Polyol Preparation by Liquefaction of Technical Lignins in Crude Glycerol

Louis C. Muller[1]*, Sanette Marx[1] and Hermanus C.M. Vosloo[2]

[1]*Energy Systems, School of Chemical and Minerals Engineering, North-West University, Private Bag X6001, Potchefstroom 2520, South Africa*
[2]*Research Focus Area for Chemical Resource Beneficiation: Catalysis and Synthesis Research Group, North-West University, Private Bag X6001, Potchefstroom 2520, South Africa*

Received July 27, 2016; Accepted September 17, 2016

ABSTRACT: This work reports a study of polyol synthesis through liquefaction of technical lignins in crude glycerol by means of ^{1}H and ^{31}P NMR spectroscopy. The polyols are intended for preparation of polyurethane foam; thus, it is important to know how different lignin types as well as crude glycerol influence and contribute to the final polyol hydroxyl contents. Polyols prepared from organosolv lignin, kraft lignin and lignosulphonate had hydroxyl numbers suitable for rigid foam of 435, 515 and 529 mgKOH/g, respectively. The polyols differed in composition with glycerol, showing significant variation. During liquefaction the glycerol content was mostly reduced through bonding with lignin, and to a lesser extent monoacylglycerol and diacylglycerol formation through transesterification with fatty acid ethyl esters. It is concluded that crude glycerol can potentially replace petroleum-derived polyols as liquefaction solvent and that different types of technical lignin have a strong impact on the resulting bio-based polyol hydroxyl contents.

KEYWORDS: Lignin, renewable polyols, polyurethane, ^{31}P NMR, biodiesel by-product, pulp and paper by-product

1 INTRODUCTION

Polyurethane is a versatile polymer used in many industries and is formed through the reaction of hydroxyl groups (OH) with isocyanate groups to yield urethane linkages [1]. Due to a move away from the use of paper, traditional pulp and paper producers are increasingly looking towards other potential markets for their products. The pulp and paper industry is the major source of technical lignin, generated as a low-value by-product [2]. Lignocellulosic ethanol production in the biofuel industry might further increase lignin-rich by-product volumes [3, 4]. Therefore lignin is receiving considerable attention as a potential feedstock for the preparation of higher value renewable materials, and because these heterogeneous macromolecules contain substantial amounts of aliphatic and phenolic OH [5], it is of interest in bio-based polyurethane applications.

Cateto *et al.* [6] determined that the differences in OH content and MW of lignin have an effect on the reactivity of technical lignin with isocyanate. They found that higher aliphatic OH content imparted higher reactivity when comparing Indulin AT kraft lignin with Alcell lignin. Similar results were found both when comparing Spruce lignins isolated with different solvents and comparing Spruce softwood and Aspen hardwood lignins [7]. Aliphatic OH in lignin are further known to be more reactive than phenolic OH [1], as primary OH is more reactive than secondary OH [7].

Lignin has often been modified through reaction with propylene oxide to improve its application in polyurethane preparation. Oxypropylation replaces phenolic OH in lignin with aliphatic OH which lowers hindrance through steric and electronic effects [8]. Phenolic OH also forms thermally labile bonds with isocyanate [9]. The chain extension further yields a reactant with improved uniformity [5] and lowers rigidity [1]. During oxypropylation, Cateto *et al.* [8] found kraft lignins (Indulin AT and Curan 27-11P) to exhibit shorter reaction times than Alcell lignin attributed in part to higher aliphatic OH content in the kraft lignins. Lignin phenolic OH-type content also affects reactivity. Nadji *et al.* [10] found that during oxypropylation hardwood organosolv lignin and grass

**Corresponding author*: 24023795@nwu.ac.za, muller.lcc@gmail.com

DOI: 10.7569/JRM.2016.634130

soda lignin had shorter reaction durations than softwood kraft and organosolv lignins. They attribute the higher reactivity of the hardwood organosolv lignin to lower MW, and in the case of grass soda lignin, to higher *p*-hydroxyphenyl unit content. According to the authors, *p*-hydroxyphenyl units are more reactive than syringyl and guaiacyl units due to less hindrance by methoxyl groups. Lignin-based polyurethane crosslinking density also depends on lignin MW and functionality and determines the mechanical properties as well as the glass transition temperature of the polyurethane [1].

An alternative modification method to oxypropylation is liquefaction of lignin in solvents such as polyethylene glycol (PEG) combined with glycerol. The resulting polyols contain mostly aliphatic OH [11]. The polyols are said to form through condensation reactions between PEG or glycerol OH and lignin phenolic and aliphatic OH as well as through self-polymerization among lignin fragments [12, 13]. Fragments are formed through lignin interunit bond cleavage during liquefaction, which also liberates phenolic OH [14]. Luo *et al.* [15] studied the conversion of crude glycerol into polyols through liquefaction. They determined that the product consisted of major fractions of monoacylglycerol (MAG), glycerol and diacylglycerol (DAG) as well as fatty acid methyl esters (FAME) and soap. The polyols were successfully employed to prepare polyurethane foam. The liquefaction of biomass in crude glycerol to prepare polyols eliminates the use of petroleum-derived compounds, such as PEG, and replaces it with a low-value, high-volume by-product of biodiesel production which subsequently increases the renewable content of polyurethane [16–18].

According to Balakshin and Capanema [19], quantitative ^{13}C and ^{31}P NMR spectroscopy are the analytical methods used most often to study the structure of lignin. ^{31}P NMR methods have been developed for quantification of various types of OH in lignin. ^{31}P NMR has also been used in the analysis of biodiesel [20] and enables quantification of glycerol, MAG, DAG, fatty acids and alcohols through phosphorylation of hydroxyl groups. The method could potentially also be useful in the study of crude glycerol, which contains mostly the same compounds as biodiesel in different proportions. Liquefaction of technical lignins from the pulp and paper industry in crude glycerol has, to the best of our knowledge, not been reported.

In this study, the results obtained by employing NMR spectroscopy to investigate the use of crude glycerol as solvent and determine the effect which different technical lignins might have on the polyol properties, which in turn will determine polyurethane foam characteristics, are reported. Three technical lignins were compared: kraft lignin, organosolv lignin and calcium lignosulphonate.

Two reagents were employed as ^{31}P NMR phosphorylation reagents, i.e., 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (RII), since it allows differentiation between various types of phenolic, aliphatic and carboxylic OH in lignin [21], and 2-chloro-1,3,2-dioxaphospholane (RI), which enables better distinction between primary and secondary aliphatic OH. ^{1}H NMR, which is frequently employed in lignin characterization [22], was used to obtain further structural information on the lignin and polyols. A crude glycerol polyol was prepared by conducting the liquefaction reaction without the addition of lignin. The spectra of the different lignins and their respective lignin polyols, the crude glycerol as well as the crude glycerol polyol were subsequently compared.

2 EXPERIMENTAL

2.1 Materials

Sugarcane bagasse was obtained from Tsb Sugar RSA (Malalane, South Africa, 24.4833°S, 31.5167°E). Organosolv lignin was extracted from bagasse according to a method described by Xu *et al.* [23] employing a solvent mixture consisting of acetic acid/formic acid/water (30/60/10, v/v/v). The lignin extraction and crude glycerol preparation through transesterification of sunflower oil and ethanol were previously described [18]. Hardwood calcium lignosulphonate was supplied by Sappi Saiccor mill (Umkumaas, South Africa, 30.2010°S, 30.7940°E). Softwood kraft lignin, pyridine, N,N-dimethylformamide (DMF), cyclohexanol, 2-chloro-1,3,2-dioxaphospholane (97%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (95%), chromium(III) acetylacetonate and chloroform-D ($CDCl_3$, 99.96% D) were bought from Sigma-Aldrich. Dimethyl sulfoxide-d_6 (DMSO-d_6, 99.96% D) was bought from Merck. Chemicals were of reagent grade or higher. Lignins were vacuum dried in an oven at 30 °C for at least 24 h before analysis.

2.2 Liquefaction

The liquefaction reaction was conducted in a temperature controlled glass reactor open to atmosphere. Catalyst, 98 wt% H_2SO_4, was first added to crude glycerol until pH 8.0 was measured. The mixture was heated to 160 °C; lignin was then added at a ratio of 9:1 (crude glycerol:lignin, wt/wt). The reaction was allowed to continue for 90 min under magnetic stirring whereafter it was immediately cooled. The

product was subsequently fractionated by addition of ethanol (15 mL g^{-1} product) while stirred, followed by centrifugation at 4000 rpm for 10 min to separate a solid product phase, and finally ethanol was removed in a rotary evaporator at 30 °C from the liquid fraction to yield a liquid product phase. The solid product was washed with ethanol and dried before analysis.

