

Preparation of polyurethane foam from lignin and crude glycerol

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PREFACE

Thesis format

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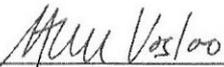
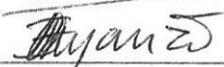
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The co-authors hereby grant permission according to 5.4.2.8 above, with regards to the below list of publications:

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Prof. S Marx proposed the project and was involved from start to end in the design of the study, interpretation of results and review of the manuscripts and thesis. Prof. HCM Vosloo was involved in the interpretation of the results and review of the manuscripts and thesis. Dr. I Chiyanzu and Prof. E Fosso-Kankeu were involved in the initial design of the study and review of the manuscripts as per the above list.

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ABSTRACT

The development and implementation of lignocellulose-based biorefineries which produce renewable fuels, chemicals and pharmaceuticals are expected to grow, but still face technological challenges. Economic feasibility could be improved through the optimization of feedstock utilisation and in this work a method is proposed and demonstrated which utilise two by-product streams from an integrated biorefinery concept to produce a higher value product.

More specifically the study focused on the preparation of biobased products rich in hydroxyl groups which could be used as polyols for polyurethane preparation. The process entails lignin liquefaction in crude glycerol. Lignin is viewed as a potentially high volume by-product of future biorefineries and is an existing by-product of the pulp and paper industry. Crude glycerol is a by-product of conventional biodiesel preparation through transesterification of fats and oils with alcohols.

In this work crude glycerol was prepared from ethanol and sunflower oil and used in the liquefaction of three technical lignins, i.e. softwood kraft lignin, hardwood lignosulphonate and organosolv lignin from sugarcane bagasse. The lignin structure differs, depending on the source and isolation method and was expected to influence product properties. ^1H and ^{31}P NMR spectroscopy was used to study the lignins, with ^{31}P NMR specifically capable of quantifying hydroxyl groups. The solid phase liquefaction products differed in degree of functionality while the liquid phase composition varied. The glycerol and fatty acid ethyl ester (FAEE) contents were reduced, while the monoacylglycerol (MAG) and diacylglycerol contents were also altered in the liquid phase.

From size-exclusion chromatography (SEC) and NMR results it was concluded that the modification of lignin was to some extent correlated with the ratio of aliphatic and phenolic hydroxyl group contents in lignin, as well as MAG and glycerol reduction during liquefaction. Higher molar mass lignin derivatives were detected with SEC in the organosolv lignin liquid phase product, supported by NMR and FTIR observations.

The solid phase products showed an increase of ether and ester bonds, as well as aliphatic content relative to that in lignin, both with FTIR and ^1H NMR spectroscopy. It was concluded that the solid phase products consisted of lignin derivatives functionalised with glycerol, MAG and FAEE.

The liquefaction products had hydroxyl contents similar to commercial polyurethane polyols and urethane bond formation through reaction with diphenylmethane-4,4'-diisocyanate was confirmed with FTIR. The product of each respective lignin was used as the sole polyol

component to prepare rigid polyurethane foam (PUF) and the variation in material and thermal properties revealed the influence of the lignin type. The biobased contents of the prepared foams were as high as 55 wt%. The thermal conductivity and compressive strength of the kraft lignin-based foams were superior with values of $0.039 \text{ W m}^{-1} \text{ K}^{-1}$ and 345 kPa. An evaluation of the biodegradability in soil of the prepared PUF and commercial petroleum-derived PUF, over a 30 month period, did not reveal significant differences in degradation. Based on the properties of the foams it is concluded that the proposed strategy can be a viable valorisation route for these by-products in biorefineries and feasibility should be further evaluated.

Keywords: lignin, kraft, organosolv, liginosulphonate, crude glycerol, polyurethane foam, polyol, SEC

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CHAPTER 1 INTRODUCTION

1.1 BACKGROUND - BIOREFINERY

The move to mitigate climate change by lowering greenhouse gas emissions has been strengthened by the enforcement of the 2015 United Nations Paris Agreement. Therefore, biofuel implementation and production are set to expand along with the growing demand for transportation fuels.¹ Currently, the main biofuels in use for this purpose are first generation ethanol and biodiesel. Next generation fuels from lignocellulose are however viewed as more sustainable and the most promising solution for the near future.²⁻³ Biodiesel is currently viewed as the preferred renewable fuel option for heavy road transport, mining and shipping.¹ Economic feasibility of both cellulosic ethanol and biodiesel production is however a problem and currently receive subsidies in many areas. There are further also justified concerns over 1st and 2nd generation biofuels use in terms of food security, deforestation and uncertainty in greenhouse gas emission benefits associated with land use change.⁴⁻⁶ This adds to the necessity to, along with development in biotechnology for next generation biofuels, optimize both the efficiency of 1st and 2nd generation biofuel production processes and utilisation of current feedstock in integrated biorefineries.^{5,7-8}

In line with the increased use of biofuels there is general agreement on the need for a move towards materials and chemicals derived from sustainable sources such as biomass, due to environmental concerns and eventual depletion of fossil fuel reserves.⁹⁻¹⁰ The function of biorefineries is described as “the sustainable processing of biomass into a spectrum of biobased products and bioenergy”.¹¹ Speciality biobased products of high value are seen as potentially crucial sources of revenue for future biorefineries.^{5,7,10}

A recent review of by-products from sustainable biorefinery concepts discusses the importance and potential of biomass-based high-value low-volume by-products, not easily prepared from petroleum feedstocks, to improve the economic feasibility of biofuel or bioenergy production. A number of case studies were discussed.⁷ In one Vlysidis et al. studied production of biodiesel through transesterification as the main product, combined with succinic acid as a by-product of fermentation of glycerol. By-product production was found to increase profits up to 60% compared to only producing fuel, although profitability was found to be highly dependent on feedstock and product prices at the time.¹² Moncada et al. studied a lignocellulose (bark) biorefinery producing cellulosic ethanol and as by-products: furfural and electricity. Furfural was produced from pentose hydrolysis. Saccharification residues, rich in lignin, were used as fuel to generate electricity and steam. Electricity and steam generation reduced production cost by 66% and reduced the environmental impact. Annual revenues from furfural and ethanol were

54% and 38%, respectively.¹³ These studies illustrate the importance of optimal utilization of feedstocks.

This work proposes an unexplored method to valorise low value by-products from an integrated biorefinery concept. In such a biorefinery, biofuel or biobased products from lignocellulose would yield a lignin-rich by-product stream. Simultaneously biodiesel production from waste oil, fats, seed crops or algae through transesterification would yield crude glycerol as a low value by-product. The proposed method would then utilise the lignin rich by-product and crude glycerol to produce a higher value product intended as reagent for polyurethane foam preparation with the aim to increase revenues for a biorefinery.

1.2 LIGNIN

The importance of lignin in the biorefinery context is evident from a number of reviews on lignin valorisation.¹⁴⁻¹⁷ Recently Rinaldi et al. presented an exhaustive discussion on the state of the art.¹⁸ It is indicated that annually over 130 million tons of lignin are liberated by the pulp and paper industry alone and that a cellulosic ethanol biorefinery could isolate lignin at 0.5–1.5 kg [kg ethanol]⁻¹. The lignin would be more than what is required for the refinery's power generation.¹⁸⁻¹⁹ Researchers therefore propose that the most feasible utilization strategies for lignin in future refineries would comprise conversion into both high value and lower value applications, depending on demand. This includes pharmaceuticals, chemicals, fuels and materials.

Industrially lignin is mainly produced in kraft pulping where it is used for steam and power generation.^{18,20} Lignosulphonate is a by-product of sulphite pulping and although sulphite pulping only accounts for a small fraction of the total industry its lignin is not employed as fuel at the mills. Lignosulphonate is the major lignin type isolated for commercial purposes with the annual production given at approximately 1 million tonnes.²⁰⁻²¹ Organosolv pulping is only employed at demonstration scale according to literature and was developed as an alternative method with less negative environmental impacts. The process yields lignin that is of comparatively higher purity, less condensed, but is said to contain more phenolic hydroxyl groups due to bond cleavage. Organosolv process severity does however vary amongst methods.^{18,21-22} Organosolv methods are viewed as potentially important for lignocellulose biorefineries based on attributes like process flexibility and efficient separation.^{19,21}

Figure 1.1a shows the three monolignols which are the primary monomers from which native lignin forms.^{19,23} Following the biosynthesis of monolignols from phenyl alanine or tyrosine, lignification occurs by enzymatic radicalisation and non-enzymatic radical coupling of the

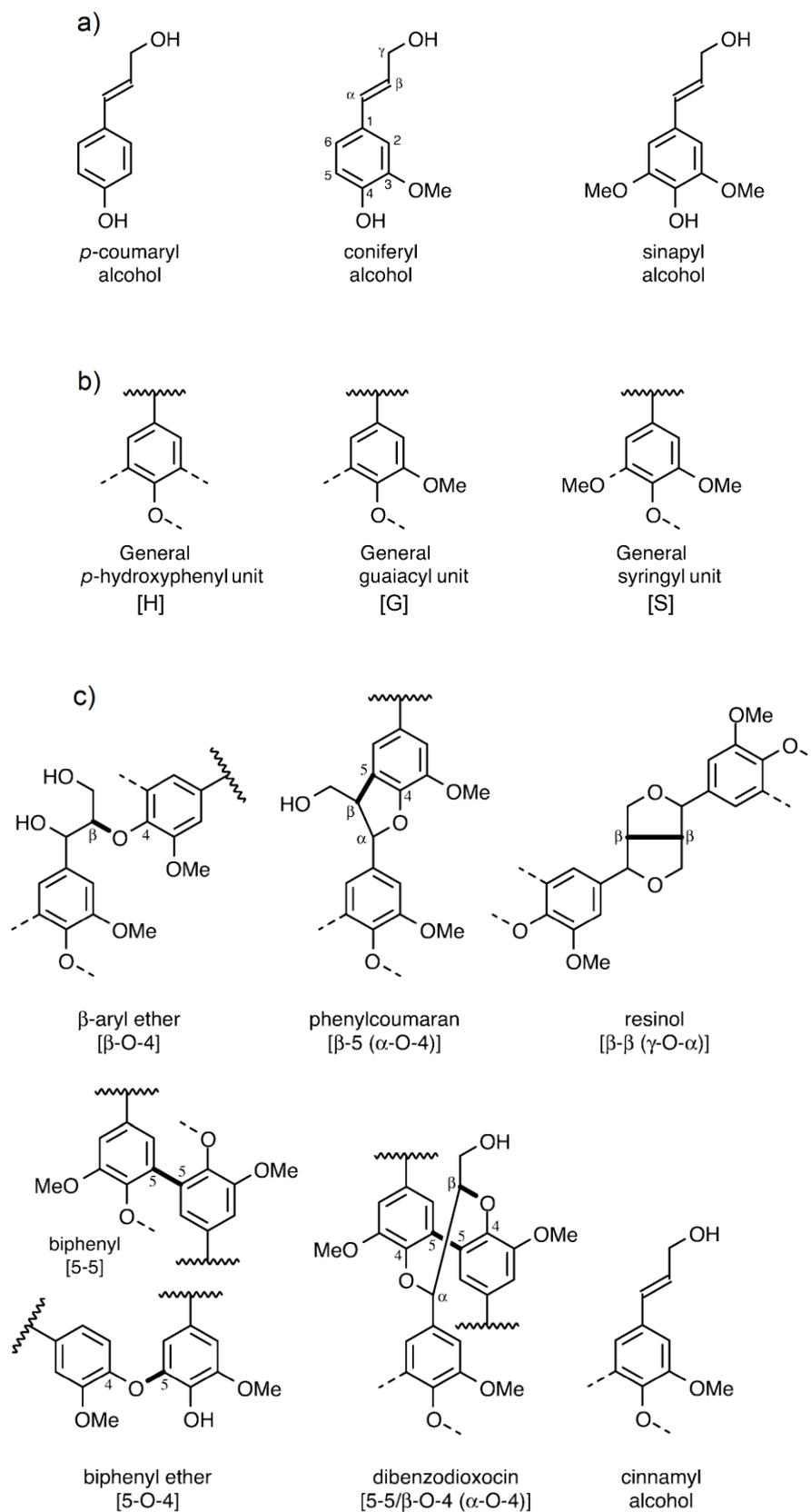


Figure 1.1: Monolignins (a), lignin polymer units (b) and characteristic structural units (c). (Adapted from Ralph et al.²³)

monolignols onto the growing polymer and forms the three respective polymer units (Figure 1.1b): *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S).^{18,23-24}

Polymerisation does not occur in a specific sequence and results in a complex and heterogeneous macromolecular structure with characteristic interunit linkages, some shown in Figure 1.1c. The monolignols are not the only monomers partaking in lignification.^{18,23} Lignin and its biosynthesis has been well defined and illustrated.^{18,23,25}

Technical lignins refer to lignin isolated from lignocellulose which can have roughly 15-40% native lignin content.^{19-20,26} Pulping or pretreatment is employed to isolate technical lignin, resulting in depolymerisation, “creating new free-phenolic” and “side chain end groups”, oxidation of side chains, degradation of their end groups and condensation.^{18,23} Technical lignins differ in structure and purity based on their isolation method and source.^{22,26}

1.3 BIODIESEL CRUDE GLYCEROL

In 2016 biodiesel consumption in the U.S. was approximately 2 billion U.S. gallons, with the majority derived from soybean oil as feedstock.²⁷⁻²⁸ Annual production growth between 2005 and 2015 was about 23%, and continued to grow despite the fall in more recent crude oil prices. Diesel use in transportation is increasing relative to petrol or gasoline and the trend is expected to continue.²⁹ The traditional biodiesel production method is transesterification of vegetable oil, algae oil or fat (triacylglycerols or TAG) with an alcohol (Figure 1.2). Crude glycerol is produced as by-product at about 1 kg per 10 kg biodiesel.³⁰⁻³¹ Data is limited but one source forecasts that Europe will consume 1.19 million tons glycerol by 2022 with the majority biodiesel-derived. In 2015 personal care products and pharmaceuticals took up 38% of the total glycerol consumption.³² Recent prices for crude glycerol and refined glycerol of € 290-390 ton⁻¹ (80 wt% purity) and € 650-700 ton⁻¹ (99.5 wt%) are reported.³³⁻³⁵ Crude glycerol is generated in high volumes and its valorisation is seen as beneficial to producers. In this work unrefined crude glycerol was used (about 25 wt% purity), intended as unprocessed by-product to demonstrate maximum potential benefit. Although alternative biomass-based diesel production methods are in use which can eliminate crude glycerol generation, glycerol volumes from biodiesel production is still expected to grow.³⁶

Crude glycerol has a low value due to the impurities which vary between producers. Impurities include water, alcohol, catalysts/salts, unreacted oil, monoacylglycerol (MAG), diacylglycerol (DAG), soap, free fatty acids and biodiesel.^{31,37-38} Conventionally, crude glycerol is refined to higher purities and, depending on the feedstock, can find application in chemicals, pharmaceuticals or food production.³⁶⁻³⁷ Due to the cost of purifying crude glycerol and the high supply, there have been many alternative valorisation strategies investigated. The ideal is to

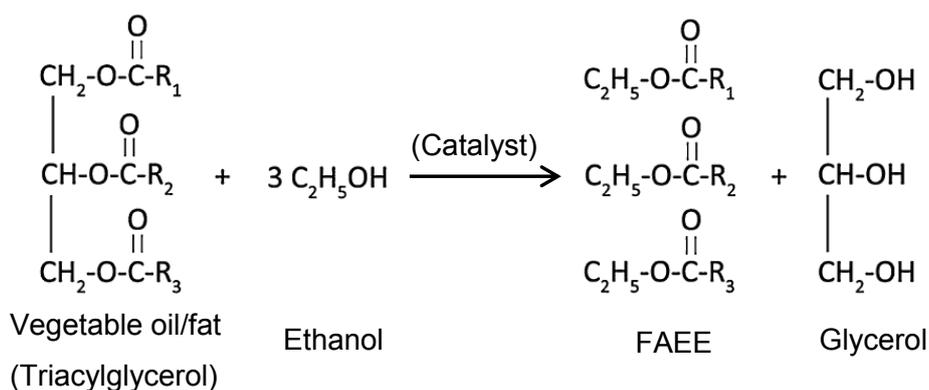


Figure 1.2: Biodiesel preparation through transesterification of triacylglycerol with ethanol to yield glycerol and fatty acid ethyl esters (FAEE). (Adapted from Sreedhar and Kishan³⁹).

minimize the processing costs by directly converting unrefined glycerol into higher value products. In recent reviews, Luo et al. discussed a number of chemicals which can be produced chemically or biologically,³⁷ while He et al. focused on renewable energy generation from crude glycerol by means of different conversion methods.³⁶

1.4 POLYURETHANE FOAM

Polyurethane is a versatile polymer with a wide range of applications in various industries. Commercial development started in the 40s.⁴⁰ Urethane bonds are formed by the reaction of isocyanate with hydroxyl groups. Urethane polymers, polyurethane, are formed through the reaction of diisocyanates and diols or polyols (Figure 1.3).⁴¹ Polyols refer to a chemical reagent used to prepare polyurethane and it typically has 2–8 hydroxyl groups and a molar mass of 200–8000 g mol⁻¹.⁴² Polyurethane comes in different forms. These can be divided into foams and solids. Foams will include rigid and flexible foams and solids: elastomers, coatings, adhesives etc.⁴⁰ In 2000 the global polyurethanes market comprised 9.3 million tonnes of which 23% was rigid and semi-rigid foams.⁴³ The main application of rigid foam is as insulation material in the construction and refrigeration industries because of its low thermal conductivity.⁴⁴ The need for energy conservation makes insulation in the building sector increasingly important.⁴⁵

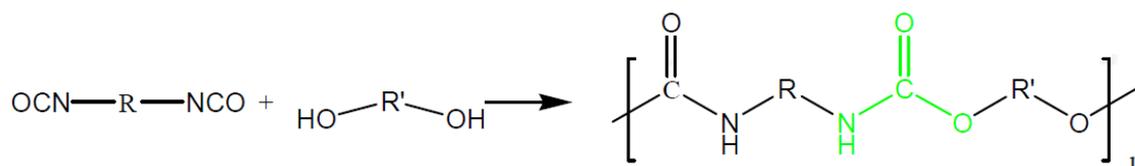


Figure 1.3: Reaction of a diisocyanate with a diol or polyol to form polyurethane. (Adapted from Sharmin and Zafar⁴⁶).

1.5 POLYURETHANE POLYOLS FROM BIOMASS

It has often been reported that lignocellulose could be thermochemically converted to polyols effective in polyurethane preparation through a liquefaction reaction, due to its high hydroxyl content.⁴⁷⁻⁴⁸ The process involves heating lignocellulose in a liquefaction solvent with a catalyst, for a specific duration. A liquid product rich in hydroxyl groups is desired. Hu et al. explained the process as degradation of biomass into lower molar mass (MM) derivatives or fragments by cleavage of chemical bonds. The biomass derivatives can then bond among themselves or with the solvent molecules to yield polyols or insoluble residues.⁴⁹ Jin et al. state that during liquefaction of lignin derived from enzymatic hydrolysis, in a mixture of polyethylene glycol (PEG) and glycerol, lignin is firstly fragmented which lowers its MM. Then the fragments bind through their hydroxyl groups with PEG and finally condensation occurs among the fragments to yield residues.⁵⁰ Various types of lignocellulose in combination with different solvents have been investigated and a summary of some studies is given in Table 1.1. Lignocellulose is seen as a viable feedstock due to wide availability, but there have also been many studies on employing lignin in polyurethane preparation. As discussed lignin is a by-product of the pulp and paper industry and its structure is also rich in hydroxyl groups.⁵¹⁻⁵² Lignin and cellulose have been found to behave differently during liquefaction,⁵³ but lignin has previously also yielded polyols suitable for polyurethane preparation.⁵⁴

Lignin is mostly employed by two approaches. It may be directly reacted with diisocyanate or it is often modified beforehand.^{21,55} As with PEG combined with glycerol (PEG/glycerol), propylene oxide as a modification reagent is often reported. Lignin reactivity with isocyanate has been shown to be dependent on lignin MM, hydroxyl group content (phenolic, primary and secondary aliphatic), source and isolation method.^{21,55-58} As an example, softwood kraft lignin was found to exhibit higher reactivity towards isocyanate than hardwood organosolv lignin, attributed to higher total and aliphatic hydroxyl group contents of the kraft lignin.⁵⁵ Recently, the same has been found in comparing reactivity of lignin fractions isolated from wheat straw with different organic solvents.⁵⁹

Table 1.1: Lignocellulose liquefaction in various reagents for polyol preparation.

