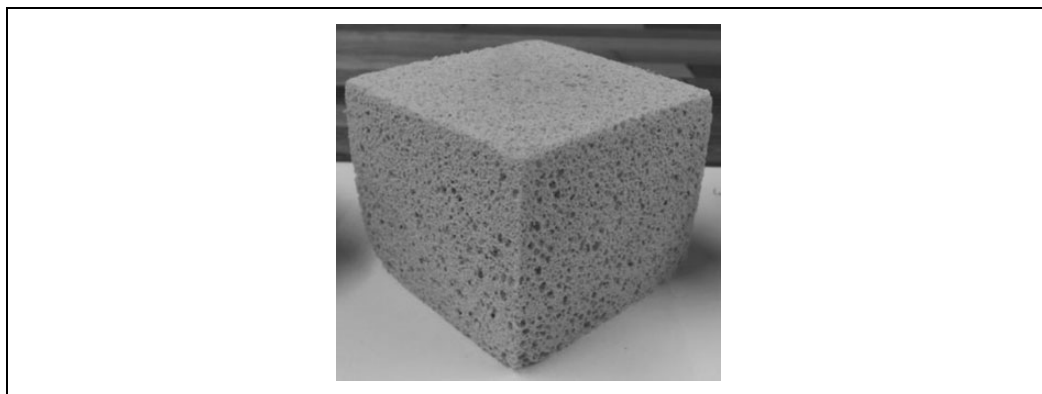


Figure 4. OL product PU foam. OL: organosolv lignin; PU: polyurethane.

Table 4. Product hydroxyl numbers and liquefaction yields.

Lignin/solvent	Hydroxyl number (mg KOH g ⁻¹)	Solid product yield (g (g lignin) ⁻¹)	Liquid product yield (g (g crude glycerol) ⁻¹)
KL	412 ± 27	1.19 ± 0.23	0.62 ± 0.16
OL	224 ± 10	0.76 ± 0.11	0.73 ± 0.06
LS	592 ± 18	1.25 ± 0.12	0.61 ± 0.07
Crude glycerol	769 ± 32		

KOH: potassium hydroxide; KL: kraft lignin; OL: Organsolv; LS: lignosulphonate.

spectrum did not show a reduction in this regard. Importantly, low amounts of aromatic content were introduced into the products, originating in the lignins, while ether bond content was also increased.

Polyurethane. The formation of urethane bonds is confirmed through the observed bands at 3310, 1736, 1528 and 1219 cm⁻¹ in the spectra of the prepared PUs (Figure 3(f)). These bands are the result of mixed absorbance assigned to N–H, C=O of urethane, coupled N–H and coupled C–N, respectively.^{29,74,75} The band at 1736 cm⁻¹ also overlaps with urea absorbance, present at approximately 1700–1640 cm⁻¹.^{76,77} The prepared PUs presented bands not seen in the liquefaction product spectra, further suggesting the formation of PU. The absorbance maxima were as follows: 1528, 1312, 1072, 816 and 764 cm⁻¹. At 1312 cm⁻¹, the absorbance is assigned to urethane,⁷⁶ at 1072 cm⁻¹ to urethane C–O–C and both at 816 and 764 cm⁻¹ to aromatic C–H.^{78,79} At 2276 cm⁻¹, excess unreacted isocyanate NCO absorbance is visible.^{29,76} Based on the specific reagents, rigid PU foam was obtained (Figure 4).

Yield and hydroxyl numbers

The crude glycerol OH content was reduced during lignin liquefaction (Table 4). The OL product had the lowest hydroxyl number, which indicates OH were removed to a greater extent than during KL and LS liquefaction.¹⁸ The product hydroxyl numbers are similar to those obtained by other workers from liquefaction of lignin (Table 3), as well as lignocellulose, generally ranging

100–600 mg KOH g⁻¹.³ The numbers also correspond with that of commercial polyols for rigid PU foam.⁸⁰ The yield of the OL liquefaction products differs significantly from that of the KL and LS. This can be explained by the FTIR results where a limited increase of aromatic content in the OL liquid product spectrum was more prominent. Similarly, the SEC analysis revealed higher MW fractions in the OL liquid product, not detected in the KL and LS liquid products. Greater incorporation of OL in the liquid phase would have lowered the yield of the solid phase.

Conclusions

The KL weight-average MW was decreased during liquefaction to form the solid-phase product, in contrast to the OL and LS which both formed products of increased MW. The MW modifications are concluded to be related to lignin aliphatic and phenolic OH contents. Glycerol and MAG consumption during liquefaction of OL and LS, respectively, correlated with the resultant product MW to some extent. The OL liquid-phase product showed the presence of low concentrations of higher MW lignin derivatives along with glycerol and MAG, whereas only glycerol and MAG were detected for the other lignins. This correlated with higher aromaticity observed in the OL liquid product with FTIR, as well as a higher yield. FTIR spectra further indicated the incorporation of aliphatic content in the solid products along with an increase of ester and ether bonds. In this specific strategy to prepare polyols from lignin, the solid phase of the product contains the majority of the higher MW components, originating in lignin, and exclusion of these components from any PU formulation would discard potentially beneficial structural features inherent to lignin.

PU formation through reaction between the liquefaction products and diisocyanate was confirmed by FTIR. The lower MW of the KL solid product could potentially have a significant effect on PU properties by increasing cross-linking density.⁸¹ Lignin type, based on its origin and isolation method, is concluded to be an important determinant of the product characteristics and its application potential. The products were intended as bio-based polyols for rigid PU preparation but could also be further modified for other applications.

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Supplemental material

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