2.3 Characterization

2.3.1 NMR Spectroscopy

A Bruker Avance III 600 MHz spectrometer with a 5 mm PA BBO 1H/D Z-GRD probe was used to acquire all spectra.

2.3.2 ^{1}H NMR Spectroscopy

Spectra were acquired according to methods described by Xue *et al.* [12] and Sun *et al.* [24]. Lignin and solid samples were dissolved in DMSO-d_6 at approximately 20 mg mL^{-1} and polyols at 40 mg mL^{-1}. The sample solutions were vortexed to aid dissolution, stored over 4 Å molecular sieves under nitrogen and left at 40 °C overnight before being transferred to 5 mm NMR tubes for analysis. ^{1}H NMR spectra were recorded at 600.17 MHz, 21 °C, 128 scans, 14 µs pulse width for a 30° flip, 12335.5 Hz spectral width, 3.98 s acquisition time and 1 s relaxation delay.

2.3.3 ^{31}P NMR Spectroscopy

Lignin and polyol samples were analyzed after phosphorylation with RI or RII [21, 25]. Lignin, 30 mg, was dissolved in 350 µL DMF and 350 µL pyridine/$CDCl_3$. A pyridine/$CDCl_3$ ratio of 1.6:1 (v/v) was used throughout ^{31}P NMR experiments [22, 26]. To this solution 100 µL each of the relaxation reagent and the internal standard solutions were added followed by 100 µL of either RI or RII. The relaxation reagent solution consisted of chromium(III) acetylacetonate in pyridine/$CDCl_3$, 5 mg mL^{-1}, and the internal standard solution of cyclohexanol in pyridine/$CDCl_3$, 10.85 mg mL^{-1}. Samples phosphorylated with RI were vortexed and shaken 1 h before being transferred to NMR tubes. With the use of RII, lignin samples were shaken 12 h before analysis to aid dissolution and were observed to be stable. RI samples, however, were found to become unstable after about 2 h. Balakshin and Capanema [19] previously reported RI to be less stable than RII. Lignin samples were analyzed in duplicate unless otherwise noted.

Polyol samples were prepared by dissolving 30 mg polyol in 700 µL pyridine/$CDCl_3$ followed by addition of relaxation reagent, internal standard and RI or RII as described above. Samples were vortexed and directly transferred to NMR tubes for analysis.

The ^{31}P NMR spectra were recorded at 242.99 MHz, 25 °C with inverse gated decoupling, 512 scans, 10.25 µs pulse width for a 30° flip, 96153.8 Hz spectral width, 0.34 s acquisition time, 65537 data points, zero filling and 5 s relaxation delay. Signals were referenced to the reaction product of RI and RII with residual water at 121.1 and 132.2 ppm, respectively [5]. The signal of the reaction product of cyclohexanol with RI and RII at approximately 133.6 ppm and 145.1 ppm, respectively, were used for intergration [12, 21]. Baseline correction with a 4th order polynomial was performed before integration [27]. Spectra were analyzed with MestReNova 10.0.0.

2.3.4 Lignin and Polyol Properties

Lignin was dried at 105 °C to constant weight before ash content was measured. Ash content was determined according to the laboratory analytical procedure NREL/TP-510-42622 in a muffle furnace at 600 °C. Elemental analysis was performed on an Exeter Analytical CE-440 elemental analyzer by combustion in oxygen. Elements C, H, and N were determined directly. O, S, Ca and Na were measured on a scanning electron microscope (FEI Quanta 250 FEG ESEM equipped with an Oxford Instruments 20 mm^2 X-Max^N silicon drift detector) by means of energy dispersive spectroscopy (EDS). Spectra of the uncovered lignin, mounted in thin layers on stubs, were recorded at an accelerating voltage of 15 kV under high vacuum.

The total hydroxyl content of the polyols (liquid product) and crude glycerol was determined according to a standard test method, ASTM D4274-11 method D, through phthalic anhydride esterification of hydroxyl groups catalyzed by imidazole. The iodometric-periodic acid method, AOCS Official Method Ca 14-56, was used to determine the free glycerol content of the crude glycerol [15].

Fatty acid ethyl ester content of crude glycerol was determined by gas chromatography (GC) after repeated extraction with diethyl ether until a clear nonpolar phase was obtained. Diethyl ether was removed by drying at 40 °C, while stirred, to a constant weight. About 130 mg sample was dissolved in hexane at about 10 wt%, mixed and filtered through a 0.2 µm PTFE filter before injection. An Agilent 7820A GC fitted with a flame ionization detector and an Agilent HP-88 column (100 m, 0.25 mm diameter, 0.2 µm film thickness) was employed. The 1 µL aliquots (in triplicate) were injected at 250 °C with the detector temperature held at 350 °C (Ramp program given in Supplementary material). The helium flow was 1 mL/

min. The system was calibrated with FAME standards of analytical grade (Sigma-Aldrich).

3 RESULTS AND DISCUSSION

3.1 Lignin Analysis

3.1.1 *Elemental Analysis*

The lignin elemental analysis results and deduced C_9 formulae are given in Table 1. The values for O, S, Na and Ca are not absolute (hydrogen free basis) and intended for comparison among the three lignins. It can be seen from the C_9 formulae that the kraft lignin has the lowest relative hydrogen content. Carbon content in isolated lignins can increase due to condensation reactions [28]. The organosolv lignin has the highest total carbon content, because it contains low amounts of impurities. The lignosulphonate has higher oxygen and sulphur content than the other lignins due to sulfonation. The lignin compositions and MW presented in Table 1 fall in the wide range of values reported for lignins isolated from different sources and by different methods [22, 28, 29].

3.1.2 *^{1}H NMR Spectroscopy*

An overlay of the ^{1}H NMR lignin spectra is given in Figure 1. The kraft lignin display a broad peak from 6.6–6.9 ppm assigned to both guaiacyl at 6.9 ppm and syringyl lignin polymer units at 6.6 ppm [24, 30].

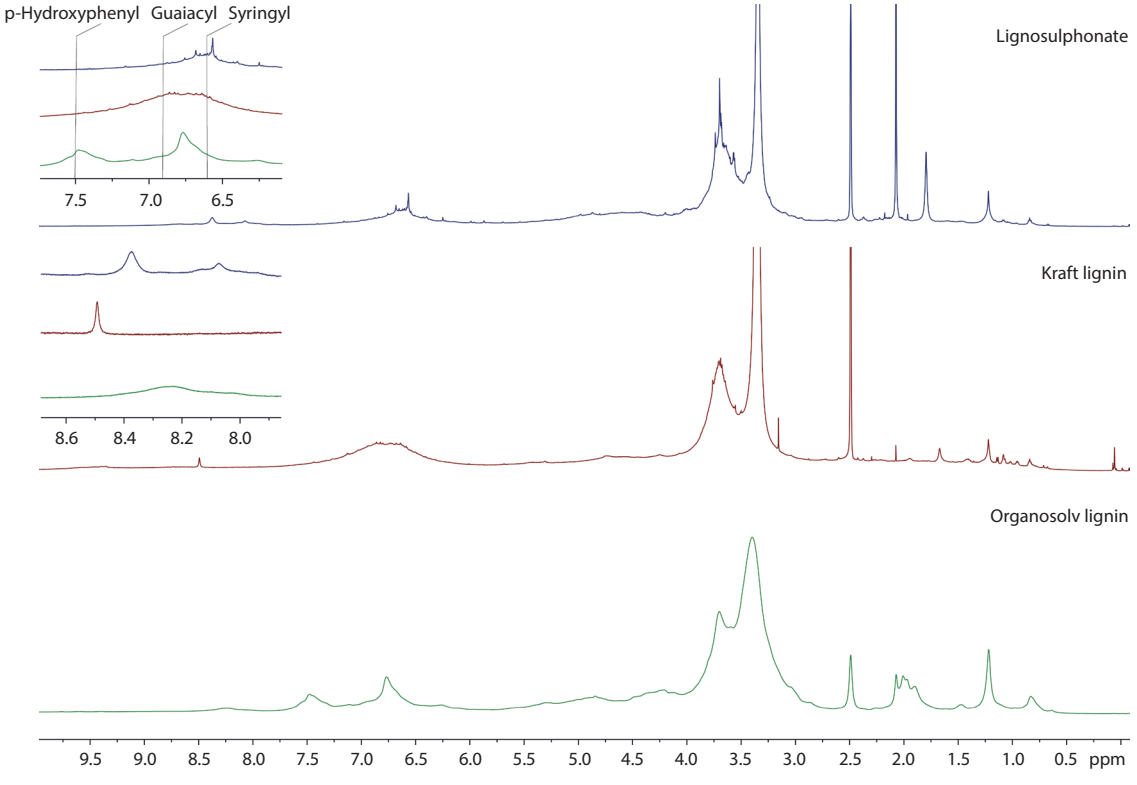

Figure 1 ^{1}H NMR spectra of lignosulphonate, kraft lignin and organosolv lignin. The areas typically assigned to the aromatic protons of the three generic lignin units are indicated in the top expansion.