Biomass	Solvent mixture	Hydroxyl number (mg KOH g ⁻¹)	MM	Reference
Wheat straw	PEG400 ^a /glycerol	250–430	1040–1950	Chen and Lu ⁶⁰
Cornstalk	PEG400/glycerol	335–365	1135–1425	Yan et al. ⁶¹
Alkaline lignin (cornstalk EHR ^b)	PEG/glycerol	191–409	-	Jin et al. ⁵⁰
Organosolv lignin (olive tree pruning)	PEG400/glycerol	176–821	-	Sequeiros et al. ⁶²
Corn stover	Crude glycerol	270–310	-	Wang et al. ⁶³
Soybean straw	Crude glycerol	440–540	-	Hu et al. ⁶⁴
Dried distillers grains	Ethylene carbonate	137–226	-	Yu et al. ⁶⁵
Sugarcane bagasse	EG ^c /phthalic anhydride	195–235	1524–2178	Nasar et al. ⁶⁶

^a PEG400 refers to PEG with a molar mass of 400 g mol⁻¹. ^b Enzymatic hydrolysis residue.

^c Ethylene glycol.

Modification through liquefaction or with propylene oxide is a means of improving the reactivity with isocyanate by replacing less reactive hydroxyl groups (such as phenolic groups) with aliphatic hydroxyl groups and also lowering steric hindrance. The introduction of aliphatic functionality further alters the lignin-based polyol properties and can, for instance, lower rigidity through decreased crosslink density in polyurethane.²¹ During modification with propylene oxide, lignin type has also been found to affect reactivity. In this regard Nadji et al. reported that higher H unit content in grass soda lignin might have imparted the observed higher than expected reactivity compared to hardwood organosolv lignin (containing mostly S and G units).⁶⁷ H units are less sterically hindered. Kurimoto et al. compared the liquefaction (in PEG400 as solvent) of various hardwood and softwood species and found that softwood liquefaction exhibited a higher rate of residue formation, as well as a greater decrease in hydroxyl group content at a higher rate than hardwood liquefaction.⁶⁸ The higher content of the more reactive G units, compared to S units, which are less predominant in softwood than hardwood, were concluded to have caused the differences.

Differences in modified or unmodified lignin structures transpire into variation in material properties of the subsequently prepared polyurethane. Polyurethane crosslink density is determined by polyol functionality and thus MM, both affected by lignin type.^{21,58} Lignin incorporation has been found by some to be beneficial to polyurethane properties. Thring et al. prepared polyurethane with PEG and lignin as polyol mixture. Optimal tensile strengths were obtained at lignin content of 15–25 wt%.^{52,58} Improved mechanical properties were also reported while employing lignin as a filler (10 wt%) in polyurethane foam and films.⁶⁹⁻⁷⁰ Glass transition

temperature has also been shown to increase through lignin addition in polyurethane formulations.²¹

No studies were found that specifically compare lignin modification through liquefaction of different technical lignins. Renewable and “green” liquefaction and modification agents have been receiving attention in an attempt to lower the petroleum-based content of the products. Crude glycerol was effectively used with corn stover and soybean straw,⁶³⁻⁶⁴ and more recently butanediol and propylene carbonate have also been found to be effective.⁷¹⁻⁷² Enzymatic hydrolysis residue, high in lignin content, has recently been combined with crude glycerol as liquefaction solvent and the polyols have been shown to form polyurethane through reaction with diisocyanate.⁷³ Liquefaction of kraft lignin, lignosulphonate or organosolv lignin (technical lignins) in crude glycerol do not appear to have been reported. Therefore, there is a potential to prepare sustainable polyols through liquefaction, as well as polyurethane with a high content of biobased material.

The slow degradation of polyurethane in the environment can lead to pollution. Enhancement of biological degradation is therefore a priority in many of the material’s applications.⁷⁴⁻⁷⁶ Ignat et al. blended lignin into polyurethane elastomer films and found that the lignin had a definitive effect on the degradation of the material through enzymatic oxidation by laccase and peroxidase (from *Aspergillus*). Surface and material properties were altered based on lignin content and enzyme type and it was concluded that lignin can have a positive effect on polyurethane biodegradation. They pointed out the limited amount of literature available on the subject.⁷⁷ Amaral et al. studied the degradation of PUF prepared from oxypropylated lignin. They found that the foam showed a higher degree of degradation than petroleum derived PUF during incubation in soil and liquid media inoculated with *Aspergillus niger*. It was concluded that lignin could enhance the degradability of PUF.⁷⁵ Cateto et al. found that blending of sorbitol based polyols and oxypropylated lignin produced PUF with enhanced degradability in soil inoculated with fungi.⁷⁸ Gomez et al. found that PUF prepared from crude glycerol based polyols had enhanced degradability in soil. Degradation of the structure was mostly attributed to fatty acid methyl esters and specifically ester groups.⁷⁴ Crude glycerol and lignin incorporation in PUF as proposed in this work, based on the aforementioned, might enhance degradability.

1.6 AIM AND OBJECTIVES

The aim of the project was therefore to evaluate the potential to prepare polyurethane foam from technical lignin and crude glycerol. The project was broken down into the following objectives:

- Prepare a polyol type product from the liquefaction of technical lignin in crude glycerol obtained from biodiesel preparation. Characterise the reagents and products and study the liquefaction reactions.
- Prepare polyurethane from the prepared “polyols”. Characterise the prepared polyurethane in terms of its application potential as rigid foam insulation.
- Evaluate the effect if any, that technical lignin type might have on the liquefaction and polyurethane properties.
- Compare degradability of the prepared polyurethane foam (PUF) with that of conventional petroleum-derived PUF to determine whether it is biodegradable.

1.7 OUTLINE

The chapters are organised as follows.

- Chapter 1: An introduction to the work is presented and provides a background through discussion of relevant literature which aims to justify the need for the specific investigation.
- Chapter 2: Liquefaction was studied by means of ^1H and ^{31}P NMR spectroscopy. The starting materials and products were characterised and compared and the liquefaction reactions subsequently discussed. This manuscript is presented as published in Journal of Renewable Materials with minor adjustments to layout.⁷⁹
- Chapter 3: The starting materials and products were further studied and compared by means of size-exclusion chromatography and FTIR. Liquefaction yield and total hydroxyl group content were compared and finally the reaction between a prepared polyol and diisocyanate was performed to obtain polyurethane. The manuscript was accepted in Polymers from Renewable Resources.
- Chapter 4: Rigid polyurethane foams were prepared from the three respective technical lignin-derived polyols. The materials were characterised, compared and finally the results of the biodegradability investigation were presented and discussed. The manuscript was accepted in Polymers from Renewable Resources.
- Chapter 5: Conclusion and future prospects.
- Annexure A: An initial paper summarizing part of the results. This manuscript is presented as published in a conference proceedings with minor adjustments and corrections.⁸⁰

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CHAPTER 2 POLYOL PREPARATION BY LIQUEFACTION OF TECHNICAL LIGNINS IN CRUDE GLYCEROL

ABSTRACT

This work reports a study of polyol synthesis through liquefaction of technical lignins in crude glycerol by means of ^1H 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 liginosulphonate had hydroxyl numbers suitable for rigid foam of 435, 515 and 529 mg KOH g $^{-1}$, 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 biobased polyol hydroxyl contents.

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

2.1 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.²¹ 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.⁸¹ Lignocellulosic ethanol production in the biofuel industry might further increase lignin rich by-product volumes.^{19,82} 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,⁵¹ it is of interest in biobased polyurethane applications.

Cateto *et al.*⁵⁵ determined that the differences in OH content and MM of lignin have an effect on the reactivity of technical lignin with isocyanate. They found 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.⁵⁷ Aliphatic OH in lignin is further known to be more reactive than phenolic OH²¹ as primary OH is more reactive than secondary OH.⁵⁷

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.⁸³ Phenolic OH also forms thermally labile bonds with isocyanate.⁸⁴ The chain extension further yields a reactant with improved uniformity⁵¹ and lowers rigidity.²¹ During oxypropylation Cateto *et al.*⁸³ 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.*⁶⁷ found that during oxypropylation hardwood organosolv lignin and grass soda lignin had shorter reaction durations than softwood kraft and organosolv lignins. They attribute the higher reactivity of the hardwood organosolv lignin to lower MM 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 cross-linking density also depends on lignin MM and functionality and determines the mechanical properties, as well as the glass transition temperature of the polyurethane.²¹

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.⁵⁴ 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-polymerisation among lignin fragments.^{56,85} Fragments are formed through lignin interunit bond cleavage during liquefaction which also liberates phenolic OH.⁸⁶ Luo *et al.*⁸⁷ studied the conversion of crude glycerol into polyols through liquefaction. They determined that the product consisted of major fractions 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.^{63,73,80}

According to Balakshin and Capanema⁸⁸ quantitative ¹³C and ³¹P NMR spectroscopy are the analytical methods used most often to study the structure of lignin. ³¹P NMR methods have been developed for quantification of various types of OH in lignin. ³¹P NMR has also been used in the analysis of biodiesel⁸⁹ 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 ³¹P 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 lignin⁹⁰ and 2-chloro-1,3,2-dioxaphospholane (RI), which enables better distinction between primary and secondary aliphatic OH. ¹H NMR which is frequently employed in lignin characterisation⁹¹ 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.

2.2 EXPERIMENTAL

2.2.1 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.*⁹² 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.⁸⁰ Hardwood calcium lignosulphonate was supplied by Sappi Saiccor mill (Umkomaas, 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 (CDCl₃, 99.96% D) were bought from Sigma Aldrich. Dimethyl sulfoxide-d₆ (DMSO-d₆, 99.96% D) was bought from Merck. Chemicals were of reagent grade or higher and used as received. Lignins were vacuum dried in an oven at 30 °C for minimum 24 h before analysis. Lignin molar mass is presented in section 3.3.1 (Table 3.1). The crude glycerol contained 25.3 wt% glycerol (Figure 2.7a), 14.8 wt% ethanol, 27.2 wt% fatty acid esters (Table 2.8) and 0.66 wt% salt. The crude glycerol pH ranged 9.6±0.1.

2.2.2 Liquefaction

The liquefaction reaction was conducted in a temperature controlled glass reactor open to atmosphere. Catalyst, 98 wt% H₂SO₄, 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 the 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. The liquefaction yields are presented in section 3.3.3 (Table 3.4).

2.2.3 Characterization

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.

¹H NMR Spectroscopy

Spectra were acquired according to methods described by Xue *et al.*⁵⁶ and Sun *et al.*⁹³ 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. ¹H 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.

³¹P NMR Spectroscopy

Lignin and polyol samples were analysed after phosphorylation with RI or RII.^{90,94} Lignin, 30 mg, was dissolved in 350 μL DMF and 350 μL pyridine/CDCl₃. A pyridine/CDCl₃ ratio of 1.6:1 (v/v) was used throughout ³¹P NMR experiments.^{91,95} 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/CDCl₃, 5 mg mL⁻¹, and the internal standard solution of cyclohexanol in pyridine/CDCl₃, 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 Capanema⁸⁸ previously reported RI to be less stable than RII. Lignin samples were analysed in duplicate unless otherwise noted.

Polyol samples were prepared by dissolving 30 mg polyol in 700 μL pyridine/CDCl₃ followed by the addition of relaxation reagent, internal standard and RI or RII as described above. Samples were vortexed and directly transferred to NMR tubes for analysis.

³¹P 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.⁵¹ The signal of the product of cyclohexanol with RI and RII at approximately 133.6 ppm and 145.1 ppm, respectively, was used for integration.^{56,90} Baseline correction with a 4th order polynomial was performed before integration.⁹⁶ Spectra were analysed with MestReNova 10.0.0.

Lignin and Polyol Properties

Lignin was dried at 105 °C to constant weight before the 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 analyser 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 20mm² 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,⁹⁷ through phthalic anhydride esterification of hydroxyl groups catalysed by imidazole.⁹⁷ The iodometric-periodic acid method, AOCS Official Method Ca 14-56,⁹⁸ was used to determine the free glycerol content of the crude glycerol.⁸⁷

The fatty acid ethyl ester content of crude glycerol was determined by gas chromatography (GC) after repeated extraction with diethyl ether until a clear non-polar phase had been 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. 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⁻¹. The system was calibrated with FAME standards of analytical grade (Sigma-Aldrich). Salt content of the crude glycerol was determined by Bio Services (Randburg, South Africa) according to AOAC 963.05. pH was determined with a Metrohm 692 pH meter.

2.3 RESULTS AND DISCUSSION

2.3.1 Lignin Analysis

Elemental Analysis

The lignin elemental analysis results and deduced C₉ formulae are given in Table 2.1. 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 C₉ formulae that the kraft lignin has the lowest relative hydrogen content. The carbon content in isolated lignins can increase due to condensation reactions.⁹⁹ 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 MM presented in Table 2.1 fall in the wide range of values reported for lignins isolated from different sources and by different methods.^{91,99-100}

Table 2.1: Lignin composition (wt% on moisture-free basis), C₉ formulae and corresponding molar mass (MM).

Lignin	Ash	C	H	N	O	S	Na	Ca	C ₉ formula ^b	MM C ₉ unit (g mol ⁻¹)
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 ₉ H _{9.1} O _{3.8} (OCH 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 ₉ H _{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 ₉ H ₉ O _{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 ³¹P NMR RII results for syringyl and guaiacyl content.

¹H NMR Spectroscopy

An overlay of the ¹H NMR lignin spectra is given in Figure 2.1. The kraft lignin displays 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.^{93,101} According to Baucher *et al.*¹⁰² 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 a similar guaiacyl and syringyl unit content. The organosolv lignin exhibit a broad signal centred 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, a higher *p*-hydroxyphenyl unit content is expected.⁹⁵ The lignosulphonate (hardwood) displays a signal with maximum intensity at 6.6 ppm, indicative of higher syringyl unit content.^{93,101}

Weaker signals between 8.0–8.5 ppm assigned to phenolic protons¹⁰³ differ for each of the lignins suggesting that the OH contents differ for each. Marchessault *et al.*¹⁰⁴ 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 ¹H NMR lignin signal assignment is summarised in Table 2.4 (Supplementary Material).

³¹P NMR Spectroscopy

The results of the quantitative ³¹P NMR analysis (Figure 2.2) are given in Table 2.2, (integration ranges are given in Table 2.5, Supplementary Material). 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

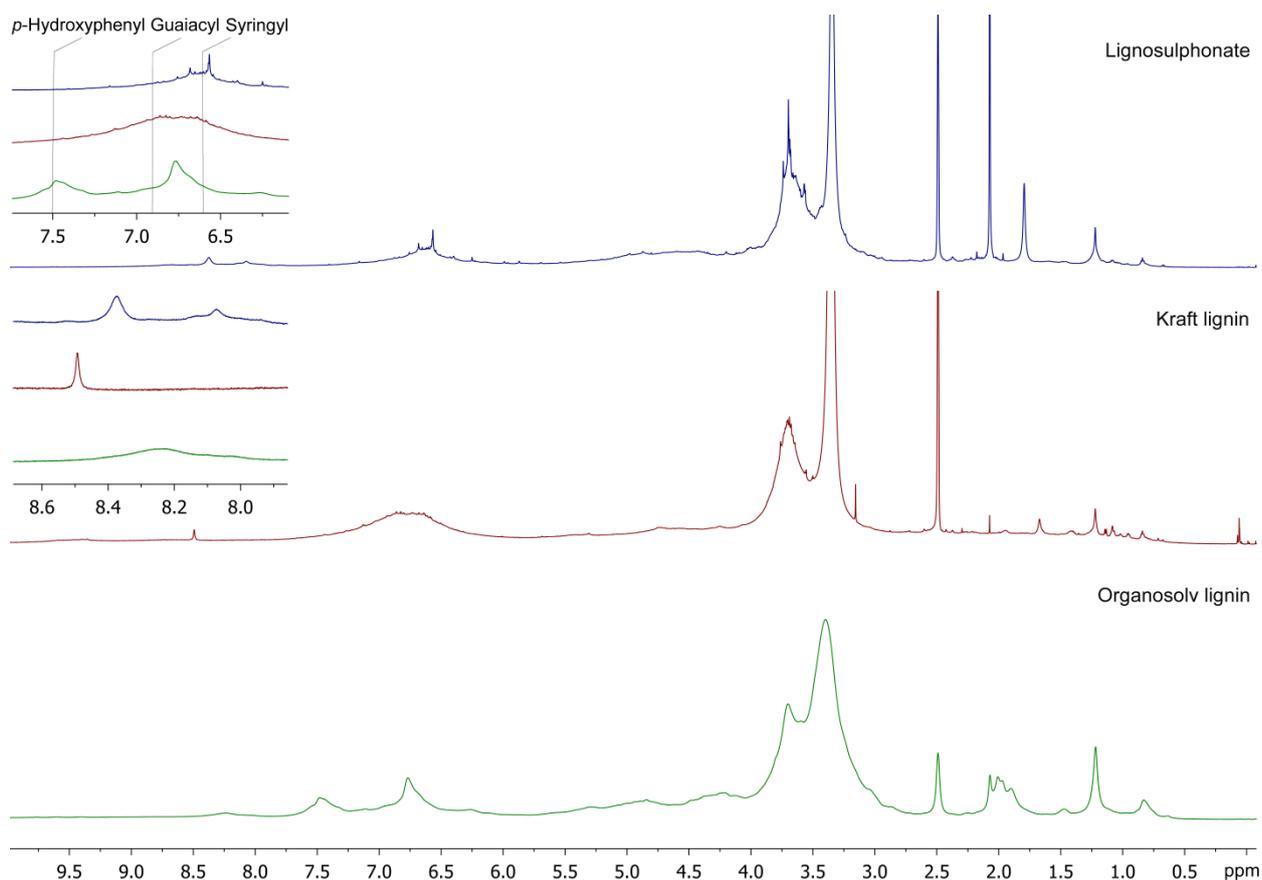


Figure 2.1: ^1H NMR spectra of lignosulphonate, kraft lignin and organosolv lignin. The areas typically assigned to the aromatic protons of the three generic lignin units are indicated in the top expansion.

the other lignins. The content of condensed phenolic structures can increase in lignin during isolation through condensation reactions,⁹⁰ but lignin from different sources do also contain different types and ratios of intermonomeric linkages.¹⁰² The organosolv lignin and lignosulphonate have a 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 the primary OH content (Table 2.2). 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.⁸⁸ The kraft lignin and lignosulphonate were only partially soluble when employing RI and did not give consistent results.

The values in Table 2.2 of the syringyl, guaiacyl and *p*-hydroxyphenyl unit contents correlate with the observations made with ^1H 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. Lignin composition is however dependent on a number of factors and variation within populations has been reported.¹⁰²

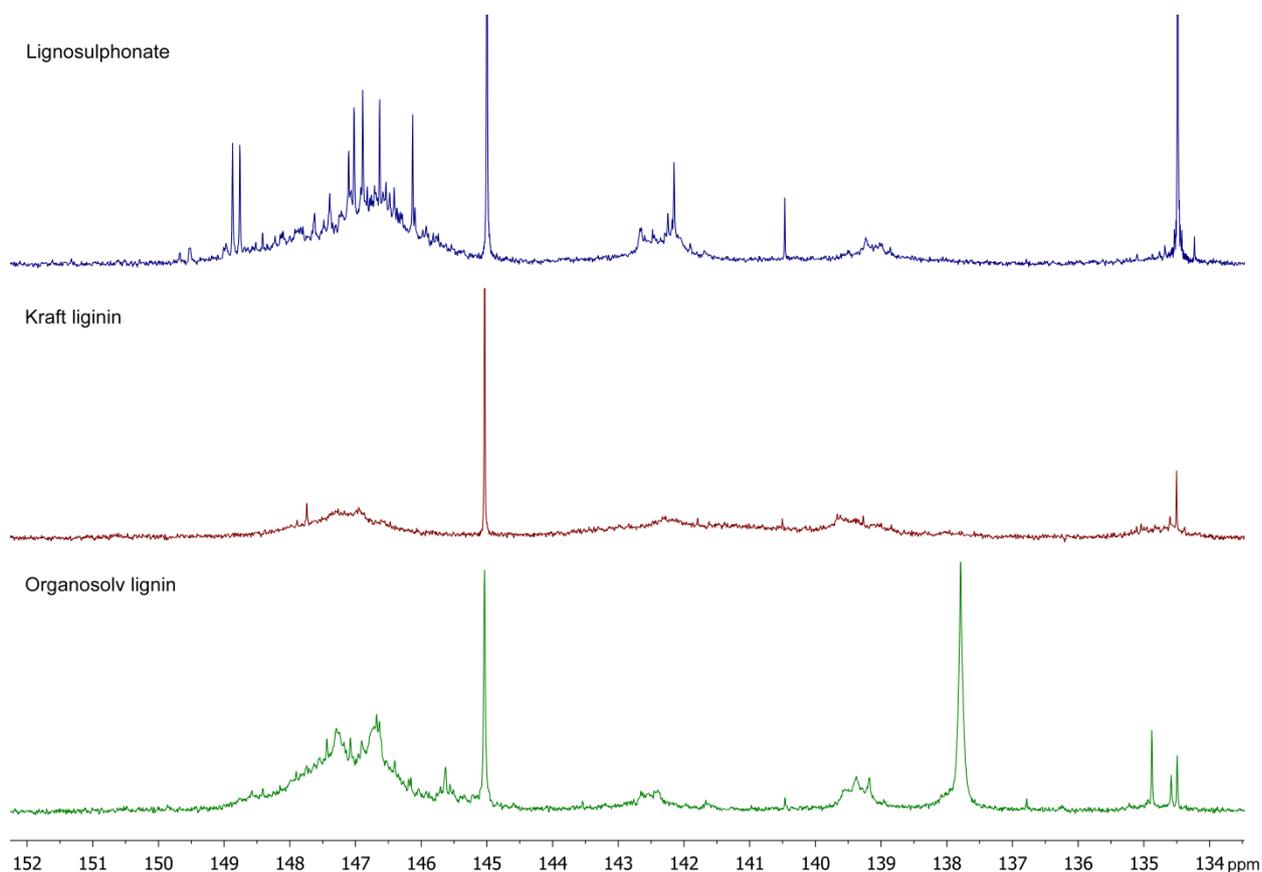


Figure 2.2: ^{31}P NMR RII spectra of lignosulphonate, kraft lignin and organosolv lignin.