Table 1 Lignin composition (wt% on moisture-free basis), C_9 formulae and corresponding molecular weight (MW).

Lignin	Ash	C	H	N	O	S	Na	Ca	C_9 formula[b]	MW C_9 unit (g/mol)
Organosolv	2.6 ± 0.2[a]	57.7 ± 0.7	5.2 ± 0.0	0.8 ± 0.1	34.1	0	0.1	0.4	$C_9H_{9.1}O_{3.8}(CHO_3)_{0.3}$	187.7
Kraft	20.2 ± 0.0	51.7 ± 0.7	3.7 ± 0.2	0.2 ± 0.0	32.1	4.1	6.3	0	$C_9H_{5.9}O_{3.7}S_{0.3}(OCH_3)_{0.9}$	210.3
Lignosulphonate	16.7 ± 0.4	42.8 ± 0.1	4.0 ± 0.1	0.2 ± 0.0	40.2	4.5	0	6.6	$C_9H_9O_{6.2}S_{0.4}(OCH_3)_{0.6}$	246.4

[a]95% Confidence interval based on triplicate analysis.
[b]The methoxyl content is an estimate based only on the ^{31}P NMR RII results for syringyl and guaiacyl content.

According to Baucher *et al.* [31], lignin in grasses consists of syringyl, guaiacyl and *p*-hydroxyphenyl units. Softwood lignin consists mostly of guaiacyl units while hardwood lignin consists of mostly syringyl and guaiacyl units. The kraft lignin used in this study is of softwood origin, but the signal intensities do not differ significantly between 6.6–6.9 ppm, indicating similar guaiacyl and syringyl unit content. The organosolv lignin exhibits a broad signal centered at 6.76 ppm assigned to both syringyl and guaiacyl units. It further displays a signal at 7.5 ppm assigned to *p*-hydroxyphenyl units and since the organosolv lignin was extracted from sugarcane bagasse, which belongs to the grass family, higher *p*-hydroxyphenyl unit content is expected [26]. The lignosulphonate (hardwood) displays a signal with maximum intensity at 6.6 ppm, indicative of higher syringyl unit content [24, 30].

Weaker signals between 8.0–8.5 ppm assigned to phenolic protons [32] differ for each of the lignins, suggesting that OH content differs for each. Marchessault *et al.* [33] assign a peak at 0.9 ppm to methyl groups and peaks at 1.2 and 1.5 ppm to methylene groups. Between 2.0–2.2 ppm they assign peaks to methyl or methylene protons next to a double bond or carbonyl group. The three lignins exhibit unique signals between 0.8–2.1 ppm, which therefore indicate differences in aliphatic group contents. The ^{1}H NMR lignin signal assignment is summarized in Table S1.

3.1.3 ^{31}P NMR Spectroscopy

The results of the quantitative ^{31}P NMR analysis (Figure 2) are given in Table 2 (integration ranges are given in Table S2). As discussed, the variation in OH content present in lignin affects reaction with isocyanate, propylene oxide and liquefaction solvents. In this regard the kraft lignin has higher phenolic and condensed phenolic content than the other lignins. The content of condensed phenolic structures can increase in lignin during isolation through condensation reactions [21], but lignin from different sources also contains different types and ratios of intermonomeric linkages [31]. The organosolv lignin and lignosulphonate have similar aliphatic OH content, which is significantly higher than that of the kraft lignin. The secondary OH content of the organosolv lignin is more than double that of primary OH content (Table 2). The total OH content determined for the organosolv lignin by RI and RII differs to some extent, which is likely due to signal overlap in the integration region of the internal standard [19]. The kraft lignin and lignosulphonate were only partially soluble when employing RI and did not give consistent results.

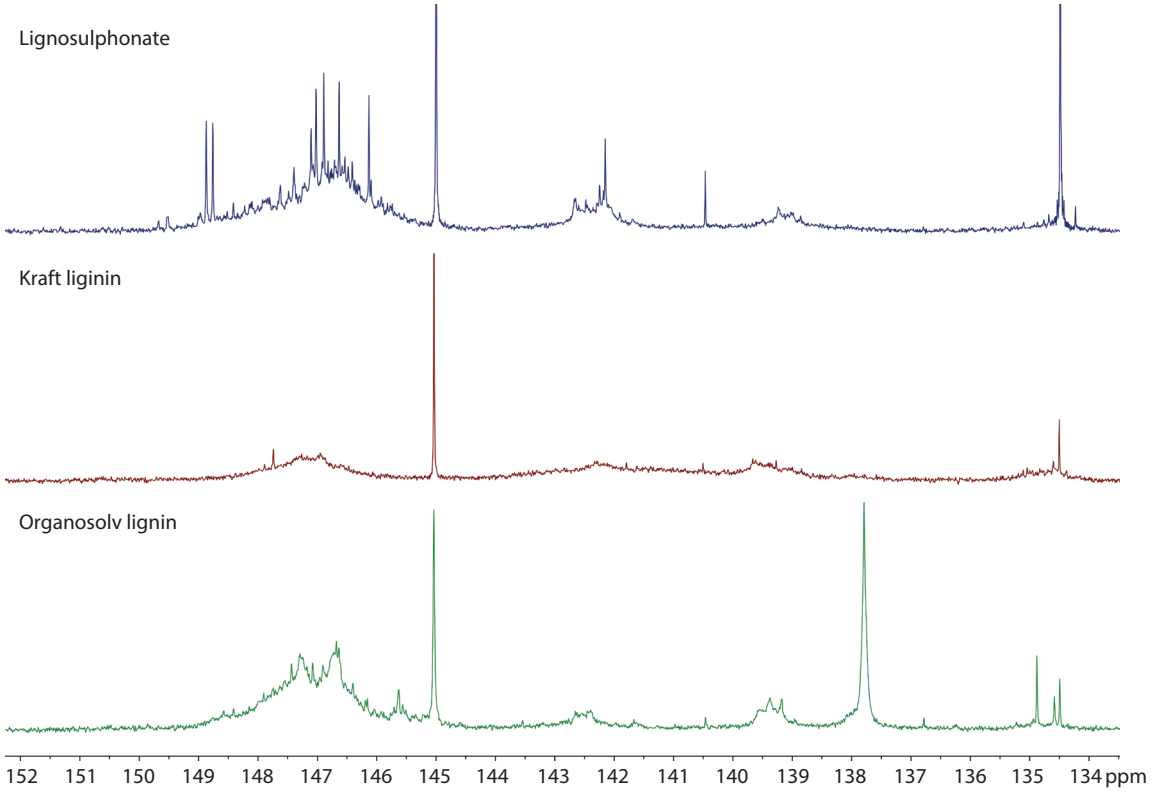

Figure 2 ^{31}P MMR RII spectra of lignosulphonate, kraft lignin and organosolv lignin.

Table 2 Lignin hydroxyl content (mmol/g, ash-free basis) determined by ^{31}P NMR spectroscopy.

Lignin OH type:	Organosolv lignin (Sugarcane bagasse)	Kraft lignin (Softwood)	Lignosulphonate (Hardwood)
RII:			
Aliphatic	4.09	2.47	4.54
Condensed phenolic	0.27	1.56	0.48
Syringyl	0.36	1.04	0.81
Guaiacyl	0.54	1.16	0.49
p-hydroxyphenyl	0.91	0.21	0.09
Carboxylic acids	0.30	0.63	0.57
Total	6.48	7.06 ± 0.56[a]	6.99
Total phenolic	2.08	3.97	1.88
Ratio of lignin units[b]	1:1.5:2.6	5:5.6:1	9.3:5.7:1
Aliphatic/Phenolic OH	1.97	0.62	2.42
RI:			
Total	5.70		
Aliphatic: Secondary/Primary	2.28		

[a]95% Confidence interval based on triplicate analysis.
[b]Ratio of syringyl:guaiacyl:*p*-hydroxyphenyl units.

The values in Table 2 of the syringyl, guaiacyl and *p*-hydroxyphenyl unit contents correlate with the observations made with ^{1}H NMR in terms of the differences in ratios among the three lignins. The similar guaiacyl and syringyl unit content of the kraft lignin is not expected for softwood. However, the dependence of lignin composition on a number of factors and variations within populations has been reported [31].