Furthermore, according to Balakshin and Capanema⁸⁸ syringyl units can be significantly overestimated in lignin spectra because a substantial fraction 5-condensed guaiacyl unit signals also resonate in the syringyl assignment region. The organosolv lignin revealed a higher content of the more reactive *p*-hydroxyphenyl units than the other lignins.

2.3.2 Crude Glycerol and Polyol Analysis

^1H NMR Spectroscopy

Liquid product

Luo *et al.*⁸⁷ 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 the 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 the soap and FAME contents were substantially reduced.

Table 2.2: Lignin hydroxyl content (mmol g⁻¹, ash-free basis) determined by ³¹P 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.

An overlay of the crude glycerol and crude glycerol polyol ¹H NMR spectra is shown in Figure 2.3 with signal assignment (Table 2.6, Supplementary Material) to fatty acid ethyl esters (FAEE), glycerol, MAG, DAG and TAG.¹⁰⁵⁻¹⁰⁹ Ethanol signal intensities at 3.43 ppm and 1.04 ppm¹¹⁰ and water at 3.43 ppm¹⁰³ 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 decrease and overlap with a doublet of doublets is apparent, indicating the presence of TAG.¹⁰⁹ Accordingly, a TAG signal at 5.3 ppm does not change substantially and therefore the TAG content remained stable during liquefaction while the FAEE content decreased.

Corresponding to the reduction at 4.0 ppm, the ethoxy signal intensity at 1.15 ppm also decrease in the crude glycerol polyol. Decreases in intensity between 3.23–3.38 ppm and between 4.3–4.7 ppm indicate a loss of glycerol OH content. The 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 3.60 ppm, also assigned to MAG and DAG do increase slightly in the crude glycerol polyol.

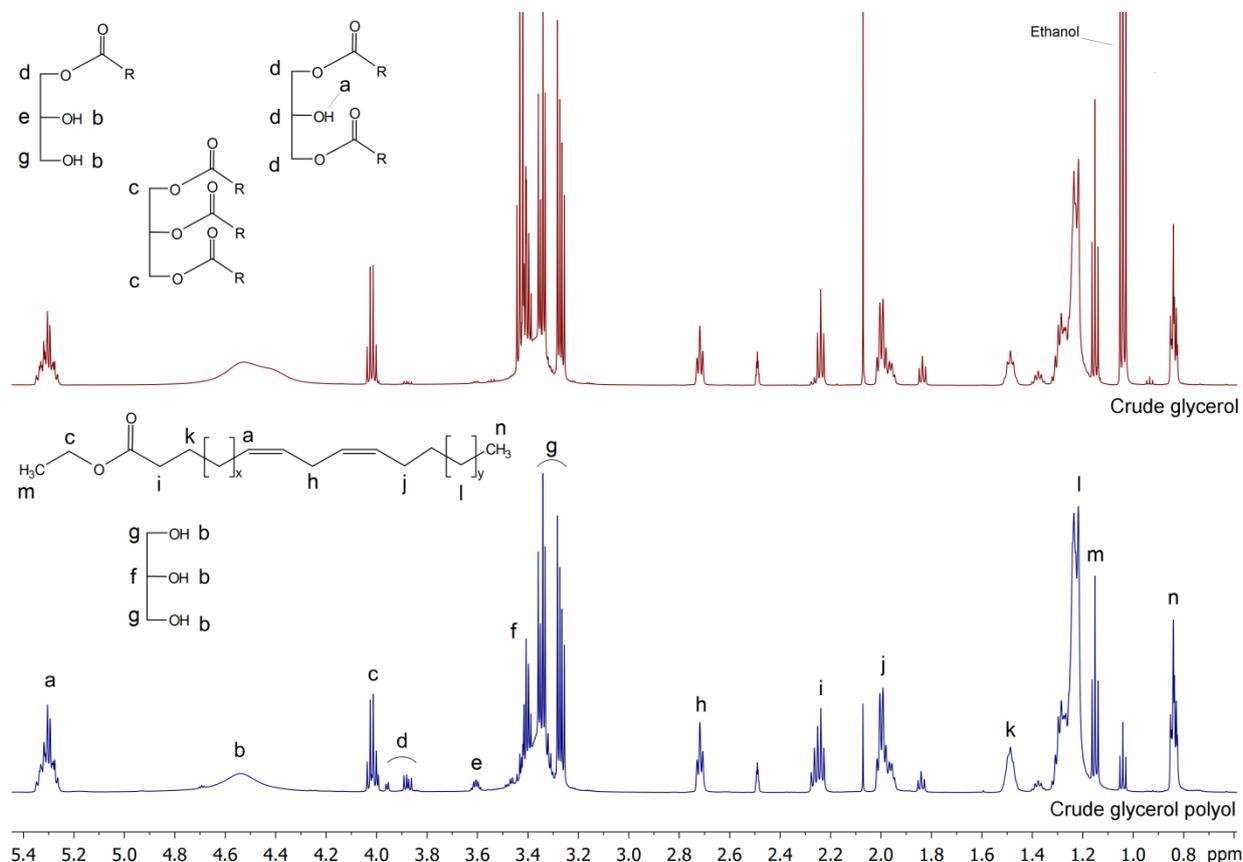


Figure 2.3: ¹H NMR spectra and signal assignment of crude glycerol and crude glycerol polyol.

Between 1.35–1.45 ppm in Figure 2.4 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.¹¹⁰ At 2.05 ppm the organosolv lignin polyol exhibit a triplet not visible in the kraft lignin and liginosulphonate polyols. Similarly, only the kraft lignin polyol exhibit a peak at 1.91 ppm. In this range the organosolv lignin and kraft lignin exhibit signals assigned to aliphatic protons adjacent to double bonds or carbonyl groups.¹⁰⁴

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 and 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 indicate differences in OH type and

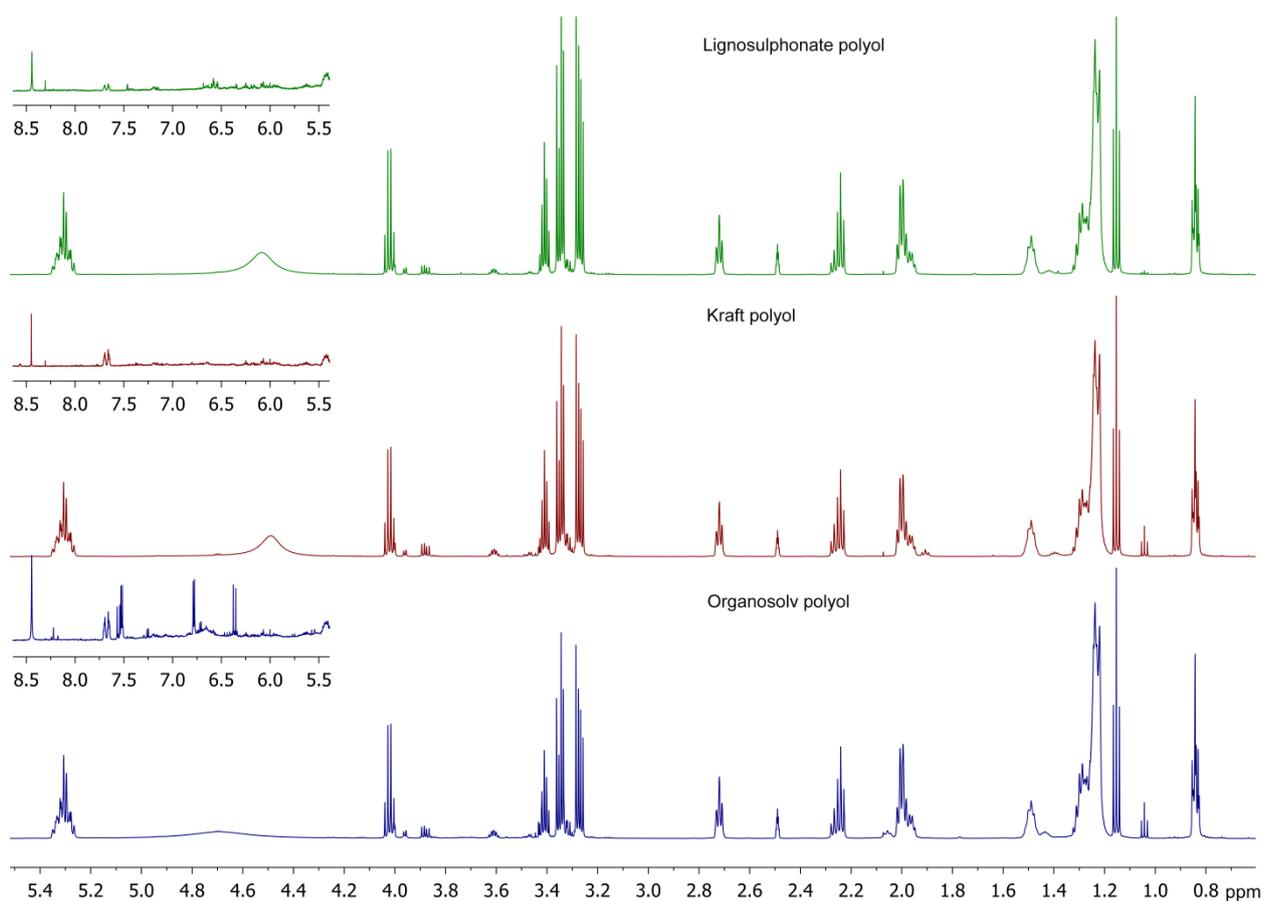


Figure 2.4: ^1H NMR spectra of lignosulphonate polyol, kraft lignin polyol and organosolv lignin polyol.

content.⁸⁴ Low intensity signals not visible in the crude glycerol polyol and crude glycerol appear in the organosolv lignin polyol between 6.0 and 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 a 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 differed among the polyols. Glycerol OH content was found to reduce significantly during liquefaction, along with FAEE ethoxy to a lesser extent.

Solid product

Figure 2.5a shows an overlay of the crude glycerol, solid product of kraft lignin liquefaction and kraft lignin ^1H NMR spectra. The relative size of the broad peak in the kraft lignin between 6.6–

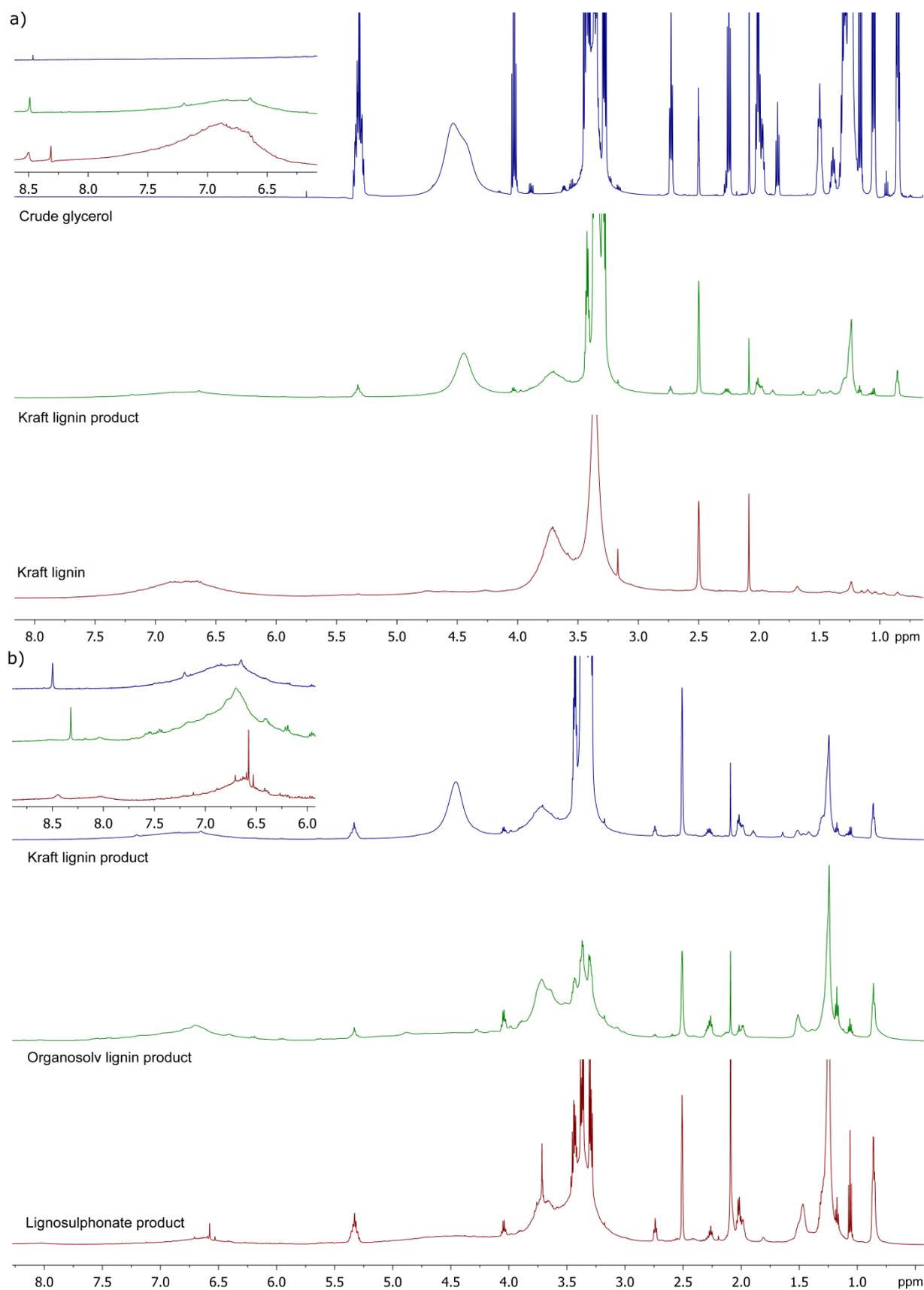


Figure 2.5: a) ^1H NMR spectra of crude glycerol, kraft lignin solid product and kraft lignin. b) ^1H NMR spectra of the solid lignin liquefaction products.

6.9 ppm is reduced in the solid product, possibly due to the removal of phenolic 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 olefinic protons. Centred 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 and 3.45 ppm intense signals arise not present in the kraft lignin. Corresponding signals in the crude glycerol are assigned to CH and CH₂ 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. Centred at 2.0 ppm a small peak appears in the product. A similar peak at 2.0 ppm in the crude glycerol is 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 2.5b), that the signal assigned to glycerol OH around 4.5 ppm is absent in the spectra of the organosolv and liginosulphonate products. Both products do however exhibit similar peaks between 3.25 and 3.45 ppm to those in the kraft lignin product, although the intensities are clearly reduced. The reason for the absence of a signal at 4.5 ppm might be the removal of glycerol OH after glycerol has bound to lignin, since the signals between 3.25 and 3.45 ppm are still present. Overall it does appear that glycerol 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, as discussed. In the other areas signals of the three solid products are similar.

³¹P NMR Spectroscopy of the liquid product

Qualitative

Figure 2.6 (Table 2.7, Supplementary Material) shows an overlay of the polyol (liquid product) and crude glycerol ³¹P NMR RII spectra and signal assignment^{89,96,111} 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 signal⁸⁹ 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 (CH₂). 2-Monoacylglycerols and DAG 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.*⁸⁷ That would correlate with the decrease in glycerol OH and FAEE content observed with ¹H NMR.

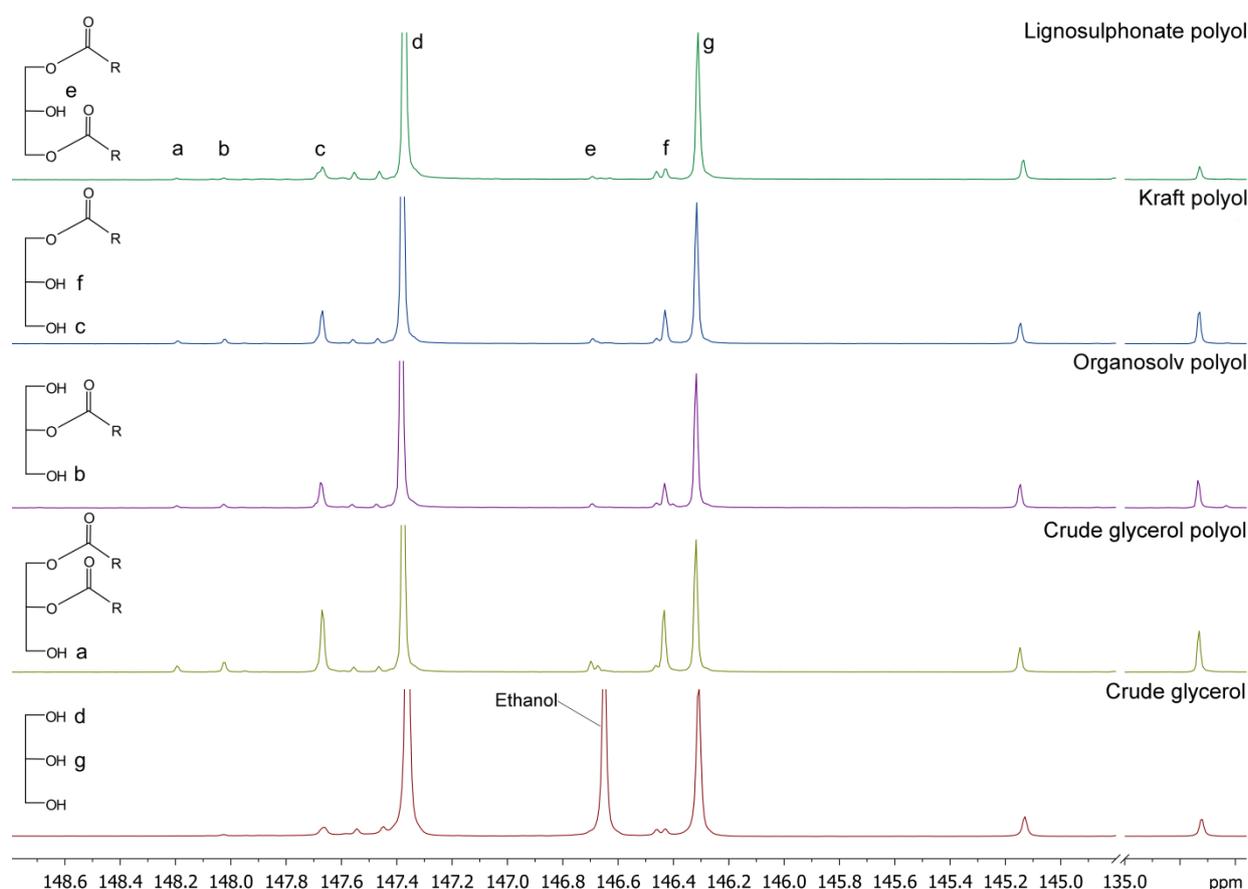


Figure 2.6: ³¹P NMR RII spectra and signal assignment of the crude glycerol and polyols.

Quantitative

The values of the OH content of the crude glycerol, crude glycerol polyol and lignin polyols (liquid product) determined with RII, as well as according to ASTM D4274-11, are given in Table

2.3. It compares with the values reported by others for lignin-derived polyols determined with ^{31}P NMR which range 3.1–8.7 mmol g^{-1} .^{54,56} The differences between the values of the lignin polyol OH contents determined by ^{31}P NMR using RII and titration after esterification with phthalic anhydride are 0–5%. D'Souza *et al.*⁸⁴ prepared polyols through oxypropylation of bark and bark alkaline extract and found values determined by the two methods differed 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.⁸³

Table 2.3: Polyol (liquid product) and crude glycerol hydroxyl content (mmol g^{-1} , unless otherwise noted) determined by ^{31}P NMR spectroscopy and compared to the ASTM standard method.

OH type:	OP ^a	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 ^b
Total (mg KOH g^{-1}) ^c	435	515	529	510	723
ASTM D4274-11 (mg KOH g^{-1})	436	491±15	555±54	466±17	758±13
RI:					
Primary / Secondary	2.1	1.7	2.3	1.2	2.4

^a OP: Organosolv lignin polyol; KP: Kraft lignin polyol; LP: Lignosulphonate polyol; CGP: Crude glycerol polyol; CG: Crude glycerol. ^b 95% Confidence interval based on triplicate analysis. ^c Values of the total hydroxyl content determined by ^{31}P NMR (mmol g^{-1}) converted to units of mg KOH g^{-1} (multiply by 56.1 [molar mass of KOH]).

It is important to note that the liquid phase products contain almost exclusively aliphatic OH, similar to polyols obtained with PEG/glycerol liquefaction and base catalysed oxypropylation.^{84,112} The original phenolic OH of lignin, as well as any phenolic OH liberated during liquefaction through lignin interunit bond cleavage therefore rather form part of the solid phase products (Figure 2.5). Furthermore, obtaining high phenolic OH content in the polyols was not expected, because of the high solvent/lignin ratio used in liquefaction.

The ratios of primary/secondary OH (Table 2.3) indicate the polyols contain significant content of both primary and secondary OH. It can be seen in Figure 2.6 that glycerol contributes the

major fraction of OH content while MAG, which also contain both primary and secondary OH, contributes to a lesser extent. The primary/secondary OH ratios affect reaction kinetics between OH and isocyanate⁸⁴ and the variation in the value among the polyols is expected to impact subsequent polyurethane foam preparation.

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 ³¹P NMR RII results. Values of 24.8 and 25.3 wt% were obtained with the respective methods. Figure 2.7a displays a comparison of the crude glycerol and polyol compositions based on the signal assignment in Figure 2.6 (Table 2.7). A comparison of the absolute change in the crude glycerol constituents during liquefaction is given in Figure 2.7b. Change is expressed as an increase or a 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. The DAG content in the crude glycerol and the 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. The FAEE content of the crude glycerol measured by GC was found to be 27.2 wt% (Table 2.8, Supplementary Material).

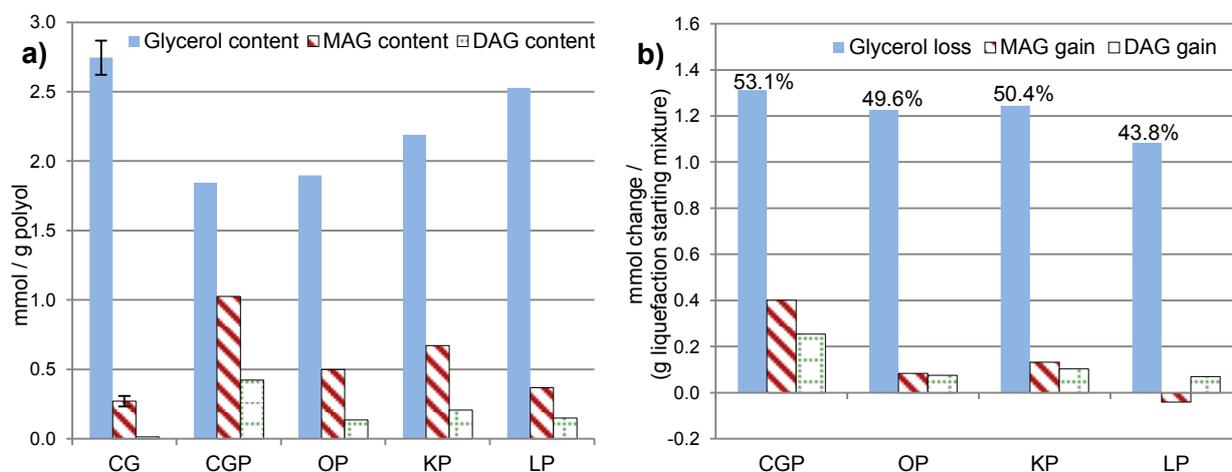


Figure 2.7: a) Comparison of the crude glycerol and polyol compositions determined with ³¹P NMR RII, (CG: crude glycerol, CGP: crude glycerol polyol, OP: organosolv polyol, KP: kraft polyol, LP: liginosulphonate polyol). b) Change in the original crude glycerol components during liquefaction determined by ³¹P 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.

The molar increase in the MAG and DAG content for each of the polyols is substantially lower than the 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. ^1H NMR spectra did not indicate significant changes in TAG contents. Based on the ^1H NMR analysis (Figure 2.3–2.5), glycerol loss is also caused by reaction with lignin OH. In the case of lignin binding at only one or two OH 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 2.6). If lignin bound at all three glycerol OH no signals would arise for the new compounds.

The crude glycerol polyol underwent greater gain in the MAG and DAG content than the lignin polyols, which helps to affirm reaction between lignin and glycerol, as well as the impact lignin has on the liquefaction product properties. If lignin additionally bound with FAEE through transesterification during liquefaction it would also lower the MAG and DAG formation. Esterification reactions with ethylene glycol during lignin liquefaction were reported by Jasiukaitytė-Grojzdek *et al.*⁸⁶ Furthermore, the primary/secondary OH ratios (Table 2.3) of the polyols decrease as the glycerol loss increases, indicating a possible preferential reaction at the primary OH of glycerol. The two quantities were determined independently with RI and RII.

Liquefaction of kraft lignin and organosolv lignin resulted in a greater glycerol loss than lignosulphonate, despite the higher aliphatic OH content in the lignosulphonate. As discussed, the organosolv lignin did have a 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 cross-linking density would be higher within the kraft lignin and organosolv lignin polyols based on increased bonding with glycerol. Higher cross-linking 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 valorised.

2.4 CONCLUSIONS

Liquefaction of lignin in crude glycerol yields a liquid product containing mostly aliphatic OH and the total OH content is similar to those 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 the formation of MAG with FAEE. Based on the ^1H 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.⁸⁰

Different technical lignins each yields polyols with unique compositions and structures which differ from polyols prepared by sole crude glycerol liquefaction and careful selection of lignin isolation methods is therefore necessary on industrial scale. ³¹P NMR spectroscopy enables the quantification of different constituents of crude glycerol before and after liquefaction which helps to determine the reactions that occur.

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2.6 SUPPLEMENTARY MATERIAL

Table 2.4: Signal assignment of the ^1H NMR lignin spectra.

δ (ppm)	Assignment	Reference
Organosolv lignin		
7.3–7.6	Aromatic protons in positions 2 and 6 of <i>p</i> -hydroxyphenyl structures	Seca <i>et al.</i> ¹¹³
6.6–6.8	Aromatic protons in syringyl and guaiacyl structures	Xu <i>et al.</i> ⁹²
4.8–5.0	H β in β -O-4 structures	Xu <i>et al.</i> ⁹²
4.2	H γ in β -O-4 structures	Sun <i>et al.</i> ⁹³
1.9–2.1	Methyl or methylene protons adjacent to double bonds or carbonyl groups	Marchessault <i>et al.</i> ¹⁰⁴
	Lignin acetoxy groups	Ralph <i>et al.</i> ¹¹⁴
0.8–1.5	Aliphatic protons in lignin or xylans	Xu <i>et al.</i> ⁹²
Kraft lignin		
8.5	Phenolic protons	Fernandez-Costas <i>et al.</i> ¹⁰³
6.6–6.9	Aromatic protons in syringyl and guaiacyl structures	Sun <i>et al.</i> ⁹³
4.0–4.8	H β , H γ in β -O-4 structure	Sun <i>et al.</i> ⁹³
0.8–1.7	Aliphatic protons	Sun <i>et al.</i> ⁹³
Lignosulphonate		
6.6–6.7	Aromatic protons in syringyl and guaiacyl structures	Sun <i>et al.</i> ⁹³
4.0–5.0	H α , H β , H γ in β -O-4 structure	Zhou <i>et al.</i> ¹¹⁵
0.8–1.8	Aliphatic protons in lignin or contaminants	Fernandez-Costas <i>et al.</i> ¹⁰³
General		
3.7	Methoxy	Xu <i>et al.</i> ⁹² , Hu <i>et al.</i> ¹¹⁶
3.4	Water	"Gottlieb <i>et al.</i> ^{110"}
3.2	Methanol (impurity)	""
2.5	DMSO	""
2.1	Acetone (impurity)	""

FAME content by GC

The temperature ramp program was as follows: Hold at 100 °C for 5 min, raise to 120 °C at 10 °C min⁻¹, hold 1 min, raise to 175 °C at 10 °C min⁻¹, hold 10 min, raise to 210 °C at 5 °C min⁻¹, hold 5 min, raise to 230 °C at 5 °C min⁻¹, hold 5 min.

Table 2.5: Quantitative ³¹P NMR OH analysis: Approximate integration ranges. ^{51,90,117}

Functional group	RII (ppm)	RI (ppm)
Aliphatic OH	145.30–150.80	Primary: 132.0–133.6 Secondary: 133.7–138.0
Internal standard (Cyclohexanol)	145.00–145.30	133.6–133.7
Condensed phenolic	143.30–145.00 & 140.30–142.00	
Syringyl	142.00–143.30	
Guaiacyl	138.55–140.30	
<i>p</i> -Hydroxyphenyl	137.30–138.55	
Carboxylic acids	133.70–135.60	

Table 2.6: Signal assignment of the crude glycerol and polyol ¹H NMR spectra.

δ (ppm)	Assignment	Reference
5.3	Olefinic protons 1,3-DAG OH	Miyake <i>et al.</i> ¹⁰⁵ Nebel <i>et al.</i> ¹⁰⁷ Sustere <i>et al.</i> ¹⁰⁶
4.5	Ethanol OH Glycerol primary and secondary OH	SDBSWeb ¹¹⁸ Nebel <i>et al.</i> ¹⁰⁷
4.0	-CH ₂ O- in FAEE and TAG	Rosset <i>et al.</i> ¹¹⁹
3.95, 3.88	Glycerol CH and CH ₂ in MAG and DAG ^a	Sustere <i>et al.</i> ¹⁰⁶
3.43	Water Ethanol CH ₂ Glycerol CH	Fernandez-Costas <i>et al.</i> ¹⁰³ SDBSWeb ¹¹⁸ Sustere <i>et al.</i> ¹⁰⁶
3.23–3.38	Glycerol CH and CH ₂	Nebel <i>et al.</i> ¹⁰⁷
2.7	Divinyl methylene	Miyake <i>et al.</i> ¹⁰⁵
2.5	DMSO	Fernandez-Costas <i>et al.</i> ¹⁰³
2.25	α -Carbonyl methylene	Monteiro <i>et al.</i> ¹⁰⁸
2.07	Acetone (impurity)	Gottlieb <i>et al.</i> ¹¹⁰
2.0	Allyl methylene	Miyake <i>et al.</i> ¹⁰⁵
1.85	Acetic acid CH ₃ Methylene adjacent to triple bond in fatty acids	Gottlieb <i>et al.</i> ¹¹⁰ AOCS ¹²⁰
1.5	β -Carbonyl methylene	Monteiro <i>et al.</i> ¹⁰⁸
1.2–1.3	Methylene protons on saturated carbon	Miyake <i>et al.</i> ¹⁰⁵
1.15	FAEE ethoxy CH ₃	Guzatto <i>et al.</i> ¹⁰⁹
1.04	Ethanol CH ₃	SDBSWeb ¹¹⁸
0.8	Terminal methyl	Monteiro <i>et al.</i> ¹⁰⁸

^a MAG and DAG additionally have numerous signals in the range 3.2–5.0 ppm which overlaps with the other signals listed above.

Table 2.7: Signal assignment of the crude glycerol and polyol ³¹P NMR RII spectra.

δ (ppm)	Assignment	Reference
148.20	1,2-Diacylglycerol	Spyros and Dais ¹¹¹
148.02	2-Monoacylglycerol	Nagy <i>et al.</i> ⁸⁹
147.65	1-Monoacylglycerol (CH ₂)	Christophoridou and Dais ⁹⁶ ; Nagy <i>et al.</i> ¹²¹
147.36–147.39	Primary OH in glycerol	Nagy <i>et al.</i> ⁸⁹
146.70	1,3-Diacylglycerol	Spyros and Dais ¹¹¹
146.65	Ethanol	Nagy <i>et al.</i> ⁸⁹
146.43–146.45	1-Monoacylglycerol (CH)	Nagy <i>et al.</i> ⁸⁹
146.32	Secondary OH in glycerol	Christophoridou and Dais ⁹⁶
134.72–134.74	Fatty acids	Lucas-Torres <i>et al.</i> ¹²²

Table 2.8: Crude glycerol FAEE, MAG, DAG and ethanol content.

Constituent	wt%
Palmitic acid ethyl ester	1.9±0.1 ^a
Stearic acid ethyl ester	1.8±0.1 ^a
Oleic acid ethyl ester	6.7±0.3 ^a
Linoleic acid ethyl ester	16.8±0.8 ^a
MAG	9.6±1.3 ^b
DAG	0.8 ^b
Ethanol	14.8±3.7 ^b / 14.6 ^c

^a Determined by GC. 95% Confidence interval based on triplicate analysis.

^b Determined by ³¹P NMR. 95% Confidence interval based on triplicate analysis.

^c Determined by drying at 40 °C to constant weight.

CHAPTER 3 FUNCTIONALIZING LIGNIN IN CRUDE GLYCEROL TO PREPARE POLYOLS AND POLYURETHANE

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 biobased polyols for polyurethane preparation. Size-exclusion chromatography (SEC) revealed that the lignins behave differently during liquefaction based on a ranging product molar mass (MM). MM 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. FTIR spectroscopy suggested that crude glycerol constituents like glycerol and fatty acid esters were bound to lignin during liquefaction through formation of ether and ester bonds. Liquefaction yield further also varied with lignin type. The products were effectively employed as biobased polyols to prepare polyurethane.

Keywords: kraft lignin, liginosulphonate, organosolv, liquefaction

3.1 INTRODUCTION

The modification of lignocellulose and lignin have been demonstrated to be effective means to prepare biobased polyols for polyurethane preparation from renewable and sustainable resources.⁴⁹ Reaction with propylene oxide, as well as liquefaction in solvents such as polyethylene glycol (PEG), diethylene glycol (DEG), ethylene glycol (EG) and glycerol is most often reported. Recently green liquefaction solvents like propylene carbonate, butanediol and crude glycerol have been employed.^{71-72,123} Other green modification strategies reported, include esterification of lignin with a fatty acid followed by functionalization¹²⁴ and depolymerisation of kraft lignin by hydrolysis with water to yield polyols.¹⁵

In the abovementioned work the molar mass (MM) of lignin and reaction products were monitored by some as a means to study the liquefaction process.^{56,85} Decreases and increases in MM are indicators of depolymerisation of lignin and formation of higher MM products during liquefaction, respectively.¹²⁵ The hydroxyl groups (OH) of lignin are important reactive sites^{49,126} and comparing functional groups in lignin and liquefaction products also gives insight into the behaviour of the solvents and lignin or lignocellulose during modification.¹²⁷ Lignin type has previously been shown to influence polyol preparation through oxypropylation due to differences in MM, OH content and structure.^{67,83}

Crude glycerol is a low value by-product of the biodiesel industry³⁷ and has only recently been employed as a lignin liquefaction solvent. Lee et al.⁷³ and Kim et al.¹²⁸ prepared polyols through crude glycerol liquefaction of saccharification residues of empty fruit bunches and sunflower stalks, respectively. The residues had high lignin contents. We 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.⁷⁹ In this work the aim was to study and compare the lignins (kraft, lignosulphonate and organosolv) and their respective liquefaction products in terms of MM and structure by means of size-exclusion chromatography (SEC) and FTIR spectroscopy. The possible formation of polyurethane through reaction of the products with diisocyanate was finally evaluated.

3.2 EXPERIMENTAL

3.2.1 Materials

Crude glycerol was prepared through KOH catalysed transesterification of sunflower oil with ethanol (Table 3.5, Supplementary Material).⁸⁰ Organosolv lignin was extracted from sugarcane bagasse (Tsb Sugar RSA, Malelane, South Africa) according to Xu et al.,⁹² employing a mixture of acetic acid, formic acid and water with HCl as catalyst, reported previously.⁸⁰ Hardwood calcium lignosulphonate was donated by Sappi's Saiccor mill (Umkomaas, South Africa).

Softwood kraft lignin, dimethyl sulfoxide (Chromasolv Plus, 99.7%), tetrahydrofuran (99.9%, containing 250 ppm BHT), 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 H₂SO₄ (98%) was obtained from Associated Chemical Enterprises (Johannesburg, South Africa). Ethanol (99.9%) was obtained from Rochelle (South Hills, South Africa). Desmodur 44V20L (diphenylmethane-4,4'-diisocyanate) was donated by Bayer Material Science (Isando, South Africa). Air Products (Kempton Park, South Africa) donated polyurethane catalysts and surfactants. Chemicals were used as received.

3.2.2 Liquefaction

The liquefaction was conducted as previously described.⁷⁹ H₂SO₄ as catalyst was added to crude glycerol to obtain pH 8. The mixture was heated to 160 °C in a glass reactor open to the atmosphere. The specific lignin was added and the liquefaction conducted for 90 minutes under magnetic stirring, whereafter 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 rpm 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.⁹⁷

3.2.3 Size-exclusion chromatography (SEC)

Molar masses of the lignins and liquefaction products were determined on a Perkin-Elmer Flexar system (Shelton, CT), 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 x 300 mm, 8 µm particle size). The eluent used was DMSO/water (9:1, v/v) containing 0.05 mol dm⁻³ LiBr,¹²⁹ and was chosen because it is reported to be a solvent which enables the analysis of underivatized lignins. The flowrate was 0.4 mL min⁻¹, oven temperature 55 °C, injection volume 100 µL and sample concentration 8 mg mL⁻¹. Samples were stirred 24h and filtered through 0.45 µm syringe filters (PALL Acrodisc, GxP/GHP) before injection. The system was calibrated with pullulan standards (Sigma-Aldrich, batch BCBR0400V) of M_{Peak max} (g mol⁻¹) 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 was processed according to Gavrilov et al.¹³⁰ and Shortt.¹³¹ Averages are

based on at least three samples. The SEC MALLS system that used THF as eluent is described in the Supplementary Material.

3.2.4 FTIR

Diffuse reflectance spectra were recorded on a Shimadzu (Kyoto, Japan) IRAffinity-1 FTIR spectrometer fitted with a PIKE Technologies (Madison, WI) EasiDiff accessory. Samples of the lignin, solid phase products and polyurethane were analysed in a KBr matrix. Spectra were recorded between 4000–400 cm^{-1} , at 4 cm^{-1} resolution with 45 scans. Intensities were aligned at the C=C aromatic band around 1600 cm^{-1} .¹³² The crude glycerol and liquid phase products were analysed by attenuated total reflectance (ATR) FTIR spectroscopy, employing the PIKE Technologies HATR accessory with a zinc selenide crystal plate. Spectra were recorded between 4000–800 cm^{-1} as above. A three point baseline correction was applied.

3.2.5 Polyurethane preparation

Polyurethane was prepared from the respective unfractionated liquefaction products (KL, OL and LS) as the polyol component. Each product was mixed with a gelling catalyst (Polycat 8, 0.86 wt% of polyol), blowing catalyst (Polycat 5, 0.67 wt% of polyol), surfactant (DC5357, 2.5 wt% of polyol) and water (1.25 wt% of polyol) and then stirred at 6000 rpm for 10–15 s, whereafter diisocyanate (Desmodur 44V20L) was added to obtain an isocyanate index of 105 (Table 4.1). Again the mixtures were stirred for 10–15 s, and left to rise and cure.⁸⁰

3.3 RESULTS AND DISCUSSION

3.3.1 Size-exclusion chromatography

The kraft lignin (KL) was found to have higher MM (Table 3.1) than the lignosulphonate (LS) and organosolv lignin (OL), which in turn did not differ significantly from each other.

Table 3.1: Lignin and liquefaction solid phase product MM.

	\overline{M}_w^a (g mol^{-1})	\overline{M}_n^b (g mol^{-1})	Dispersity ($\overline{M}_w / \overline{M}_n$)
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

^a Weight-average MM. ^b Number-average MM.

Table 3.2 shows values reported for lignins either extracted by similar methods, from similar sources or analysed on similar SEC systems.

Table 3.2: Literature MM data of technical lignins.