Furthermore, according to Balakshin and Capanema [19], syringyl units can be significantly overestimated in lignin spectra because a substantial fraction of 5-condensed guaiacyl unit signals also resonate in the syringyl assignment region. The organosolv lignin revealed higher content of the more reactive *p*-hydroxyphenyl units than the other lignins.

3.2 Crude Glycerol and Polyol Analysis

3.2.1 ^{1}H NMR Spectroscopy

3.2.1.1 Liquid Product

Luo *et al.* [15] studied the preparation of polyols through the liquefaction of crude glycerol and determined the major reactions which took place. Transesterification of triacylglycerol (TAG) and DAG with glycerol significantly increased DAG and MAG content. Fatty acids and FAME with glycerol through esterification and transesterification, respectively, also formed MAG and DAG. After liquefaction the product did not contain any TAG while soap and FAME content were substantially reduced.

An overlay of the crude glycerol and crude glycerol polyol ^{1}H NMR spectra is shown in Figure 3 with signal assignment (Table S3) to fatty acid ethyl esters (FAEE), glycerol, MAG, DAG and TAG [34–38]. Ethanol signal intensities at 3.43 ppm and 1.04 ppm [39] and water at 3.43 ppm [32] are significantly reduced in the crude glycerol polyol. Ethanol and water were expected to be removed through evaporation during liquefaction at 160 °C. At 4.0 ppm the FAEE quartet intensity decreased and overlap with a doublet of doublets becomes apparent, indicating the presence of TAG [38]. Accordingly, a TAG signal at 5.3 ppm does not change substantially and therefore TAG content remained stable during liquefaction while FAEE content decreased.

Corresponding to the reduction at 4.0 ppm, the ethoxy signal intensity at 1.15 ppm also decreased in the crude glycerol polyol. Decreases in intensity between 3.23–3.38 ppm and between 4.3–4.7 ppm indicate a loss in glycerol OH content. Removal of ethanol OH will also decrease peak areas around 4.5 ppm. MAG and DAG signals overlap with those of glycerol between 3.23–3.38 ppm as well as with signals of ethanol and water downfield of 3.40 ppm, which makes any conclusions difficult, but the peak areas at 3.88 and

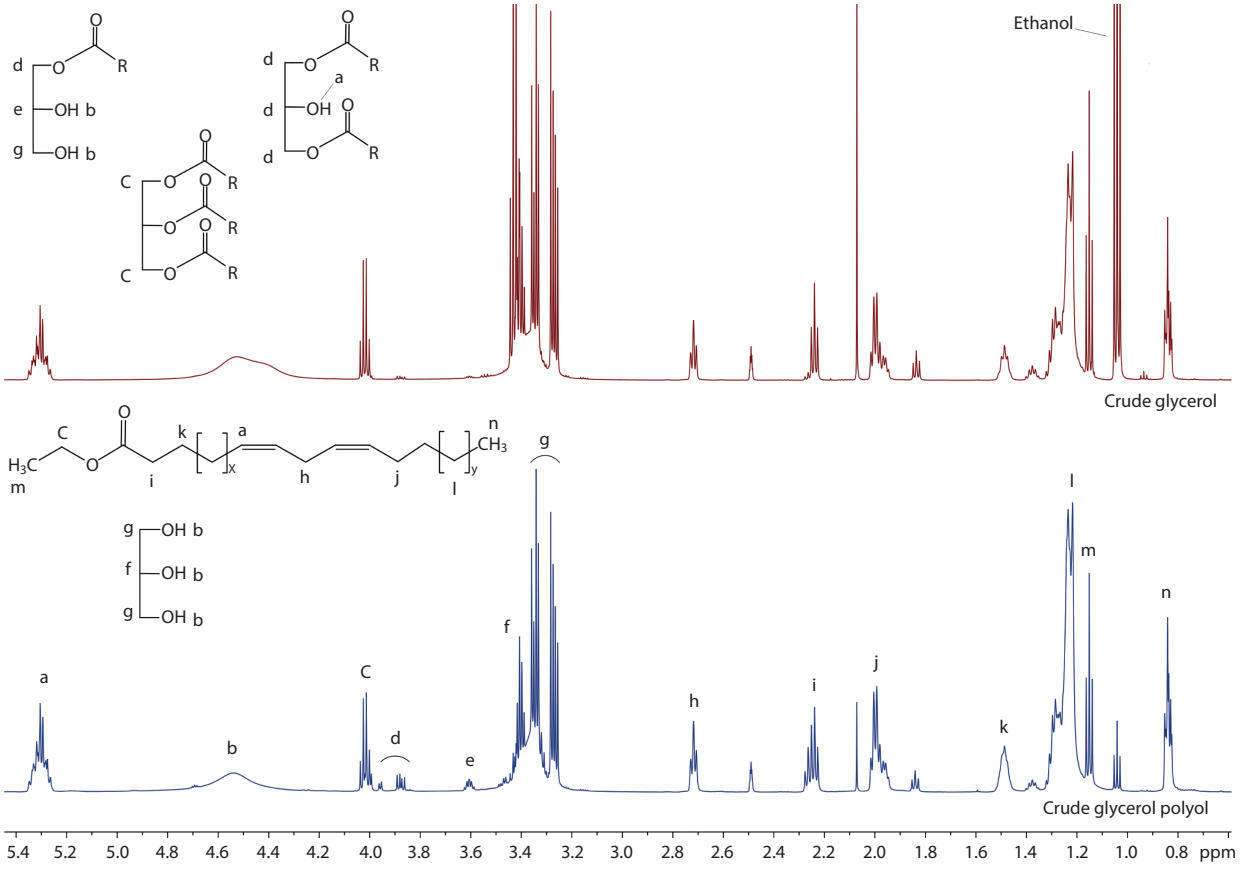

Figure 3 [1]H NMR spectra and signal assignment of crude glycerol and crude glycerol polyol.

3.60 ppm also assigned to MAG and DAG do increase slightly in the crude glycerol polyol.

Between 1.35–1.45 ppm in Figure 4 the spectra differ slightly among the crude glycerol polyol and each of the lignin polyols (liquid products referred to as polyols). This region was assigned to aliphatic protons both in lignin and fatty acids. The crude glycerol polyol and crude glycerol show a weak signal at 1.85 ppm, not present in the lignin polyols**.** In this area, acetyl protons of acetic acid in DMSO-d_6 exhibit a signal at 1.91 ppm [39]. At 2.05 ppm the organosolv lignin polyol exhibits a triplet not visible in the kraft lignin and lignosulphonate polyols. Similarly only the kraft lignin polyol exhibits a peak at 1.91 ppm. In this range the organosolv lignin and kraft lignin exhibited signals assigned to aliphatic protons adjacent to double bonds or carbonyl groups [33].

Changes in the spectra of the lignin polyols are similar to those in the crude glycerol polyol at 1.04, 1.15, 4.0 and 4.5 ppm discussed above. Between 3.2–3.5 ppm intensities differ among the polyols, indicating variation in content of glycerol, MAG and DAG. At 4.5 ppm the broad peak changes in position and width in all the spectra, which indicates differences in OH type and content [9]. Low intensity signals not visible in the crude glycerol polyol and crude glycerol appear in the organosolv lignin polyol between 6.0–8.5 ppm. Lignin signals in this region were assigned to *p*-hydroxyphenyl, guaiacyl and syringyl unit aromatic protons. Weak signals are also visible around 6.6 ppm in the lignosulphonate polyol. Signals in the kraft lignin polyol are not distinguishable from noise in this region. Although the signals are weak, it shows that the organosolv lignin and lignosulphonate polyols have higher content of aromatic structures than the kraft lignin polyol.

In summary, the lignin polyols were found to possess varying levels of aromaticity imparted by lignin during liquefaction. The OH content also differs among the polyols. Glycerol OH content was found to reduce significantly during liquefaction along with FAEE ethoxy to a lesser extent.