Lignin isolation	Source	\overline{M}_w (g mol ⁻¹)	\overline{M}_n (g mol ⁻¹)	Dispersity	Eluent	Detector/ Standards	Authors
Kraft	Birch	19650	7523	2.69	Aqueous	RI	Chen and Li ¹³³
Kraft	Softwood / Hardwood	10844–15195	4530–8071	1.8–2.4	LiBr, DMSO.	RI, Pullulan.	Zhu et al. ¹³⁴
Indulin (Kraft)	Softwood	3060	1900	1.6	THF/H ₂ O	Diode array, Polystyrene/PMMA. ^e	Andrianova et al. ¹³⁵
Formic acid / acetic acid / water ^a	Wheat straw	4170	2660	1.57	Aqueous	RI, Pullulan.	Xu et al. ⁹²
"Organosolv"	"Wheat straw"	5000	860	5	THF, acetobromination. ^b	"RI and diode array detector, Polystyrene."	Lange et al. ¹³⁶
""	""	13600	750	18	THF, acetylation. ^b	""	
NaOH and H ₂ O ₂	Sugarcane bagasse	2180	1460	1.49	0.02M NaCl, aqueous.	Pullulan	Sun et al. ¹³⁷
Organosolv	Wheat straw	8420	480	17.54	"0.5% LiBr, DMSO."	"RI and UV, Polystyrene sulfonate."	Sulaeva et al. ¹³⁸
Indulin (Kraft)	Softwood	2887	375	7.71	""	""	
Lignosulphonate	Spent sulphite liquor	8302	842	9.86	""	""	
Lignosulphonate	Hardwood	3833	2041		0.5M NaOH, aqueous.	UV, Polystyrene sulfonate.	Baumberger et al. ¹⁰⁰
Lignosulphonate	Hardwood	6600	1200	5.5	"0.05M LiBr, DMSO/H ₂ O."	"Multiple ^c , Pullulan."	Ringena et al. ¹²⁹
Curan (kraft)	Softwood	9900	1300	7.6	""	""	
Soda lignin	Bagasse	3600	1100	3.3	""	""	
Curan (kraft)	Softwood	11000	2000	5.5	0.11M LiCl, DMAc. ^d	Multiple ^c , Polyethylene glycol / oxide.	
Formic acid / water. ^a	M. x giganteus	2679	1564	1.7	THF	UV, Polystyrene.	Wang et al. ¹³⁹
Acetic acid- or formic acid / water. ^a	M. x giganteus	6024 / 6656	1444 / 2122	4.17 / 3.14	THF, acetylation. ^b	UV	Villaverde et al. ¹⁴⁰
Formic acid / acetic acid / water. ^a	Alfa grass	3230	1300	2.48	THF	RI, Polystyrene.	Abdelkafi et al. ¹⁴¹

^a Mixture of solvents. ^b Sample derivatisation. ^c RI, UV, viscosimetric, LALLS. ^d Dimethylacetamide. ^e Poly(methyl methacrylate).

The aforementioned factors are known to influence the measurement of lignin MM.¹⁴² Values of lignin MM vary in literature, but there is some agreement between values in Table 3.1 and 3.2 for each lignin type. Specifically softwood kraft lignin analysed by Ringena et al. had MM values similar to that of the KL in this work.¹²⁹ The \overline{M}_w of the hardwood liginosulphonate studied by Baumberger et al. was similar to that of the LS.¹⁰⁰ The OL \overline{M}_w corresponded to values previously reported for soda lignin from bagasse and alfa grass organosolv lignin.^{129,141} Figure 3.1a shows an overlay of the lignin molar mass distributions. The OL and LS show more peaks in the low MM region, representing lower MM lignin fractions and impurities.^{129,143} The higher MM of the KL is concluded to be a result of condensation reactions during isolation.¹⁰¹ Previous characterisation by ³¹P NMR spectroscopy of the same lignins⁷⁹ 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.

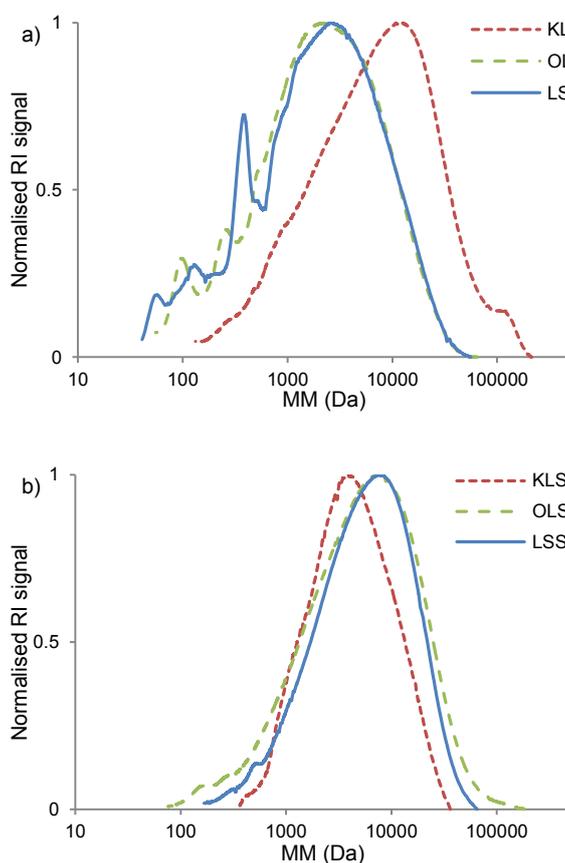


Figure 3.1: Molar mass distributions of the lignins (a) and solid phase products (b). KLS, OLS and LSS refer to the KL, OL and LS solid products, respectively.

Figure 3.1b shows a molar mass distribution overlay for the solid phase liquefaction products. In the case of OL and LS the respective solid phase products have increased \overline{M}_w and \overline{M}_n , while the KL product \overline{M}_w decreased (Table 3.1). 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.⁷⁹ The similar aliphatic OH contents of the OL and LS could have resulted in their similar MM changes, opposed to that of the KL with the higher phenolic OH content.^{50,86} Dispersion 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 ethylene glycol, polyethylene glycol (PEG) and glycerol.^{50,86} The KL seems to be fragmented more extensively during the liquefaction. The KL solid phase product \overline{M}_n however remained stable, indicating that larger MM fractions are preferentially fragmented, reducing \overline{M}_w . In the case of LS the \overline{M}_w and \overline{M}_n increased in the product. The same was seen for the OL, but \overline{M}_n increased less, relative to \overline{M}_w , indicating a greater degree of modification among larger MM fragments. The crude glycerol constituent contents were previously found to undergo differing changes during liquefaction of each of the three lignins (Figure 3.4, Supplementary Material).⁷⁹ The most significant change with regards to the aforementioned SEC results firstly appears to be a 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 MM LS fractions to a greater extent, affecting the increase in \overline{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 \overline{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 FAEE) and glycerol.

Table 3.3 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 MM, with both increases and decreases reported. It can also be seen that liquefaction of lignin in PEG/glycerol might produce higher MM polyols than crude glycerol liquefaction.

Figure 3.2a shows an overlay of the crude glycerol and liquid phase liquefaction product chromatograms. MAG eluted at close to 16.5 mL and glycerol at 17.0 mL in each of the samples. The OL liquid product showed an additional peak at 16.1 mL. That might have been a lower MM lignin derivative formed during liquefaction.⁸⁵⁻⁸⁶ Sunflower oil (triacylglycerol), diacylglycerol and fatty acid ethyl esters (FAEE) were found to be insoluble in the mobile phase

Table 3.3: Lignin and corresponding lignin-derived polyol MM reported.

Lignin type	Lignin MM (g mol ⁻¹)	Polyol MM (g mol ⁻¹)	Hydroxyl number (mg KOH g ⁻¹)	Liquefaction	Reference
Olive tree pruning, organosolv lignin	4209 / 3.77 ^a	2117 / 3.54	176–821	PEG/glycerol, H ₂ SO ₄ ^b	Sequeiros Echeverria et al. ¹⁴⁴
Empty fruit bunch, kraft lignin	1564 / 2.62	16730 / 13.94	-	PEG/glycerol, H ₂ SO ₄	Faris et al. ¹⁴⁵
Alkaline lignin	2726	1079	462	PEG/glycerol, H ₂ SO ₄	Li et al. ¹⁴⁶
Lignosulphonate	19000 / 1.1	2226 / 1.6	321–494	Glycerol/DEG, PTSA ^c	Gao et al. ¹⁴⁷
Corncob, alkaline lignin	2792 / 3.07	1108 / 2.43	-	PEG/glycerol, H ₂ SO ₄	Xue et al. ⁵⁴
Birch, ethanol /water lignin	2560 / 1.67	4990 / 1.08	4.4 (mmol g ⁻¹)	PEG/glycerol, H ₂ SO ₄	Xue et al. ⁵⁶
Beech, milled wood lignin	5800 / 1.9	2950 / 2–5500 / 8	-	EG, PTSA ^c	Jasiukaitytė-Grojzdek et al. ⁸⁶

^a Dispersity. ^b Catalyst. ^c *p*-Toluene sulfonic acid monohydrate.

(DMSO/H₂O). The liquid phase products exhibited similar chromatograms when analysed with THF as the mobile phase (Figure 3.2b and 3.5, Supplementary Material). 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,⁷⁹ which indicated that the OL liquid product had increased lignin-derived aromatic content compared to the KL and LS liquid products (Figure 3.6, Supplementary Material).

3.3.2 FTIR spectroscopy

Lignin

The spectra (Figure 3.3a) of the three lignins resemble those reported in literature.^{92,148} There are differences at 1715 cm⁻¹ where the OL has a band assigned to C=O in carbonyl or carboxyl, formed through oxidation during isolation.⁹² The lignins also differ in terms of syringyl (S), guaiacyl (G) and *p*-hydroxyphenyl (H) unit content due to their various origins.¹⁴⁹ The OL has a broad signal at 833 cm⁻¹ assigned to S, G and H units of a grass type lignin.¹³⁷ This band is absent in the KL and LS. The KL has a band at 855 cm⁻¹ indicative of G units,¹⁴⁹ while bands in this area of the LS are difficult to distinguish. A higher ratio of band intensities between 1505

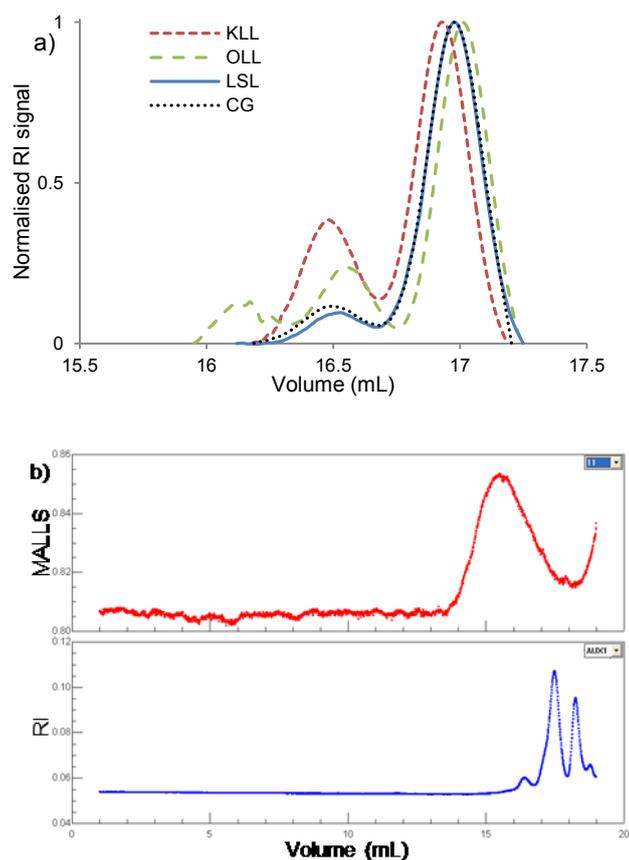


Figure 3.2: Liquid phase product SEC elution profiles: a) DMSO/H₂O system (KLL, OLL, LSL and CG refer to KL, OL, LS liquid product and crude glycerol, respectively). b) OL liquid product analysed on the THF system (Peaks from 18 mL onwards are due to solvent effects, not attributable to the samples).

and 1595 cm^{-1} is related to a higher level of condensation or cross-linking in lignin by some,¹⁵⁰⁻¹⁵¹ also indicative of a higher G relative to S unit content.¹⁵²⁻¹⁵³ 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.^{21,152}

Solid phase products

In the FTIR overlay (Figure 3.3b–d) of the KL and the solid phase product the intensity of the OH absorbance band^{101,145,154} between $3600\text{--}3100\text{ cm}^{-1}$ differ, indicating a change in the OH contents during liquefaction. There is a decrease in the intensity of the LS product in this band while OL intensities are also changed, but to a lesser extent. At 2926 and 2855 cm^{-1} the KL product show increased intensities, attributed to stretching vibrations of methyl and methylene groups.¹²⁷ The same is observed in the case of the OL and LS, indicating introduction of aliphatic chains.⁵⁰ A new band becomes visible around 1728 cm^{-1} in the KL product spectra,

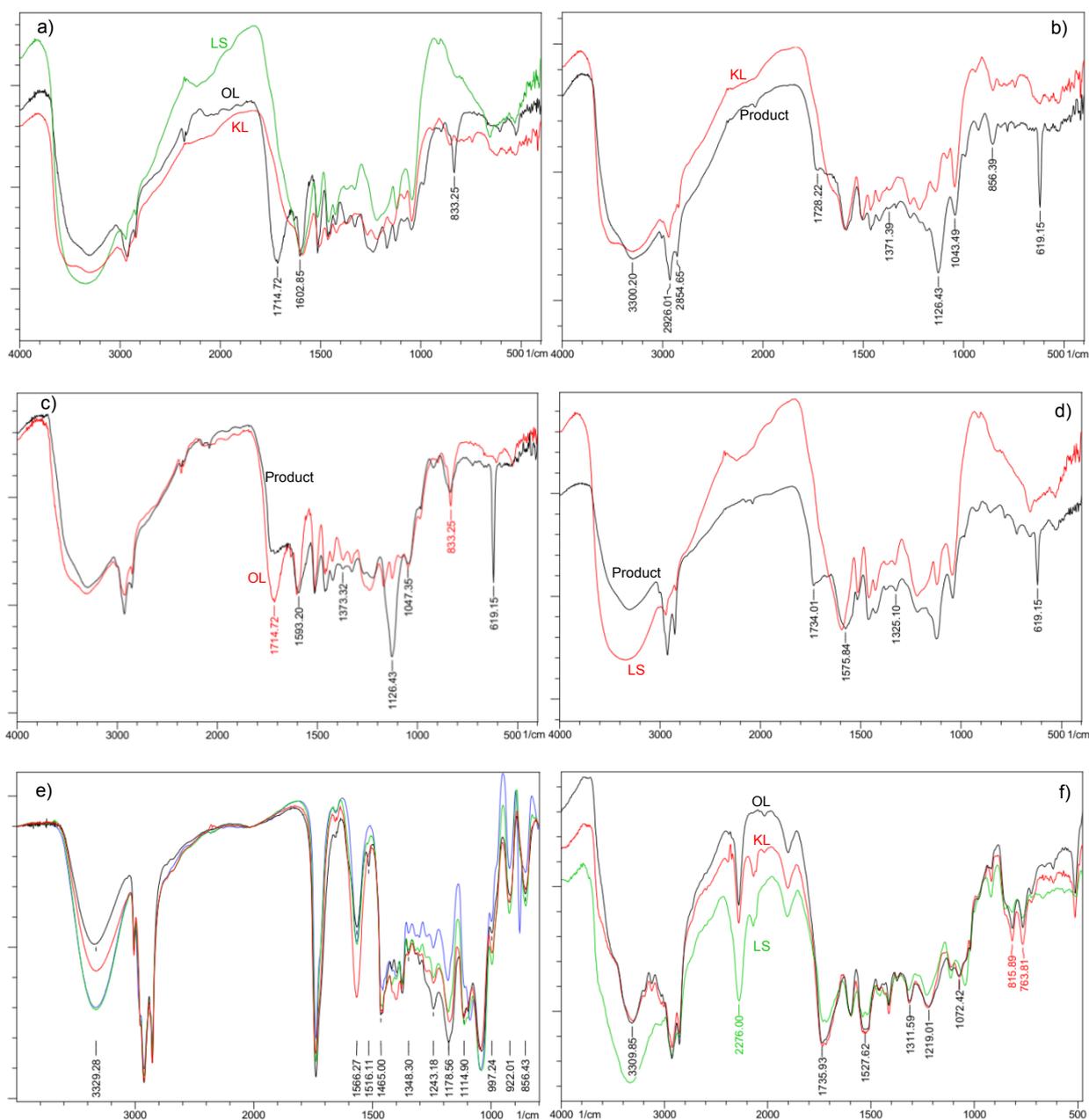


Figure 3.3: FTIR spectra: a) Lignin, b) KL and solid product, c) OL and solid product, d) LS and solid product, e) Crude glycerol and liquid products (black-OL, red-KL, green-LS, blue-crude glycerol), f) Polyurethanes.

assigned to the C=O stretch of aliphatic ester bonds.¹²⁷ The OL show a band at 1714 cm^{-1} assigned to C=O stretching in carboxyl or carbonyl groups of lignin,⁹² which is 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 exhibit similar changes than the KL in this area. A band is formed at 1126 cm^{-1} in the product spectra of all three lignins. This band is assigned to ether C-O-C stretching.^{50,155} Similarly, a band is formed at about 619 cm^{-1} in the spectra of the solid products,

which is absent in the starting lignin spectra. S-O stretching bands are assigned in this area.^{154,156}

To summarise, a change in the OH content of the lignins during liquefaction was observed. Aliphatic methyl and methylene absorbance increased in the products, likely indicating the introduction of fatty acid chains from MAG and FAEE.¹⁵⁷ This is supported by the appearance of aliphatic ester bond signals. The ester bonds absorb in the band assigned to aliphatic groups,¹⁵⁸ 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.⁸⁶ Since signals of aliphatic OH (1040 cm^{-1}) and phenolic OH^{127,159-160} (1370 cm^{-1}) were still present in the solid product spectra the lignin OH was only partially consumed. The introduction of glycerol OH was also expected to cause absorbance around 1040 cm^{-1} .¹¹⁸

Crude glycerol and liquid phase products

Absorbance is decreased in the OH band around 3329 cm^{-1} for the OL and KL liquid products compared to the crude glycerol (Figure 3.3e). Around 1566 cm^{-1} absorbance is intensified for the KL product. This band is assigned to soap COO^- in crude glycerol.¹⁶¹ 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).¹⁵³ The products show somewhat increased intensities around 1465 cm^{-1} . The band is assigned to C-O-H bending in crude glycerol¹⁶¹ and C-H deformation of lignin methoxyl.¹⁵³ Intensities are higher in the product spectra range $1350\text{--}1115\text{ cm}^{-1}$, most noticeably at 1243 , 1179 and 1115 cm^{-1} . Absorbance in the aforementioned bands has been assigned to aromatic C-O, ester C-O⁹² and aromatic C-H in S units^{153,160} 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 show 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 glycerol¹⁶¹⁻¹⁶² and C-H deformation of G units in lignin.¹⁴⁹ Ethanol¹¹⁸ 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 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 are confirmed through the observed bands at 3310 , 1736 , 1528 and 1219 cm^{-1} in the spectra of the prepared polyurethanes (Figure 3.3f). These bands are the result of mixed absorbance assigned to N-H, C=O of urethane, coupled N-H and

coupled C-N, respectively.^{77,163-164} The band at 1736 cm⁻¹ also overlaps with urea absorbance, present at approximately 1700–1640 cm⁻¹.¹⁶⁵⁻¹⁶⁶ The prepared PUFs present bands not seen in the liquefaction product spectra, further suggesting the formation of polyurethane. The absorbance maxima are as follows: 1528, 1312, 1072, 816 and 764 cm⁻¹. At 1312 cm⁻¹ the absorbance is assigned to urethane,¹⁶⁵ at 1072 cm⁻¹ to urethane C-O-C and both at 816 and 764 cm⁻¹ to aromatic C-H.^{70,167} At 2276 cm⁻¹ excess unreacted isocyanate NCO absorbance is visible.¹⁶⁴⁻¹⁶⁵

3.3.3 Yield and hydroxyl numbers

The crude glycerol OH content was reduced during lignin liquefaction (Table 3.4). The OL product has the lowest hydroxyl number, which indicates OH was removed to a greater extent than during KL and LS liquefaction.¹²⁶ The product hydroxyl numbers are similar to those obtained by other workers from liquefaction of lignin (Table 3.3), as well as lignocellulose, generally ranging 100–600 mg KOH g⁻¹.⁴⁹ The numbers also correspond with that of commercial polyols for rigid polyurethane foam.¹⁶⁸ 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 limited increase of aromatic content in the OL liquid product spectra was more prominent. Similarly, the SEC analysis revealed higher MM 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.

Table 3.4: 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)
Kraft lignin	412±27	1.19±0.23	0.62±0.16
Organosolv lignin	224±10	0.76±0.11	0.73±0.06
Lignosulphonate	592±18	1.25±0.12	0.61±0.07
Crude glycerol	769±32		

3.4 CONCLUSIONS

The KL weight-average MM was decreased during liquefaction to form the solid phase product, in contrast to the OL and LS which both formed products of increased MM. The MM 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 MM to some extent. The organosolv lignin liquid phase products showed the presence of low concentrations of higher MM 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. The OL and KL liquid products showed decreases in OH content, while increases in ether bond content were seen for all. The results indicate that the products were proposedly formed through modification of lignin by formation of new ether and ester bonds with glycerol, MAG and FAEE. Polyurethane formation through reaction between the products and diisocyanate was confirmed by FTIR. The lower MM of the KL solid product could potentially have a significant effect on polyurethane properties by increasing crosslink density.⁵⁹ Lignin type, based on its origin and isolation method, is thus an important determinant of the product characteristics and its application potential. The products were intended as biobased polyols for rigid polyurethane preparation, but could also be further modified for other applications.

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3.6 SUPPLEMENTARY MATERIAL

EXPERIMENTAL

THF size-exclusion chromatography (SEC)

The SEC-MALLS analysis procedure used, was described by Otto et al.¹⁶⁹ In short: The system consisted of an HPLC (Agilent 1100) with a MALLS detector (Wyatt Corp DAWN DSP photometer, Santa Barbara, CA) using a 5mW He-Ne laser set at 632.8 nm. The concentration was monitored by a RI detector (Agilent 1100 series). The column set consisted of a PLGel mixed bed type C column (7.6 mm x 300 mm, exclusion range 300–2,000,000 g mol⁻¹, particle size of 5 µm) and a Phenogel column (Phenomenex, 7.8 mm x 300 mm, exclusion range > 5000 g mol⁻¹, particle size of 5 µm). The eluent used, was THF containing 250 ppm BHT as inhibitor. The flowrate was 1 mL min⁻¹, system temperature was set at 30 °C and the injection volume was 100 µL. The dn/dc value was determined for each sample using the online method described by Lee and Chang.¹⁷⁰ Polystyrene ($\overline{M}_w = 30000$ g mol⁻¹, dispersity < 1.05) was used as standard.

Liquid phase product samples were prepared by first derivatizing the material according to the method described by Guerra et al.¹⁷¹ About 20 mg of sample was reacted with a mixture (0.25 mL mg⁻¹) of acetic acid/acetyl bromide (92:8, v/v) for 2 h at 50 °C under constant stirring in a closed vial. Afterwards the solvent was removed in a rotary evaporator. THF was immediately added to yield a sample concentration of 2mg mL⁻¹. Samples were stirred for 12 h and then left to stand a further 48h before the filtered samples (0.45 µm PALL Acrodisc GxF/GHP syringe filters) were analysed.

RESULTS AND DISCUSSION

Table 3.5: Crude glycerol composition.⁷⁹

Constituent	wt%
FAEE	27.2±1.3 ^a
MAG	9.6±1.3 ^b
Diacylglycerol	0.8 ^b
Ethanol	14.8±3.7 ^b
Glycerol	25.3±0.5 ^b

^a Determined by GC. 95% Confidence interval based on triplicate analysis.

^b Determined by ³¹P NMR. Based on triplicate analysis.

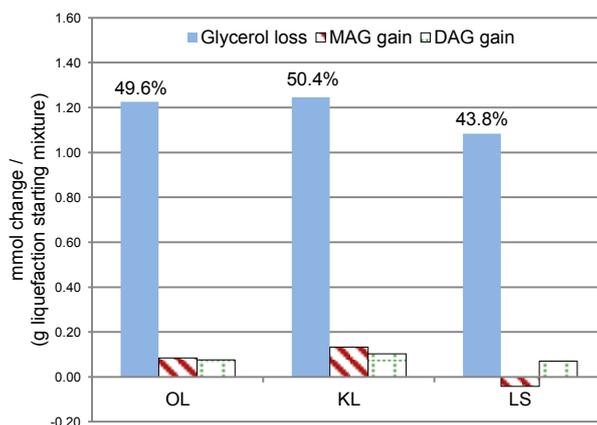


Figure 3.4: Change in crude glycerol constituent contents during liquefaction of the respective lignins, determined with ^{31}P NMR spectroscopy.⁷⁹

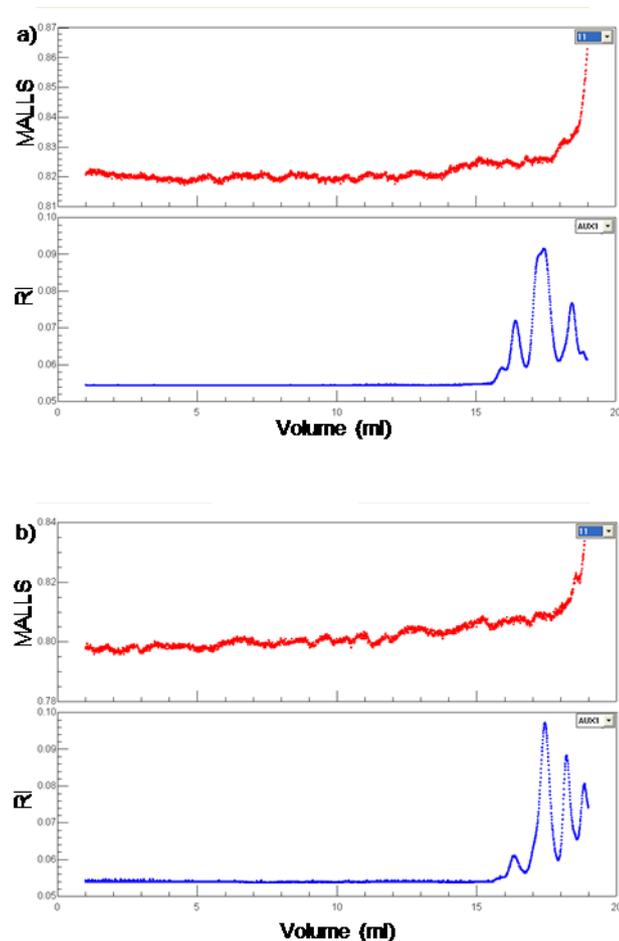


Figure 3.5: Liquid phase product elution profiles on the THF system: a) KL liquid product, b) LS liquid product (Peaks from 18 mL onwards are due to solvent effects, not attributable to the samples).

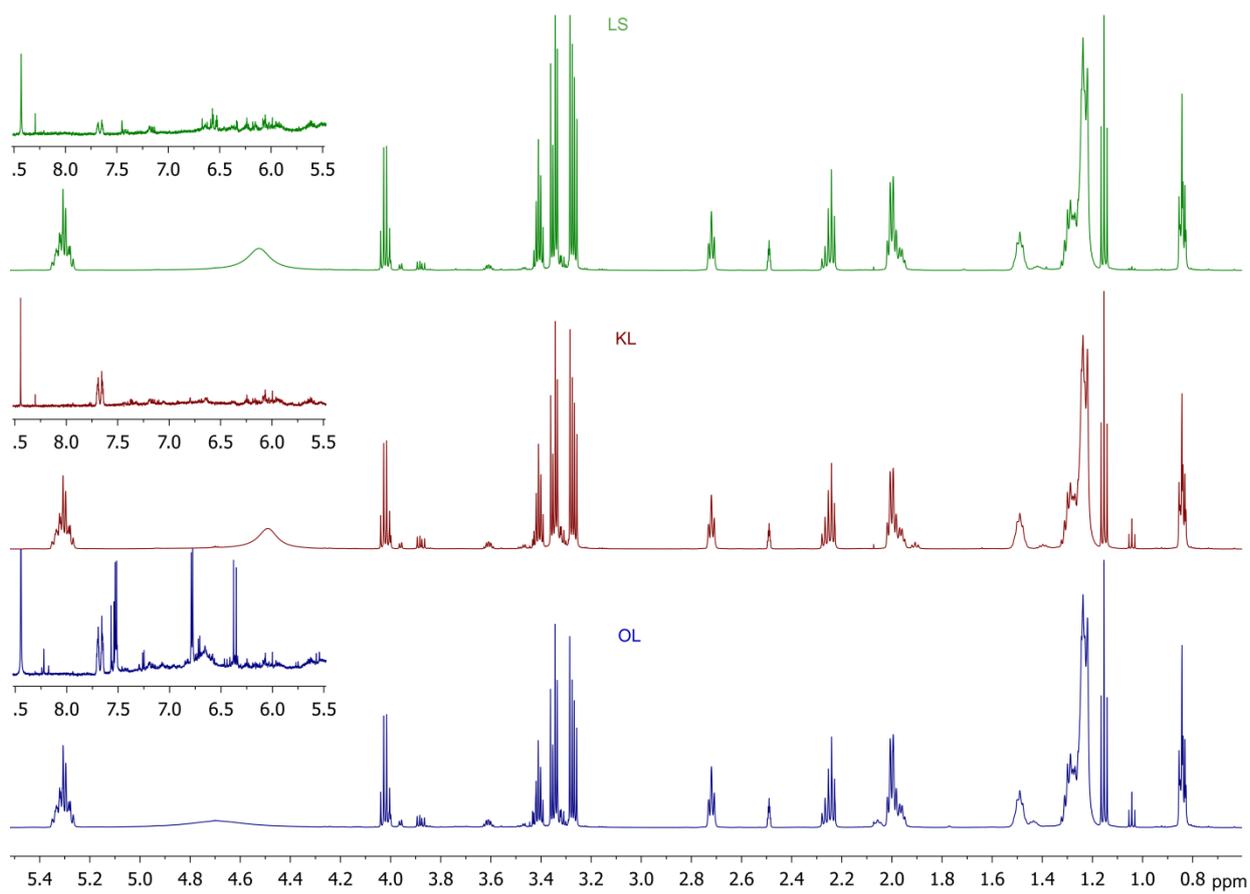


Figure 3.6: ^1H NMR spectra of liquid phase products.⁷⁹

CHAPTER 4 VALORISATION OF BIOREFINERY BY-PRODUCTS: RIGID POLYURETHANE FOAMS FROM LIGNINS AND CRUDE GLYCEROL

ABSTRACT

Driven by the need for green materials rigid polyurethane foam has been prepared in part from many biomass types in the past. The present study aims at increasing biobased content further by utilizing by-products from both the pulp and paper and biodiesel industries. Biobased polyols from respective liquefaction of kraft lignin, organosolv lignin or liginosulphonate in crude glycerol were successfully employed to prepare rigid polyurethane foams. The highest foam compressive strength achieved was 345 kPa with density 79 kg m^{-3} ; thermal conductivity was $0.039 \text{ W m}^{-1} \text{ K}^{-1}$ and the corresponding material had 44 wt% renewable content derived from wood or sugarcane bagasse, seed oil and ethanol. Thermal characteristics and biodegradability were also evaluated. Technical lignin type was found to determine product properties to a large extent. The findings of this work can be beneficial for present and future biorefineries in the valorisation of by-products.

Keywords: kraft lignin, organosolv lignin, liginosulphonate, crude glycerol, rigid polyurethane foam

4.1 INTRODUCTION

There have been many efforts and progress in the preparation of rigid polyurethane foams from biobased polyols (biopolyols) in an attempt to increase their renewable content. This is due to a global move towards limiting dependence on crude oil and addressing environmental concerns.^{15,49,82} Rigid polyurethane foam (PUF) specifically is employed as insulation material which lowers energy consumption, a further drive for its increased use and development.⁴⁵ Initially there was a focus on biopolyols prepared through modification of agricultural and forestry residues. Such residues however contain various valuable compounds such as cellulose, hemicellulose, terpenes etc., and therefore some work has also focused on utilising only the lignin fraction, which is widely studied as a renewable and sustainable feedstock for biofuels, chemicals and materials.^{16,49,82} Lignin is currently produced globally at industrial scale as a by-product in the pulp and paper industry.^{15,19}

Lignin has been used in its isolated form as a biopolyol to prepare polyurethane,^{15,21} but is often modified to improve reactivity and the properties of the polyurethane product. Biomass liquefaction in petroleum-derived reagents such as polyethylene glycol and diethylene glycol or oxypropylation with propylene oxide are most often used as modification strategies, and the resulting rigid polyurethane foams (PUFs) possess acceptable properties.^{21,49} The use of “green” modification reagents such as crude glycerol or bio-butanediol to further increase the final product’s biobased content has more recently been reported.^{49,71} Crude glycerol, a major by-product from the biodiesel industry, is currently in oversupply and actively being studied as a low cost feedstock for renewables.³⁷ Biodiesel production from sources such as waste oils yields crude glycerol as a sustainable feedstock.¹⁷²

Polyurethane preparation based on biopolyols derived from both lignin and crude glycerol has only recently been reported by *Lee et al.*⁷³ and *Kim et al.*¹²⁸ who liquefied empty fruit bunches and sunflower stalk saccharification residues in crude glycerol, respectively. This study focuses on using biopolyols obtained from liquefaction of technical lignins in unrefined crude glycerol to prepare rigid PUF, which has not, to the best of our knowledge, been reported.⁷⁹ The two major technical lignin types available as by-products from the pulp and paper industry, kraft lignin and liginosulphonate,¹⁵⁻¹⁶ were selected, as well as a lignin extracted from a major grass crop residue (sugarcane bagasse) by an organosolv method, intended as representative of a cellulosic biorefinery by-product. The ultimate goal is to increase the economic feasibility of biorefineries.

Lignin, crude glycerol and the catalyst made up the liquefaction reagents and the biopolyols were used as the sole polyol component in order to maximise the renewable content of the PUFs. The rigid PUFs obtained were characterised and compared to determine the effect of

different lignin types on the product. Material properties relevant to rigid foam insulation were investigated and included compressive strength, density, thermal conductivity and closed cell content. The three foams were compared in terms of microstructure through the use of scanning electron microscopy (SEM), as well as thermal behaviour through thermogravimetry (TG) and dynamic mechanical analysis (DMA). Due to the higher biobased content of the PUFs, biodegradability is of interest and was evaluated by CO₂ evolution during soil incubation, SEM and FTIR spectroscopy.

4.2 EXPERIMENTAL

4.2.1 Materials

As previously reported organosolv lignin (OL) was extracted from sugarcane bagasse (kindly supplied by Tsb Sugar RSA (Malalane, South Africa, 24.4833°S, 31.5167°E)) according to a method reported by Xu *et al.*⁹² employing a mixture of acetic acid, formic acid and water. Lignin extraction and crude glycerol preparation through KOH catalysed transesterification of sunflower oil and ethanol were previously described.⁸⁰ Hardwood calcium lignosulphonate (LS) was kindly donated by Sappi Technology Centre from Sappi's Saiccor mill (Umkomaas, South Africa, 30.2010°S, 30.7940°E). Softwood kraft lignin (KL), polyethylene glycol (PEG) of average molar mass 400 g mol⁻¹, sulphuric acid (98 wt%), hydrochloric acid (37 wt%), potassium hydroxide (0.5 mol dm⁻³) and diammonium hydrogen phosphate were obtained from Sigma-Aldrich (Kempton Park, South Africa). Diphenylmethane-4,4'-diisocyanate (MDI), Desmodur 44V20L, was kindly donated by Bayer Material Science (Isando, South Africa). Catalysts and surfactants for polyurethane preparation were kindly donated by Air Products (Kempton Park, South Africa). *Aspergillus* ATCC 16404 was obtained from Quantum Biotechnologies (Randburg, South Africa). Soluble starch was bought from Associated Chemical Enterprises (Johannesburg, South Africa). All chemicals were of reagent grade or higher and used as received. Commercial polyester-polyether polyol-based rigid PUF insulation was kindly donated by Rigifoam (Benoni, South Africa) to serve as representative of petroleum-derived PUF.

4.2.2 Preparations

The preparation and characterization of the biopolyols have previously been reported.⁷⁹ In short: crude glycerol, adjusted to pH 8 with 98 wt% H₂SO₄, was heated to 160 °C in a glass reactor open to atmosphere. The respective lignins were then added at a weight ratio 9:1 (crude glycerol:lignin). Reactions were performed for 90 minutes under magnetic stirring, where after products were immediately cooled to room temperature. The respective products are further referred to as biopolyols and were used without further processing. The hydroxyl numbers of the biopolyols were determined according to the standard method, ASTM D4274-11 method D.⁹⁷

The rigid PUF formulations are shown in Table 4.1.^{146,173-174} Polyol, catalysts, surfactant and water were premixed in a beaker at 6,000 rpm for 15 to 20 seconds with a hand blender. The required amount of diisocyanate (MDI) was weighed off into the mixture and it was similarly stirred for 10 to 15 seconds. The PUF was left to rise and cure for at least 24 h before being removed from the beaker. A mixture of PEG and glycerol was used as a polyether polyol to prepare rigid PUF employed as representative of petroleum-derived PUF during part of the biodegradability study discussed below.

Table 4.1: Polyurethane foam formulation.

Reactants	Biopolyol PUF	PEG/Glycerol PUF
	(KL, OL or LS polyol)	(PEG/Glycerol)
Parts by weight		
Polyol	100	100 ^b
Gelling catalyst (Polycat 8)	0.86	0.86
Blowing catalyst (Polycat 5)	0.67	1.16
Surfactant (DC5357)	2.5	2.5
Blowing agent (Water)	1.25 ^a	2.75
Isocyanate index	105 ^c	105

^a Value of 1.1 employed for LS biopolyol-based PUF. ^b PEG:glycerol at 9:1 (wt/wt).
^c Isocyanate index of 105 indicates 5% excess isocyanate is used, relative to the theoretical equivalent of the total hydroxyl content of the other reactants. Corresponding “parts by weight” of isocyanate were as follow for KL, OL and LS: 127, 78 and 171, respectively.

4.2.3 Polyurethane foam characterization

Scanning electron microscopy (SEM) micrographs of the different PUFs were taken with a FEI Quanta 250 FEG Environmental SEM (Hillsboro, Oregon). Samples were cut with a scalpel. Spectra of gold/palladium sputter-coated PUF samples were recorded at an acceleration voltage of 5 kV under high vacuum.

The compressive strength of the PUFs was determined according to a standard method, ASTM D1621-10,¹⁷⁵ on a custom built compression testing instrument (Figure 4.9, Supplementary Material). Cubic samples with side dimensions ca. 55 mm were prepared and weighed in order to determine apparent density before testing.¹⁷⁶ The movable member speed was set at 2.5 mm min⁻¹ per 25.4 mm specimen height, along the foam’s rise direction. Measurements were done at room temperature on at least five specimens for each material. All sample dimensions were measured with a Vernier calliper accurate to 0.02 mm.

Closed cell contents of samples in cubic form with side dimensions ca. 17 mm, were analysed in a Quantachrome Instruments Stereopycnometer (Boynton Beach, FL). The small cell was fitted and pressurised to an initial pressure of 3 psi with nitrogen. At least three measurements were taken per sample.

Thermal conductivity measurements were done on a Hot Disk TPS 500 (Gothenburg, Sweden) thermal constant analyser employing the Kapton 5501 sensor with radius 6.4 mm. Each sample consisted of two halves, each with dimensions: diameter 70 mm, height 15 mm. Three measurements were averaged for each sample. The laboratory was maintained at 24 °C.

Thermogravimetry (TG) was performed on a Mettler Toledo TGA/SDTA851e. Crushed samples of approximately 5 mg were analysed under nitrogen flow of 100 mL min⁻¹, heated in sealed aluminium pans from 25 to 600 °C at 10 °C min⁻¹. Differential TG (DTG) curves were calculated from the TG data.

Dynamic mechanical analysis (DMA) was performed on a Perkin Elmer Diamond DMA (Waltham, MA). Measurements (duplicate) were performed in compression mode at 1 Hz frequency, with temperature ramps of 3 °C min⁻¹ and initial force of 2.5 N. Sample height was 3 mm and diameter 10 mm.

4.2.4 Polyurethane foam biodegradability evaluation

CO₂ evolution was evaluated in soil. Briefly, degradability of biopolyol-based PUF (KL PUF) was compared to that of petroleum-derived PUF (Rigifoam, polyester-polyether polyol-based) through a standard test method: ASTM D5988-12.¹⁷⁷ Fertile soil was collected from various locations on a farm (Warden, South Africa, s27°43.408' e028°52.481'). The test setup consisted of desiccators each filled with 500 g soil (adjusted to 28.8 wt% moisture, Supplementary Material). PUF and starch (control) sample sizes were adjusted to consist of 1000 mg carbon taking into account the material elemental compositions. The soil was inoculated with *Aspergillus* (ATCC 16404) sporal suspension to obtain approximately 100000 spores g⁻¹ soil according to Amaral *et al.*⁷⁵ PUF samples in the form of cubes with sides ca. 3 mm or starch were mixed into the soil. Two glass beakers, one containing 20 mL of 0.5 mol dm⁻³ KOH solution and the other 50 mL deionized water, were placed above the soil surface on a perforated plate in each desiccator. The desiccators were sealed with vacuum grease and kept in a laboratory maintained at 22 °C. The quantity of CO₂ evolved in each desiccator was determined by periodic titration of the KOH solutions with 0.25 mol dm⁻³ HCl solution to a phenolphthalein endpoint. The test consisted of three desiccators for each of the following: biopolyol PUF, commercial PUF, starch control, blank soil samples and technical control

samples (containing no soil or samples). Further details can be found in the Supplementary Material.