3.2.1.2 Solid Product

Figure 5a shows an overlay of the crude glycerol, solid product of kraft lignin liquefaction and kraft lignin [1]H NMR spectra. The relative size of the broad peak in the kraft lignin between 6.6–6.9 ppm is reduced in the solid product, possibly due to removal of phenolic

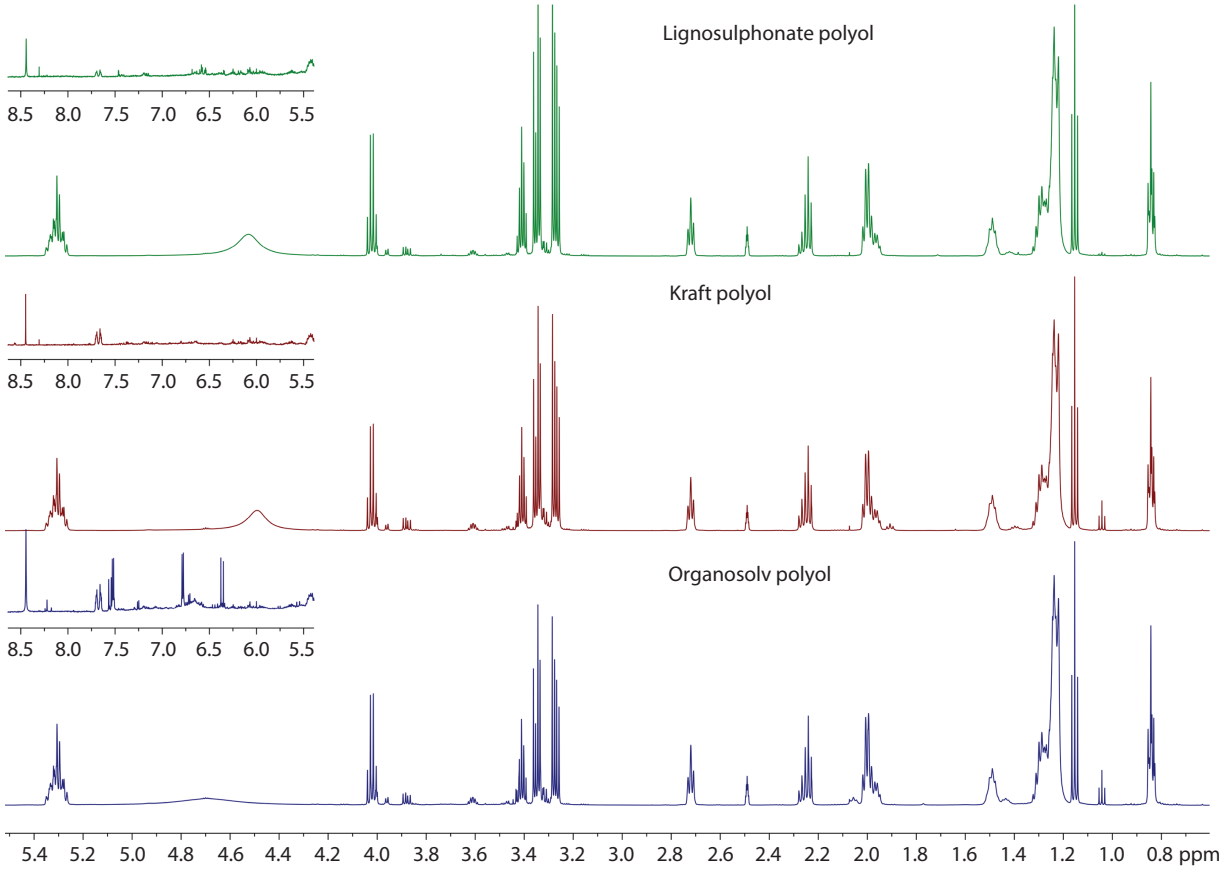

Figure 4 ^{1}H NMR spectra of lignosulphonate polyol, kraft lignin polyol and organosolv lignin polyol.

OH. At 5.3 ppm a signal appears in the product which is absent in the kraft lignin, corresponding with the crude glycerol signal assigned to olefenic protons. Centered around 4.45 ppm, the solid product shows a broad peak not present in the kraft lignin, but similar to a peak assigned to glycerol OH in the crude glycerol. Likewise, between 3.25–3.45 ppm intense signals arise which are not present in the kraft lignin. Corresponding signals in the crude glycerol are assigned to CH and CH_2 in glycerol, MAG and DAG. The kraft lignin therefore seems to have bound with glycerol. The methoxy signal intensity at 3.70 ppm is lowered in the solid product. Although the intensities are low, signals at 2.73 and 2.25 ppm appear in the product. Strong signals in these positions are assigned to divinyl and α-carbonyl methylene protons in the crude glycerol. Centered at 2.0 ppm a small peak appears in the product. A similar peak at 2.0 ppm in the crude glycerol was assigned to allyl methylene protons. The signal intensity of a peak at 1.24 ppm in the kraft lignin is increased in the product. Intense signals in the crude glycerol spectra in this area are assigned to methylene protons on saturated carbons. The product signal appearing at 0.85 ppm corresponds with terminal methyl proton signals in the crude glycerol spectra. The signals in the product at 5.3, 2.73, 2.25, 2.0, 1.24 and 0.85 ppm indicate the binding of fatty acid esters, MAG or DAG onto the kraft lignin macromolecules during liquefaction. The product signals arising due to introduction of glycerol are, however, more intense.

It is apparent from the overlay of the solid liquefaction products of the lignins (Figure 5b), that the signal assigned to glycerol OH around 4.5 ppm is absent in the spectra of the organosolv and lignosulphonate products. Both products do, however, exhibit similar peaks between 3.25–3.45 ppm to those in the kraft lignin product, although the intensities are clearly reduced. The reason for the absent signal at 4.5 ppm might be the removal of glycerol OH after glycerol is bound to lignin since the signals between 3.25–3.45 ppm are still present. Overall it does appear that glycerol is bound to kraft lignin to a greater extent.

Compared to the organosolv lignin, the *p*-hydrophenyl unit OH signal at 7.5 ppm is absent in the organosolv product, whereas the S and G unit phenolic OH signals are still present. This is possibly indicative of higher reactivity of the *p*-hydrophenyl unit OH,

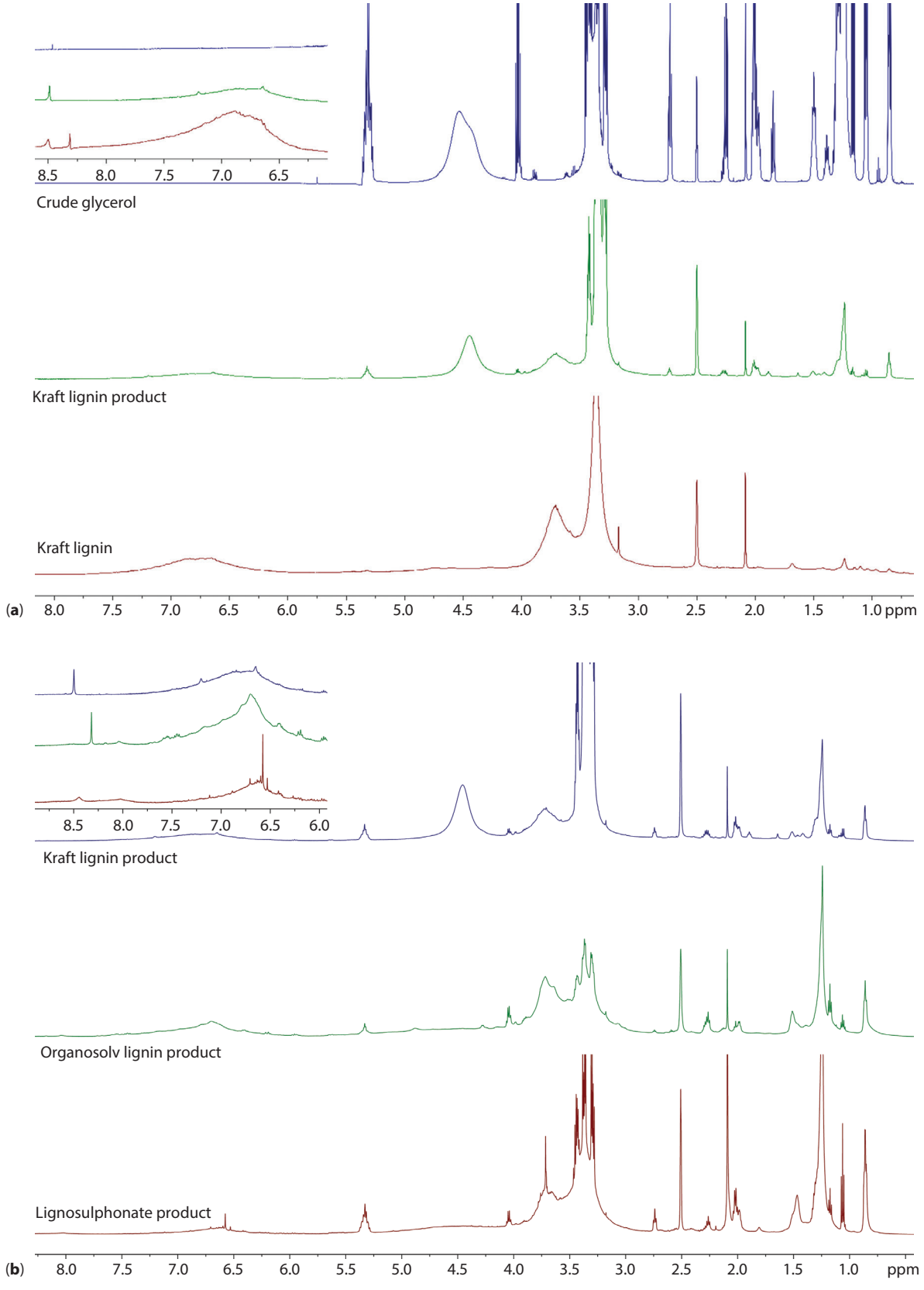

Figure 5 (**a**) ^{1}H NMR spectra of crude glycerol, kraft lignin solid product and kraft lignin. (**b**) ^{1}H NMR spectra of the solid lignin liquefaction products.

as discussed. In the other areas signals of the three solid products are similar.

3.2.2 *^{31}P NMR Spectroscopy of the Liquid Product*

3.2.2.1 Qualitative

Figure 6 (Table S4) shows an overlay of the polyol and crude glycerol ^{31}P NMR RII spectra and signal assignment [20, 27, 40] of characteristic peaks due to various acylglycerols. The polyols have similar signals, but the crude glycerol spectrum differs significantly in three areas. A sharp signal in the polyols at 146.44 ppm, which is almost absent in the crude glycerol spectra, is assigned to 1-monoacylglycerol (CH). At 146.65 ppm the intense ethanol signal [20] in the crude glycerol is absent in the polyols. The last major difference is the appearance of a signal at 147.67 ppm in the polyols, assigned to 1-monoacylglycerol (CH_2). DAG and 2-monoacylglycerols show weak signals only in the polyols, indicating limited formation of these compounds. The original lignin aliphatic signals are not visible in the spectra of the polyols. Signal intensities of the carboxylic acids around 134.73 ppm also differ among the polyols.

The most significant change during liquefaction, based on the aforementioned, is MAG formation through transesterification of glycerol and FAEE, as reported by Luo *et al.* [15]. That would correlate with the decrease in glycerol OH and FAEE content observed with ^{1}H NMR.

3.2.2.2 Quantitative

The values of OH content of the crude glycerol, crude glycerol polyol and lignin polyols determined with RII as well as according to ASTM D4274-11 are given in Table 3. It compares with the values reported by others for lignin-derived polyols determined with ^{31}P NMR which range between 3.1–8.7 mmol/g [11, 12]. The difference in the values of the lignin polyol OH contents determined by ^{31}P NMR using RII and titration after esterification with phthalic anhydride is between 0–5%. D'Souza *et al.* [9] prepared polyols through oxypropylation of bark and bark alkaline extract and found values determined by the two methods differed

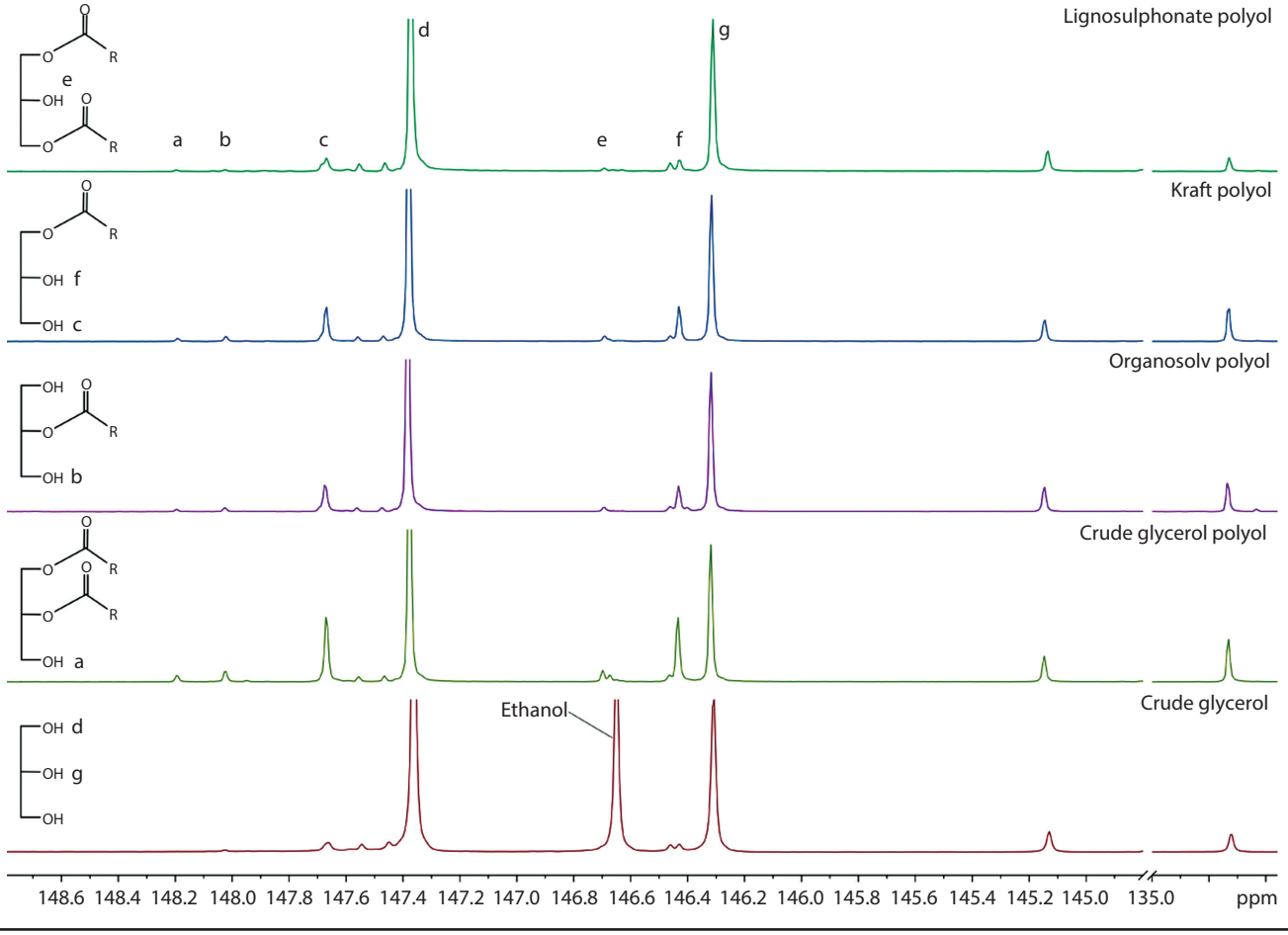

Figure 6 ^{31}P NMR RII spectra and signal assignment of the crude glycerol and polyols.

Table 3 Polyol (liquid product) and crude glycerol hydroxyl content (mmol/g, unless otherwise noted) determined by ^{31}P NMR spectroscopy and compared to the ASTM standard method.

OH type:	OP	KP	LP	CGP	CG
RII:					
Aliphatic	7.14	8.63	9.03	8.43	12.43
Phenolic	0.20	0.04	0.19	0.09	0.06
Carboxylic acids	0.40	0.50	0.20	0.58	0.40
Total:	7.75	9.17	9.42	9.09	12.89
Total excl. ethanol OH					9.67 ± 0.27[a]
Total (mg KOH/g)	435	515	529	510	723
ASTM D4274-11 (mg KOH/g)	436	491 ± 15	555 ± 54	466 ± 17	758 ± 13
RI:					
Primary/Secondary	2.1	1.7	2.3	1.2	2.4

[a]95 % Confidence interval based on triplicate analysis.
OP: Organosolv lignin polyol; KP: Kraft lignin polyol; LP: Lignosulphonate polyol; CGP: Crude glycerol polyol; CG: Crude glycerol.