A Shimadzu (Kyoto, Japan) IRAffinity-1 FTIR spectrometer fitted with a PIKE Technologies (Madison, WI) EasiDiff accessory was used to record diffuse reflectance spectra in a KBr matrix. Transmittance spectra were recorded between 4000 and 400 cm^{-1} , at 4 cm^{-1} resolution with 45 scans. Samples taken from the soil were washed with water and dried before being powdered with a pestle and mortar. The more flexible PEG/glycerol PUF was not powdered, but analysed by attenuated total reflectance (ATR) FTIR spectroscopy on a Bruker (Madison, WI) VERTEX 80 spectrometer, fitted with a diamond ATR accessory – 32 scans were recorded at 4 cm^{-1} resolution, between 4000 and 400 cm^{-1} . Comparison of the spectra were based on the intensity of the absorption band at 1413 cm^{-1} , assigned to the MDI phenyl C=C. These are considered to be the bonds found in the PUFs that are the most resistant to degradation.⁷⁷

4.3 RESULTS AND DISCUSSION

4.3.1 Polyurethane foam preparation

The hydroxyl numbers of the kraft lignin, organosolv lignin and liginosulphonate-based biopolyols were previously found to be 412 ± 27 , 224 ± 10 and 592 ± 18 mg KOH g^{-1} , respectively.⁸⁰ Further details of the crude glycerol and biopolyol compositions are given in the Supplementary Material (Section 2.2.1, Table 2.8 & Figure 2.7a), as reported previously.⁷⁹

Subsequently the biopolyols were used to prepare PUFs and the fracture-surface microstructure of the resulting PUFs are shown in Figure 4.1. The KL biopolyol-based PUF (KL PUF) structure most closely resembles that of polyurethane aerogels.¹⁷⁸ A porous network of polymer microparticles is visible. The OL PUF structure is similar but the particles appear larger. The LS PUF structure does not show particles at this scale, rather the surface appears smooth with a large number of small holes. *Chidambareswarapattar et al.*¹⁷⁸ found that polyurethane aerogel particle size, porosity and interparticle connectivity, which affect material properties, are dependent on monomer size, functional group density (OH per aromatic ring) and molecular functionality (OH per monomer). Their polyurethane aerogel network consists of primary particles which assembled into secondary particles which then aggregated to form the mass-fractal agglomerates which made up the network. Since the lignins and lignin-based biopolyols each differ in terms of the three properties given above it is expected that when used to prepare polyurethanes, the resulting microstructures would differ. The size of microparticles in polyurethane aerogel networks are determined by the degree of phase separation due to differences in solubility of the monomers and products.¹⁷⁹ Lower solubility leads to smaller

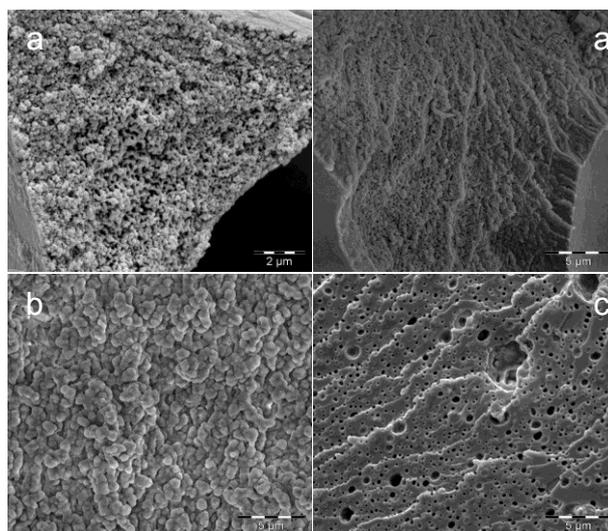


Figure 4.1: Biopolyol-based PUF microstructure by SEM. a) KL PUF, b) OL PUF, c) LS PUF.

primary particles whereas higher solubility leads to less phase separation and subsequent larger particles. In the latter case excess monomer in solution bind on the surface of the primary particle aggregates to eliminate mesoporosity and gives the appearance of a smooth polymer covering over an underlying network of “fused particles”.¹⁷⁸ The formulations of the respective PUFs differed in the weight of isocyanate used relative to the polyol component, because of the variation in hydroxyl number, which should have affected the phase separation. Grunbauer and Folmer¹⁸⁰ illustrated that when the isocyanate index of rigid PUF increases there is a morphology transition from surface fractal to mass fractal (due to increased phase segregation) with the effect that surface roughness of the phase boundaries decreases to yield smoother surfaces. Ignat *et al.*⁷⁷ blended lignin into polyurethane elastomers and found that the surface porosity and granulation increased. Based on the above discussion, the smaller particle size seen in the KL PUF might be as a result of the original kraft lignin which had the highest phenolic OH content and thus the highest functional group density which could translate into faster phase separation.¹⁷⁸ The absence of visible particles in the LS PUF microstructure is likely due to the higher isocyanate content used, based on the higher hydroxyl number of the LS biopolyol, resulting in a smoother surface as described by Grunbauer and Folmer.¹⁸⁰ The lower hydroxyl number of the OL biopolyol might have led to delayed phase separation resulting in the larger particles seen. It would be a combination of parameters leading to the final microstructure of the respective PUFs, including biopolyol MM.

4.3.2 Material properties

A comparison of the PUFs' morphology is shown in Figure 4.2. Similarly the specific compressive strength values (Table 4.2) differ significantly among the PUFs. In terms of desirable cell structure the PUFs deteriorate in the order KL > OL > LS, with the LS PUF exhibiting highly irregular cell shapes and sizes with thicker cell walls.

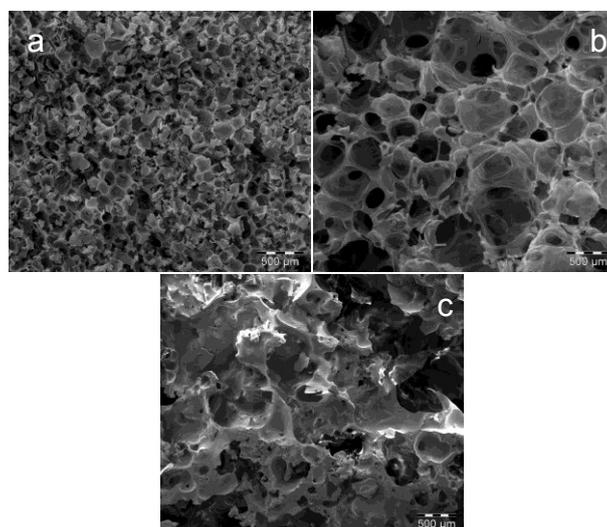


Figure 4.2: SEM micrographs of biopolyol PUF morphology. a) KL PUF, b) OL PUF and c) LS PUF.

Table 4.2: Material properties of biopolyol-based PUFs.

	KL PUF	LS PUF	OL PUF
Compressive strength at 10% strain (kPa)	345±63 ^a	245±51	50±26
Density (kg m ⁻³)	79±24	154±8	70±22
Specific ^b compressive strength (kPa kg ⁻¹ m ³)	4.4±0.8	1.6±0.4	0.7±0.4
Thermal conductivity (W m ⁻¹ K ⁻¹)	0.039±0.003	0.048±0.001 ^c	0.042±0.005
Closed cell content (vol%)	3.3±0.6	6.9±0.9 ^c	3.0±1.0

^a 95% confidence interval. ^b Ratio of the compressive strength to the apparent density. ^cThe LS PUF structure was optimized to allow measurement of thermal conductivity since the original material was too porous. Blowing agent content was reduced and the resulting foam had a density of 123±5 kg m⁻³. Cell uniformity improved, while size and wall thickness reduced.

Regular cell shapes of smaller sizes impart higher strength as do thicker cell walls.^{157,181} It appears that the gel formation in the case of the LS biopolyol with MDI was less balanced with the foaming reaction than it was for the other biopolyols. A low rate of gel formation would cause MDI to react with water to produce excess CO₂ and urea at a too early stage, which

would lead to irregular open cells with thicker walls and a higher apparent foam density.^{61,146} The LS PUF however presents a higher specific compressive strength than the OL PUF. The LS biopolyol had a significantly higher hydroxyl number, enabling higher crosslink density which imparts strength.^{59,182-183} Increased urea content can also increase stiffness.^{157,184} Excessive crosslinking due to a too high hydroxyl number can however cause an irregular cell structure.¹⁶⁶ Conversely the OL biopolyol had the lowest hydroxyl number. The biopolyols further differed in composition with the LS biopolyol having the lowest monoacylglycerol (MAG) content and the highest glycerol content (Figure 2.7a). MAG acts as a chain extender which lowers crosslinking density,¹⁶⁶ while unreactive dangling fatty acid chains of MAG, diacylglycerol and fatty acid ethyl esters lower compressive strength, acting as plasticizers.¹⁷⁴ The superior specific compressive strength of the KL PUF is attributed to a combined effect of its more regular and smaller cell shapes, microstructure, high crosslink density and lignin-specific properties such as MM, since various types of lignin have been found to perform differently in polyurethane systems.^{58,185} The values of compressive strength and density reported for biomass-based PUFs range widely, for example: 40–400 kPa and 10–80 kg m⁻³ for foams derived from bark, bamboo, wood, lignin-molasses and crude glycerol-castor oil, respectively.¹⁸⁶⁻¹⁸⁷ Commercial products can have compressive strength as low as 100 kPa, depending on the application. Density for insulation varies, normally 30–45 kg m⁻³, but can also be higher.¹⁸⁸⁻¹⁸⁹

The thermal conductivities of the prepared PUFs (Table 4.2) are above that of some commercial polyurethane products, 0.022–0.040 W m⁻¹ K⁻¹, but within the range of values reported for the many available conventional and alternative insulation materials.^{45,189-190} Heat transfer in polyurethane foams occurs through conduction, radiation and convection.^{188,191-192} Conduction and radiation contribute most and are dependent on the cellular structure. Closed cells are desirable to lower conduction through the gas phase by separating cells and retaining low conductivity blowing agents in the cells, such as CO₂, while limiting air ingress.^{188,193} Conduction in the solid phase is lowered by decreased density.¹⁸⁸ Heat flow by radiation is lowered by higher density, a decrease in cell size and higher fraction closed cells.^{188,191-192,194} Based on the aforementioned, the higher thermal conductivity of the LS PUF is caused by its irregular structure (Figure 4.2), with larger and fewer cells, thick cell walls and corresponding higher density.¹⁹⁵ The KL PUF has a lower density, smaller cell sizes with a corresponding higher number of cells and therefore the lowest thermal conductivity. The foams however exhibit a fully open cell structure, which increases thermal conductivity as mentioned (Table 4.2). Formation of closed cells can be controlled by surfactant optimization,¹⁹⁶⁻¹⁹⁸ as well as through balancing the blowing rate.^{188,193} In this regard rigid PUF made in part from biopolyols has been reported to yield inferior cell structures compared to conventional petroleum-derived polyols, when used at higher substitution levels. That includes biopolyols derived from lignin, crude glycerol, crude glycerol-castor oil, soy oil-castor oil, sawdust and bark (1–4% closed cells) while substituting

50–100 wt% of conventional polyols in the respective PUF formulations.^{186-187,195,199-201} Low reactivity, limited flexibility due to shorter chain lengths and lower functionality were suggested as causes for the lower quality structures and the introduction of chain extenders, such as PEG or ricinoleic acid from castor oil, into the biopolyols are examples of proposed improvement strategies.^{187,200}

4.3.3 Thermal characteristics

The TG and DTG curves of the prepared PUFs are shown in Figure 4.3. The LS PUF shows higher initial weight loss from about 90 °C than the KL PUF and OL PUF. This is close to a peak in the loss modulus seen with DMA (Figure 4.4), discussed below. In this temperature range weight loss is associated with escape of volatiles or moisture.²⁰²⁻²⁰⁴ Onset of significant weight loss (5 wt%) appeared earliest in the KL PUF (Table 4.3). Lignin degradation onset has been reported around 180 °C by some, but it is also known to degrade over a wide range of temperatures.^{146,205} Urethane bond dissociation presents the initial stages of polyurethane thermal degradation and is reported to degrade even up to 360 °C, but more often below 250 °C.^{202,204-205}

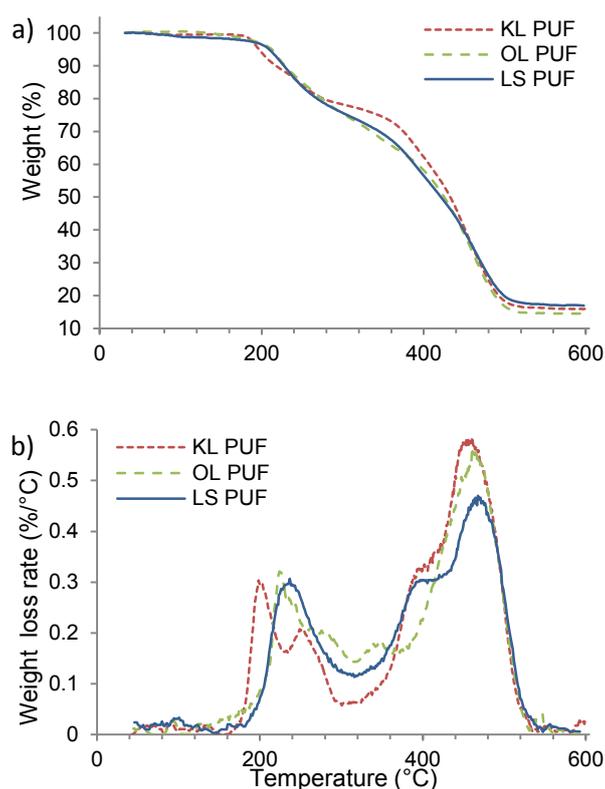


Figure 4.3: Biopolyol PUF TG (a) and DTG (b) curves.

Table 4.3: Biopolyol PUF thermogravimetry summary.

	Weight loss (%) _{T=90°C} ^a	T _{5%} (°C) ^b	T _{25%} (°C) ^b	T _{max1} (°C) ^c	T _{max2} (°C) ^c	T _{max3} (°C) ^c	T _{max4} (°C) ^c	Residue (%) ^d
KL PUF	0.6	197	344	193	244	379	454	15.9
OL PUF	0	213	302	218	275	339	458	14.5
LS PUF	0.8	209	306	223	-	380	456	17.1

^a Weight loss at 90 °C. ^b Temperatures at which 5 and 25 % weight loss was reached, respectively. ^c 1st, 2nd, 3rd and 4th maxima in the DTG curve, respectively. ^d Weight of residue remaining at 600 °C.

The KL had a higher content of phenolic OH (Table 4.4, Supplementary Material) which forms less stable urethane bonds than aliphatic OH, which was predominant in the OL and LS.^{202,206} In the range 280–350 °C the rate of weight loss in the KL PUF is lower than in the other materials (DTG). Once the more labile urethane bonds are broken, a lower rate in the KL PUF due to a higher thermal stability in the remaining urethane network caused by higher crosslink density or a differing biopolyol structure is possible.²⁰² A peak at 244 °C, possibly urethane, is present in the KL PUF's DTG curve. The OL PUF shows a maximum around 339 °C in the DTG curve. Wang *et al.*²⁰⁵ reported lignin C-C bond degradation in this area. Peaks in the KL PUF and LS PUF appear later around 380 °C. Urea degradation is also reported over a wide range of 250–320 °C.^{166,202} The maximum rate of degradation occurred similarly around 450–460 °C in all three materials, attributed to fatty acid ester chains of the biopolyols and possibly intermediate degradation products.^{166,202,204} The final char residues of the PUFs increase in the order OL < KL < LS, corresponding with the increasing weight percentage MDI (based on hydroxyl number) in the formulations of the respective PUFs. MDI increases aromaticity in the PUFs.²⁰⁷ The TG profiles indicate that the three materials differ in certain regions, but all have thermal stabilities comparable to reported values of rigid PUF prepared from either petroleum-derived or biobased polyols.

In Figure 4.4 the loss modulus (E'') of the LS PUF shows a peak at about 71 °C with a corresponding change in slope in the storage modulus (E'), which indicates a transition.^{186,208} Javni *et al.*²⁰⁹ reported glass transition temperatures (T_G) in polyisocyanurate foam in this region, but T_G were highly dependent on isocyanate index and polyol type. Li *et al.*¹⁶⁶ assigned a transition at 85 °C to enthalpy relaxation of urea hard segments in crude glycerol-based PUF. The LS PUF has a higher E' than the other materials, caused by the higher hydroxyl number of the LS biopolyol, which should lead to a higher crosslink density^{69,183,186} and required higher MDI content in the formulation which can increase isocyanurate formation and stiffness.²¹⁰ The E'' of the KL PUF and OL PUF show peaks at 141 and 122 °C, respectively, likely indicating the start of glass transitions with a corresponding drop in E' and rise in tan δ (= E''/E') which follows.

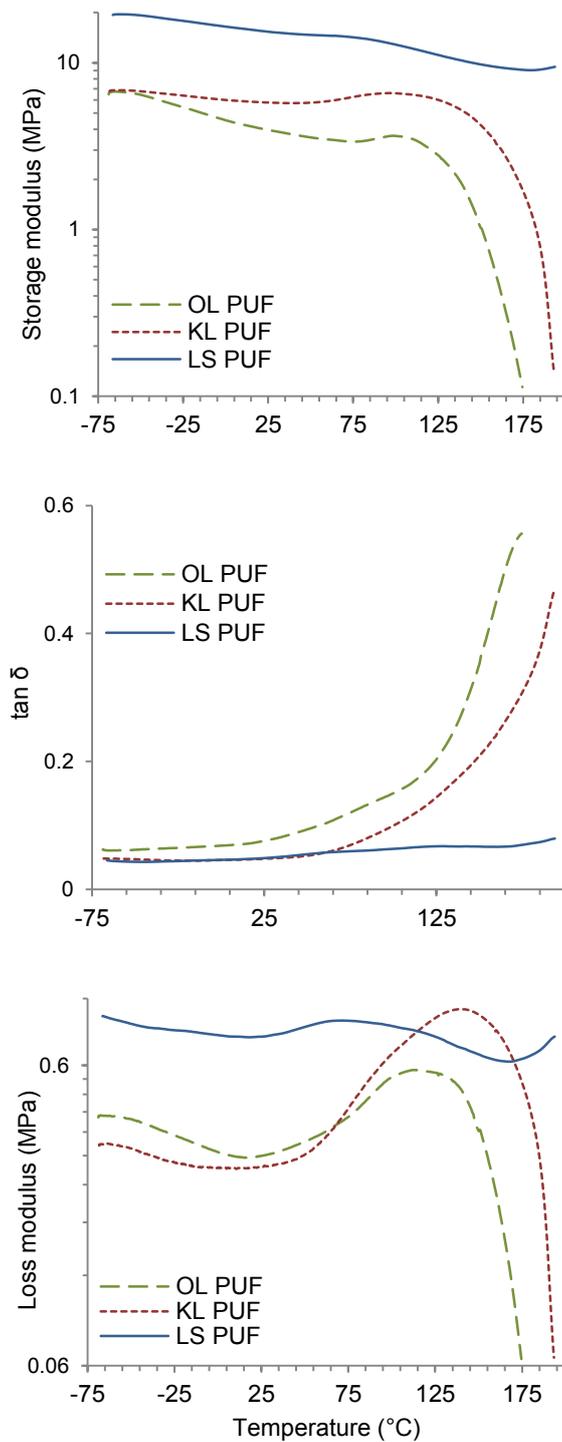


Figure 4.4: Storage modulus (E'), $\tan \delta$ and loss modulus (E'') variation with temperature of the biopolyol PUFs.

The LS PUF does not show similar changes in E' and $\tan \delta$ in this region and remains more stable. The highly rigid LS PUF might undergo collapse of cells during testing at increased temperatures which can cause anomalies in the DMA results.²¹¹ From the DMA results it can be concluded that the KL PUF shows slightly higher resistance to transition and rigidity than the OL

PUF, likely due to higher functionality in the KL biopolyol, while the LS PUF exhibits substantially increased rigidity. The behaviour is similar to that of biobased rigid PUFs reported by others.^{69,186,207}

4.3.4 Polyurethane foam biodegradability evaluation

CO₂ evolution

The results of the biodegradability evaluation by means of CO₂ evolution during soil incubation are shown in Figures 4.5, 4.6 and 4.10. The rates of CO₂ evolution in the biopolyol-based PUF (KL PUF) and starch samples were higher than for the petroleum-derived PUF (polyester-polyether polyol) and soil samples during the initial phase of the experiment. After the first measurement the rates lowered and from about 50 days the PUFs showed similar rates. At approximately 170 days the starch rate approached that of the PUFs as the starch likely became depleted. From 435 days onwards the four rates were similar and their confidence intervals started to overlap. The higher initial rate of the biopolyol PUF compared to the commercial PUF might indicate that the material provided additional substrate during this stage. The fact that the PUF rates eventually became similar to that of the soil means that the PUFs did not provide substantial amounts of viable substrate in addition to that which originates in the soil for the remainder of the experiment. Possible explanations for the higher initial rate of the biopolyol PUF might include the higher porosity of the PUF which could impact on aeration of the soil matrix, as well as the presence of excess reagents. Isocyanate is highly reactive with water and the reaction generates CO₂.⁴¹ The commercial PUF however appeared to contain more unreacted isocyanate, discussed below.