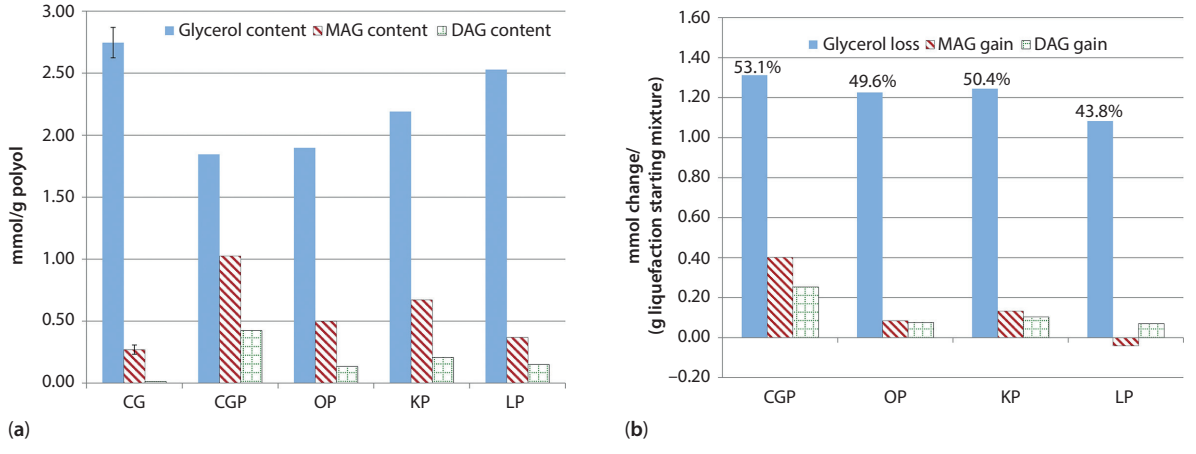

Figure 7 (**a**) Comparison of the crude glycerol and polyol compositions determined with ^{31}P NMR RII, (CG: crude glycerol, CGP: crude glycerol polyol, OP: organosolv polyol, KP: kraft polyol, LP: lignosulphonate polyol). (**b**) Change in the original crude glycerol components during liquefaction determined by ^{31}P NMR RII. Loss of glycerol is also given as a percentage of the original content. The CGP, OP, KP and LP had secondary/primary OH ratios of 0.81, 0.48, 0.59 and 0.43, respectively.

by 8–13%, similar to the results of this study. The OH contents of the polyols fall in the range of values suitable for rigid polyurethane foam preparation [8].

It is important to note that the lignin polyols almost exclusively contained aliphatic OH, similar to polyols obtained with PEG/glycerol liquefaction and base catalyzed oxypropylation [9]. The original phenolic groups of lignin as well as any phenolic groups liberated during liquefaction through lignin interunit bond cleavage were therefore not markedly retained in the polyols, but were rather consumed by reaction. Furthermore, obtaining high phenolic OH content in the polyols is not expected, because of the high solvent/lignin ratio used in liquefaction. The ratios of primary/secondary OH (Table 3) indicate that the polyols contain significant content of both primary and secondary OH. It can be seen in Figure 6 that glycerol contributes the major fraction of OH content while MAG, which also contains both primary and secondary OH, contributes to a lesser extent. The primary/secondary OH ratios affect reaction kinetics between OH and isocyanate [9] and the variation in the value among the polyols is expected to impact subsequent polyurethane foam preparation.

3.2.3 *Polyol Composition Comparison*

The free glycerol content of the crude glycerol was determined according to AOCS Official Method Ca 14-56 and compared to the ^{31}P NMR RII results. Values of 24.8 and 25.3 wt% were obtained with the respective methods. Figure 7a displays a comparison of the

crude glycerol and polyol compositions based on the signal assignment in Figure 6 (Table S4). A comparison of the absolute change in the crude glycerol constituents during liquefaction is given in Figure 7b. Change is expressed as increase or decrease in mmol of glycerol, MAG and DAG based on starting with 1 gram reaction mixture and taking into account the polyol yield obtained for each lignin type. DAG content in the crude glycerol and DAG gains are only an estimate since a 1,2-diacylglycerol signal at 146.7 ppm would be overlapped by the intense ethanol signal in the crude glycerol. FAEE content of the crude glycerol measured by GC was found to be 27.2 wt%. (Table S5).

The molar increase in MAG and DAG content for each of the polyols are substantially lower than glycerol loss and therefore their formation through transesterification of glycerol with FAEE would only partly contribute to the total loss in glycerol. The lignosulphonate polyol even showed a loss in MAG content. A major fraction of the glycerol OH is therefore removed via other routes. ^{1}H NMR spectra did not indicate significant changes in TAG contents. Based on the ^{1}H NMR analysis (Figures 3–5), glycerol loss was also caused by reaction with lignin OH. In the case of lignin binding at only one or two OH groups per glycerol molecule, ^{31}P NMR signals could arise in new areas or new signals might coincide with the MAG and DAG signals. Signals in new areas were not observed in the polyols (Figure 6). If lignin is bound at all three glycerol OH groups no signals would arise for the new compounds.

The crude glycerol polyol underwent greater gain in MAG and DAG content than the lignin polyols, which helps to affirm the reaction between lignin and glycerol as well as the impact lignin has on the liquefaction product properties. If lignin is additionally bound with FAEE through transesterification during liquefaction it would also lower MAG and DAG formation. Esterification reactions with ethylene glycol during lignin liquefaction have been reported by Jasiukaitytė-Grojzdek *et al.* [14]. Furthermore, the primary/secondary OH ratios (Table 3) of the polyols decrease as glycerol loss increases, indicating possible preferential reaction at primary OH of glycerol. The two quantities were determined independently with RI and RII.

Liquefaction of kraft lignin and organosolv lignin resulted in greater glycerol loss than lignosulphonate, despite the higher aliphatic OH content in the lignosulphonate. As discussed, the organosolv lignin did have higher *p*-hydroxyphenyl unit content, which is expected to impart higher reactivity. The higher phenolic OH content of the kraft lignin did not lower the observed reactivity with glycerol. It is expected that the polyol crosslinking density would be higher within the kraft lignin and organosolv lignin polyols based on increased bonding with glycerol. Higher crosslinking densities in the polyols would subsequently impact the mechanical and thermal properties of polyurethane foam, as mentioned in the introduction. It is therefore important to consider the effect on lignin properties when selecting isolation methods for industrial processes if the lignin is to be valorized.

4 CONCLUSIONS

Liquefaction of lignin in crude glycerol yields a liquid product containing mostly aliphatic OH and the total OH content is similar to that of lignin-derived polyols prepared with PEG or propylene oxide, suitable for rigid polyurethane foam applications. During lignin liquefaction the largest fraction of glycerol loss is concluded to have occurred through reaction with lignin followed by formation of MAG with FAEE. Based on the ^{1}H NMR analysis the solid liquefaction products consisted of lignin modified with glycerol and fatty acids. The degree of functionality differed among the three lignin products. The liquid and solid phase products are to be used as polyol without prior separation to prepare polyurethane foam [18].

Different technical lignins each yield polyols with unique compositions and structures, which differed from polyols prepared by sole crude glycerol liquefaction, and careful selection of lignin isolation methods are therefore necessary at industrial scale. ^{31}P NMR spectroscopy enabled the quantification of different constituents of crude glycerol before and after liquefaction, which helps to determine the reactions which occur.

ACKNOWLEDGMENTS

The financial assistance of the National Research Foundation (NRF) towards this research is hereby acknowledged. Opinions expressed and conclusions arrived at are those of the authors and are not necessarily to be attributed to the NRF. The authors would like to thank Mr. André Joubert and Dr. Johan Jordaan from the Laboratory for Analytical Services of the North-West University (NWU) for recording the NMR data and offering helpful discussions, as well as Dr. Louwrens Tiedt from the Laboratory for Electron Microscopy (NWU) for recording the EDS data and Dr. Roelf Venter for his advice on characterizing crude glycerol.

REFERENCES

1. A. Duval and M. Lawoko, A review on lignin-based polymeric, micro- and nano-structured materials. *React. Funct. Polym.* **85**, 78–96 (2014).
2. A. Llevot, P.-K. Dannecker, M. von Czapiewski, L.C. Over, Z. Söyler, and M.A.R. Meier, Renewability is

not enough: Recent advances in the sustainable synthesis of biomass-derived monomers and polymers. *Chem. Eur. J.* **22**, 11510–11521 (2016).
3. A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, *et al.*, Lignin valorization: Improving lignin processing in the biorefinery. *Science* **344**(6185) (2014).
4. A. Gandini and T.M. Lacerda, From monomers to polymers from renewable resources: Recent advances. *Prog. Polym. Sci.* **48**, 1–39 (2015).
5. B. Ahvazi, O. Wojciechowicz, T.M. Ton-That, and J. Hawari, Preparation of lignopolyols from wheat straw soda lignin. *J. Agric. Food Chem.* **59**(19), 10505–10516 (2011).
6. C.A. Cateto, M.F. Barreiro, A.E. Rodrigues, and M.N. Belgacem, Kinetic study of the formation of lignin-based polyurethanes in bulk. *React. Funct. Polym.* **71**(8), 863–869 (2011).
7. D.V. Evtuguin, J.P. Andreolety, and A. Gandini, Polyurethanes based on oxygen-organosolv lignin. *Eur. Polym. J.* **34**(8), 1163–1169 (1998).
8. C.A. Cateto, M.F. Barreiro, A.E. Rodrigues, and M.N. Belgacem, Optimization study of lignin oxypropylation in view of the preparation of polyurethane rigid foams. *Ind. Eng. Chem. Res.* **48**(5), 2583–2589 (2009).
9. J. D'Souza, B. George, R. Camargo, and N. Yan, Synthesis and characterization of bio-polyols through the oxypropylation of bark and alkaline extracts of bark. *Ind. Crops. Prod.* **76**, 1–11 (2015).
10. H. Nadji, C. Bruzzese, M.N. Belgacem, A. Benaboura, and A. Gandini, Oxypropylation of lignins and preparation of rigid polyurethane foams from the ensuing polyols. *Macromol. Mater. Eng.* **290**(10), 1009–1016 (2005).
11. B.L. Xue, J.L. Wen, and R.C. Sun, Producing lignin-based polyols through microwave-assisted liquefaction for rigid polyurethane foam production. *Materials* **8**(2), 586–599 (2015).
12. B.L. Xue, J.L. Wen, F. Xu, and R.C. Sun, Polyols production by chemical modification of autocatalyzed ethanol-water lignin from *Betula alnoides*. *J. Appl. Polym. Sci.* **129**(1), 434–442 (2013).
13. E. Jasiukaitytė, M. Kunaver, and C. Crestini, Lignin behaviour during wood liquefaction-characterization by quantitative ^{31}P, ^{13}C NMR and size-exclusion chromatography. *Catal. Today* **156**(1–2), 23–30 (2010).
14. E. Jasiukaitytė-Grojzdek, M. Kunaver, and C. Crestini, Lignin structural changes during liquefaction in acidified ethylene glycol. *J. Wood Chem. Technol.* **32**(4), 342–360 (2012).
15. X.L. Luo, S.J. Hu, X. Zhang, and Y.B. Li, Thermochemical conversion of crude glycerol to biopolyols for the production of polyurethane foams. *Bioresour. Technol.* **139**, 323–329 (2013).
16. J.H. Lee, J.H. Lee, D.K. Kim, C.H. Park, J.H. Yu, and E.Y. Lee, Crude glycerol-mediated liquefaction of empty fruit bunches saccharification residues for preparation of biopolyurethane. *J. Ind. Eng. Chem.* **34**, 157–164 (2016).
17. Y. Wang, Wu, J., Wan, Y., Lei, H., Yu, F., Chen, P. *et al.*, Liquefaction of corn stover using industrial biodiesel glycerol. *Int. J. Agric. Biol. Eng.* **2**(2), 32–40 (2009).
18. L. Muller, S. Marx, I. Chiyanzu, and H. Vosloo, Preparation of polyurethane from lignin and crude glycerol, in *Setting the Course for a Biobased Economy: Proceedings of the 23rd European Biomass Conference, Vienna, Austria, June 1–4, 2015*, I. Obernberger, D. Baxter, A. Grassi, and P. Helm (Eds.), pp. 1070–1074, ETA-Florence Renewable Energies, Florence (2015).
19. M. Balakshin and E. Capanema, On the quantification of lignin hydroxyl groups with ^{31}P and ^{13}C NMR spectroscopy. *J. Wood Chem. Technol.* **35**(3), 220–237 (2015).
20. M. Nagy, B.J. Kerr, C.J. Ziemer, and A.J. Ragauskas, Phosphitylation and quantitative ^{31}P NMR analysis of partially substituted biodiesel glycerols. *Fuel* **88**(9), 1793–1797 (2009).
21. A. Granata and D.S. Argyropoulos, 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a reagent for the accurate determination of the uncondensed and condensed phenolic moieties in lignins. *J. Agric. Food Chem.* **43**(6), 1538–1544 (1995).
22. C.A. Cateto, M.F. Barreiro, A.E. Rodrigues, M.C. Brochier-Solan, W. Thielemans, and M.N. Belgacem, Lignins as macromonomers for polyurethane synthesis: A comparative study on hydroxyl group determination. *J. Appl. Polym. Sci.* **109**(5), 3008–3017 (2008).
23. F. Xu, J.X. Sun, R.C. Sun, P. Fowler, and M.S. Baird, Comparative study of organosolv lignins from wheat straw. *Ind. Crops Prod.* **23**(2), 180–193 (2006).
24. Y.C. Sun, J.L. Wen, F. Xu, and R.C. Sun, Fractional and structural characterization of organosolv and alkaline lignins from *Tamarix austromogoliac*. *Sci. Res. Essays* **5**(24), 3850–3864 (2010).
25. D.S. Argyropoulos, Quantitative phosphorus-31 NMR analysis of lignins, a new tool for the lignin chemist. *J. Wood Chem. Technol.* **14**(1), 45–63 (1994).
26. W. Hoareau, W.G. Trindade, B. Siegmund, A. Castellan, and E. Frollini, Sugar cane bagasse and curaua lignins oxidized by chlorine dioxide and reacted with furfuryl alcohol: characterization and stability. *Polym. Degrad. Stab.* **86**(3), 567–576 (2004).
27. S. Christophoridou and P. Dais, Novel approach to the detection and quantification of phenolic compounds in olive oil based on ^{31}P nuclear magnetic resonance spectroscopy. *J. Agric. Food Chem.* **54**(3), 656–664 (2006).
28. M.G. Chua and M. Wayman, Characterization of autohydrolysis aspen (P. tremuloides) lignins. Part 1. Composition and molecular weight distribution of extracted autohydrolysis lignin. *Can. J. Chem.* **57**(10), 1141–1149 (1979).
29. S. Baumberger, A. Abaecherli, M. Fasching, G. Gellerstedt, R. Gosselink, B. Hortling, J. Li, B. Saake, and E. De Jong, Molar mass determination of lignins by size-exclusion chromatography: Towards standardisation of the method. Holzforschung **61**(4), 459–468 (2007).
30. A. Tejado, C. Pena, J. Labidi, J.M. Echeverria, and I. Mondragon, Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis. *Bioresour. Technol.* **98**(8), 1655–1663 (2007).
31. M. Baucher, B. Monties, M. Van Montagu, and W. Boerjan, Biosynthesis and genetic engineering of lignin. *Crit. Rev. Plant Sci.* **17**(2), 125–197 (1998).

32. C. Fernandez-Costas, S. Gouveia, M.A. Sanroman, and D. Moldes, Structural characterization of kraft lignins from different spent cooking liquors by 1D and 2D nuclear magnetic resonance spectroscopy. *Biomass Bioenergy* **63**, 156–166 (2014).
33. R. Marchessault, S. Coulombe, H. Morikawa, and D. Robert, Characterization of aspen exploded wood lignin. *Can. J. Chem.* **60**(18), 2372–2382 (1982).
34. Y. Miyake, K. Yokomizo, and N. Matsuzaki, Determination of unsaturated fatty acid composition by high-resolution nuclear magnetic resonance spectroscopy. *J. Am. Oil Chem. Soc.* **75**(9), 1091–1094 (1998).
35. Z. Sustere, R. Kampare, E. Liepins, and V. Kampars, The composition of commercial acetylated glycerol samples determined by ^{13}C and ^{1}H NMR. The comparison with gas chromatography. *J. Anal. Chem.* **69**(8), 763–768 (2014).
36. B. Nebel, M. Mittelbach, and G. Uray, Determination of the composition of acetylglycerol mixtures by ^{1}H NMR followed by GC investigation. *Anal. Chem.* **80**(22), 8712–8716 (2008).
37. M.R. Monteiro, A.R.P. Ambrozin, L.M. Liao, and A.G. Ferreira, Determination of biodiesel blend levels in different diesel samples by ^{1}H NMR. *Fuel* **88**(4), 691–696 (2009).
38. R. Guzatto, D. Defferrari, Q.B. Reiznautt, I.R. Cadore, and D. Samios, Transesterification double step process modification for ethyl ester biodiesel production from vegetable and waste oils. *Fuel* **92**(1), 197–203 (2012).
39. H.E. Gottlieb, V. Kotlyar, and A. Nudelman, NMR chemical shifts of common laboratory solvents as trace impurities. *J. Org. Chem.* **62**(21), 7512–7515 (1997).
40. A. Spyros and P. Dais, Application of ^{31}P NMR spectroscopy in food analysis. 1. Quantitative determination of the mono- and diglyceride composition of olive oils. *J. Agric. Food Chem.* **48**(3), 802–805 (2000).

Supplementary Document Available Online

http://www.scrivenerpublishing.com/journalsuppl/jrm/JRM-2016-0041/jrm_JRM-2016-0041_supp1.docx