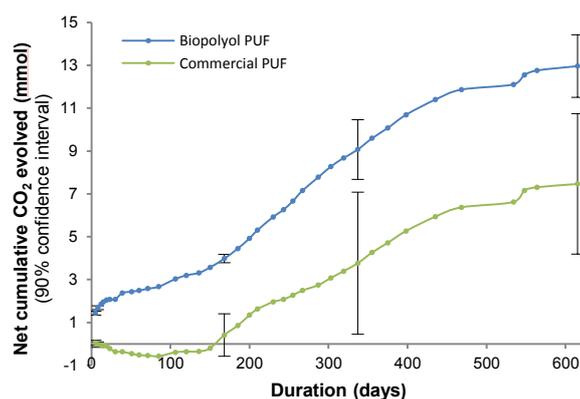


Figure 4.5: Net cumulative CO₂ evolved during soil incubation of biopolyol PUF and commercial petroleum-derived PUF. [Net CO₂ = PUF in soil CO₂ – blank soil CO₂]

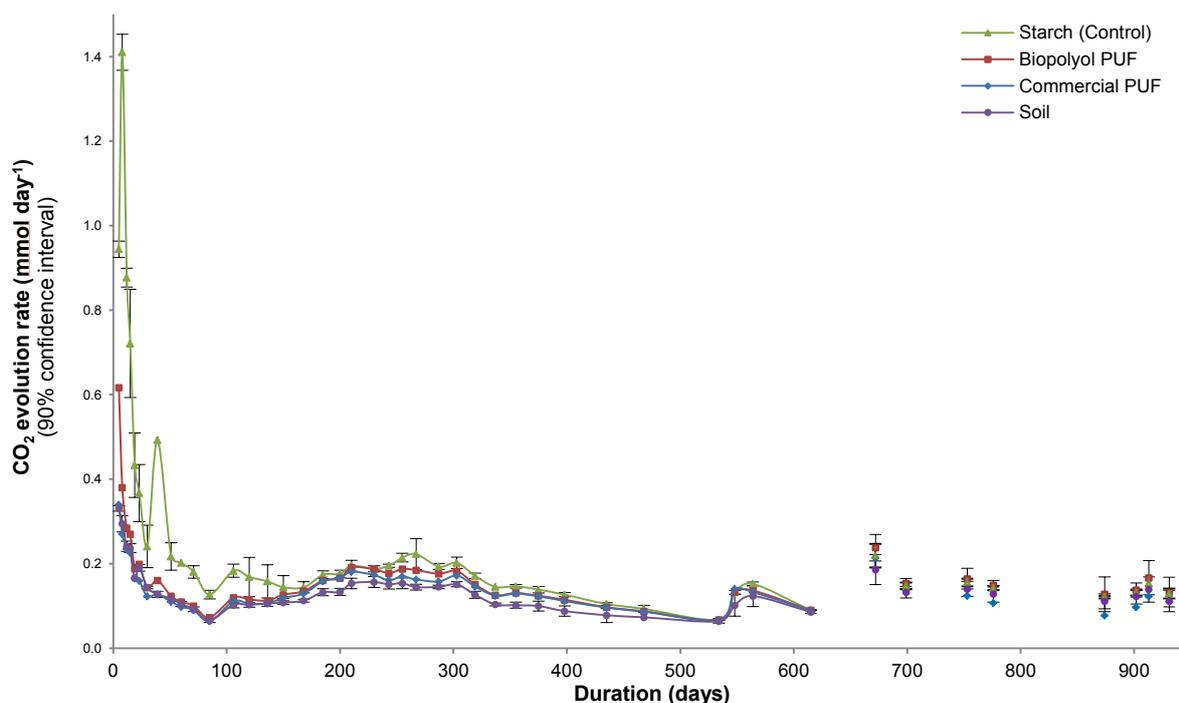


Figure 4.6: Rate of CO₂ evolution during soil incubation of biopolyol PUF, commercial petroleum-derived PUF and starch, as well as soil without test material.

The biopolyol PUF would also contain low amounts of unbound glycerol, acylglycerols and FAEE. Shogren *et al.*²¹² also found high initial rates during vegetable oil-based polyurethane biodegradation assays in soil. The CO₂ production diminished quickly and they attributed this to the degradation of low MM fractions while the bulk of the high MM material was resistant. Their CO₂ production stabilised around 7.5 % (of theoretical). Similar mineralisation rates in compost of less than 10 wt% in 30 days for polyricinoleic acid based polyurethane,²¹³ 11.2 wt% over 320 days for crude glycerol-based polyurethane⁷⁴ in soil and about 2 mmol CO₂ evolution over 90 days from oxypropylated lignin polyurethane⁷⁵ in soil have been reported. The apparent theoretical mineralisation for the biopolyol PUF after 615 days was 18.5 wt%.

SEM analysis

SEM micrographs of the biopolyol PUF (KL PUF) incubated in soil for various durations show that the material does contain cracks, many broken cells, pores, fungal hyphae, bacteria and insects (Figure 4.7). The physical deterioration of the structure does however not increase substantially over time. One does not see signs of material damage usually associated with extensive microbial degradation such as colour changes, dense microbial growth and severe disintegration.²¹⁴⁻²¹⁶ It is not expected that extensive microbial degradation of highly crosslinked biobased PUF would necessarily occur in the given timeframe.^{78,217-218}

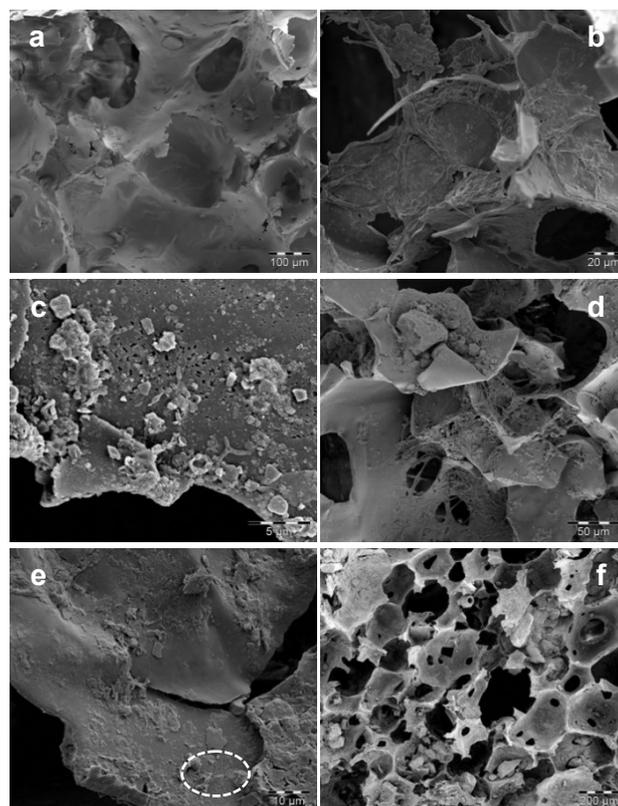


Figure 4.7: Micrographs of the biopolyol PUF incubated in soil for increasing durations. a) Original material; b) 2 months; c) 1 year; d) 18 months with *Aspergillus* addition; e) 31 months (pores encircled); f) 30 months with *Aspergillus* addition.

If ester, urethane or urea bonds do deteriorate slowly over time due to hydrolysis or oxidation it would lead to a loss in strength which would result in material breakage in weaker areas of the structure.^{217,219} The polyether polyol-based PUF was also incubated in soil without addition of *Aspergillus* to study biodegradation. The micrographs of the petroleum-derived PUFs are given in the Supplementary Material (Figure 4.11). The materials show fewer broken cells and in general less breakage of the structure. This might be due to higher material strength and therefore higher resistance to biodegradation cannot be concluded from the SEM results.

FTIR analysis

FTIR spectroscopy is often used to study PUF degradation^{75,77} and was employed here to compare the possible change in structure of the PUFs during soil incubation. Figure 4.8a shows an overlay of the biopolyol PUF (KL PUF) spectra at different stages of the degradation experiment, (no *Aspergillus* addition). The broad band with maximum around 3308 cm^{-1} exhibit increased intensity during the 1st year, thereafter intensity remains relatively constant. This band

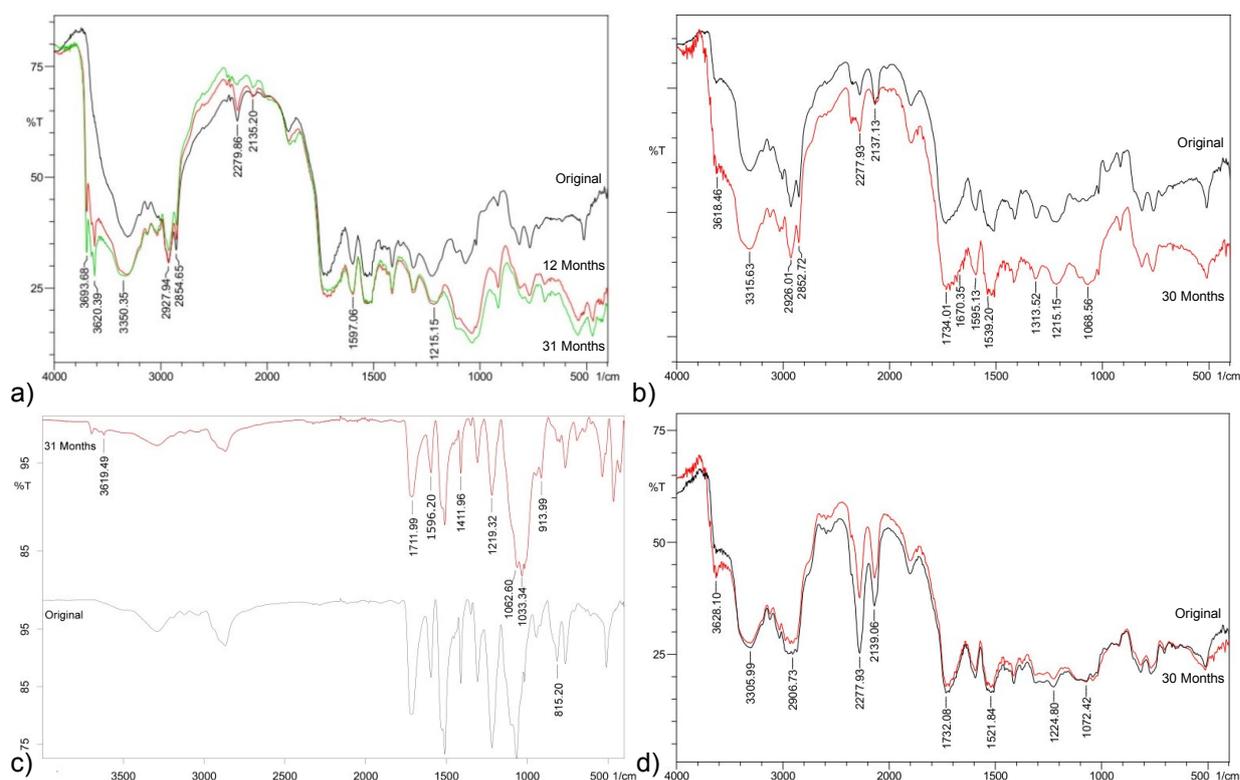


Figure 4.8: FTIR spectra: a) Comparison of the original biopolyol PUF and the aged samples that were incubated in soil for different durations (12 months and 31 months); b) Biopolyol PUF before and after 30 months incubation in soil with *Aspergillus* addition; c) PEG/glycerol (polyether) PUF before and after 31 months incubation in soil; d) Polyester-polyether polyol PUF before and after 30 months incubation in soil with addition of *Aspergillus*.

is assigned mostly to N-H with some contribution from O-H stretching.^{75,77,167} Broadening of the band and an upfield shift over time of the maximum towards 3400 cm^{-1} , indicate an increase in non-hydrogen bonded N-H and O-H bonds.⁷⁷ Intensities lower throughout the experiment at 2928 and 2855 cm^{-1} , assigned to C-H stretching.^{167,173} An isocyanate (NCO) band and a low intensity carbodiimide (NCN) band are present at 2280 and 2135 cm^{-1} , respectively.²²⁰ The isocyanate intensity decrease over time. At 1597 cm^{-1} the band intensity assigned to the MDI aromatic ring is stable.^{77,221} Downfield of 1200 cm^{-1} intensity increase over the complete spectrum for the aged foam. Increases are less during the 2nd and 3rd year. Based on a comparison with spectra of the soil used for incubation it is concluded that the increase is due to soil constituents trapped in the foam pores (Figure 4.12). The same is concluded for the increases at around 3620 and 3694 cm^{-1} .

Figure 4.8b shows an overlay of the biopolyol PUF FTIR spectra (KL PUF) before and after the degradation experiment with addition of *Aspergillus*. As in Figure 4.8a the intensity of the band with maximum around 3316 cm^{-1} increases, shifts upfield and broadens slightly. Intensities at 2926 and 2853 cm^{-1} remain stable. The carbodiimide band intensity at 2137 cm^{-1} decreases compared to the isocyanate intensity at 2278 cm^{-1} . Carbodiimides can undergo further reaction with for instance isocyanates,⁴¹ carboxylic acids or water.²²² The reactions with water and carboxylic acid generate anhydride acid and urea or an acetyl urea, respectively. Carbonyl (C=O) bands between 1735 - 1670 cm^{-1} remain stable. The MDI aromatic C=C band intensity at 1595 cm^{-1} is stable. There is minimal change in intensity around 1539 cm^{-1} in the broad band assigned to C-C stretch, C-N stretching, as well as N-H bending.¹⁶³ This absorption band is affected by chain conformation and hydrogen bonding. The combined C-N and N-H vibration band intensity at 1314 cm^{-1} does not change.⁷⁷ At 1215 cm^{-1} the band's intensity is stable and assigned to C-N deformation and N-H stretching of urethane groups.^{164,221} There is an increase in intensity over the region between 1155 - 933 cm^{-1} . Zhang *et al.*²⁰³ found increases at 1172 , 1037 and 916 cm^{-1} and attributed it to oxidation of ether bonds in soft segments of degraded liquefied wood-based PUF. The spectra resemble that of Figure 4.8a in this region and the increases are concluded to be caused by soil constituents, which would mask absorption by potential degradation products. Based on the limited change in the carbonyl and urethane group signals, degradation was very limited, but the mentioned changes in the N-H and O-H bands around 3316 cm^{-1} indicate chemical changes did occur to some extent. Chemical changes at the surface due to degradation is reported to also result in changes in hydrogen bonding, which also effect the FTIR spectra of polyurethane.⁷⁷ Similar changes in the spectra of Figure 4.8a and 4.8b indicate that *Aspergillus* addition did not have a noticeable enhancing effect on PUF degradation in soil.

Figure 4.8c shows an overlay of the polyether polyol PUF FTIR spectra before and after the degradation experiment. There is an intensity increase around 3300 cm^{-1} . Apparent around 1219 cm^{-1} is a decrease in intensity which indicates changes occur around the urethane bond.²²³ There are low intensity bands forming at 3619 and 3694 , while at 1063 , 1033 , 1017 and around 914 cm^{-1} bands increase significantly. Bands around 1067 cm^{-1} have been assigned to urethane or ether bonds.^{75,221} Urethane bond degradation is reported to yield amine and hydroxyl containing products.^{75,224} These groups can absorb in the areas where increases were seen.¹⁵⁶ The urethane carbonyl band around 1712 cm^{-1} is however not significantly altered. Intensity decreases at 815 cm^{-1} in the band assigned to aromatic C-H of MDI,^{77,167} but not around 1600 and 1411 cm^{-1} , bands also assigned to MDI aromatic rings. As for the spectra discussed above, increases upfield of 3600 cm^{-1} and downfield of 1100 cm^{-1} are mostly attributed to trapped soil constituents.

Figure 4.8d shows an overlay of the polyester-polyether polyol PUF FTIR spectra before and after the degradation experiment with *Aspergillus* addition. At 3628 cm^{-1} there is an increase in intensity. This is likely caused by soil constituents, but the band is also present in the original material and therefore could indicate formation of hydroxyl groups. The bands around 3305 and 2907 cm^{-1} remain stable. At 2278 cm^{-1} the isocyanate band intensity is reduced.^{165,167,220} The isocyanate possibly underwent further reaction with water to form urea.⁷⁴ There are however not significant increases in the bands assigned to urea at 3315 cm^{-1} and $1540\text{--}1500\text{ cm}^{-1}$.^{166,225} At 2139 cm^{-1} the carbodiimide intensity appears stable. Bands assigned to ester bonds^{74,77} around 1730 and 1225 cm^{-1} and ether bonds^{75,226} around 1072 cm^{-1} are not significantly affected. If ester, urethane or ether bonds are degraded to some extent it might yield hydroxyl containing compounds absorbing in the region around 3628 cm^{-1} .^{75,77,156} To end this discussion the most significant change found by FTIR was that three of the four PUFs showed limited changes in the N-H and O-H absorption band around 3300 cm^{-1} . In general the PUF degraded to a very limited degree in the given period and *Aspergillus* cannot be concluded to have an enhancing effect on degradation.

4.4 CONCLUSIONS

The three biopolyols were each successfully employed to prepare rigid PUF as the sole polyol component. The biobased contents of the PUFs were 44 wt% (KL), 55 wt% (OL) and 32 wt% (LS). These were amongst the higher values reported previously, and were achieved through the use of crude glycerol as a renewable and sustainable liquefaction reagent. The foams were shown to compare well with other biobased PUFs, as well as commercial products in terms of material and thermal properties. To lower the thermal conductivity further the closed cell content should be improved, while the densities could be lowered to conform to the requirements of more applications. Open cell rigid foams are however currently employed to produce vacuum insulation panels. There is a significant difference in the material properties of PUFs prepared from the respective biopolyols, with the kraft lignin clearly yielding foams with superior qualities. These findings will hopefully aid current lignin producers as well as designers of future biorefineries in terms of lignin and crude glycerol valorisation strategies. The polyurethane showed limited degradation during a 3 year period in soil to evaluate biodegradability. Further work in terms of eliminating the use of isocyanate is currently receiving attention and could be a means to incorporate building blocks more susceptible to degradation for applications where it is a desirable attribute.

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4.6 SUPPLEMENTARY MATERIAL

EXPERIMENTAL



Figure 4.9 **Compression testing instrument.**

Polyurethane foam biodegradability evaluation

CO₂ evolution in soil: The soil had a pH of 6.3. Rocks and large plant debris were removed. The composition was 58.8 wt% sand, 22.9 wt% silt and 18.2 wt% clay after being sieved to less than 2 mm particle size, determined by Eco Analytica (Noordbrug, South Africa). Moisture content was adjusted to 100 % of field capacity which was found to be 36.2 % (volume) taken at -20 kPa. Moisture and volatiles content were determined as 14.4±0.8 wt% in the original soil and 11.8±0.8 wt% on a dry weight basis according to standard methods APHA-AWWA-WPCF 2540 D and G, respectively.²²⁷ The compositions of the PUF samples were determined by elemental analyser (Exeter Analytical CE-440), to be as follows: biopolyol PUF – 69.07±1.12 % C, 6.75±0.13 % H, 6.99±0.14 % N; commercial PUF – 66.55±0.95 % C, 5.67±0.14 % H, 7.33±0.1 % N. Ammonium phosphate solution (4.72 g dm⁻³) was added to the soil as nitrogen supplement to obtain a ratio of 1:10 of N:C based on the carbon added as sample. Sporal suspensions were prepared by growing inoculum of *Aspergillus* ATCC 16404 on potato dextrose agar plates for 16 days at room temperature. 10 mL sterile water was then added and the spores scraped off with a sterile loop. The resulting suspension was collected and adjusted to the required concentration by the use of a counting chamber.

RESULTS AND DISCUSSION

Crude glycerol, lignin and biopolyol characteristics

Table 4.4: Lignin hydroxyl content^a (mmol g⁻¹, ash-free basis).⁷⁹

Lignin OH type:	Organosolv lignin (OL)	Kraft lignin (KL)	Lignosulphonate (LS)
Aliphatic	4.09	2.47	4.54
Total phenolic	2.08	3.97	1.88
Total	6.48	7.06±0.56 ^b	6.99

^a Determined by ³¹P NMR spectroscopy. ^b 95% Confidence interval based on triplicate analysis.

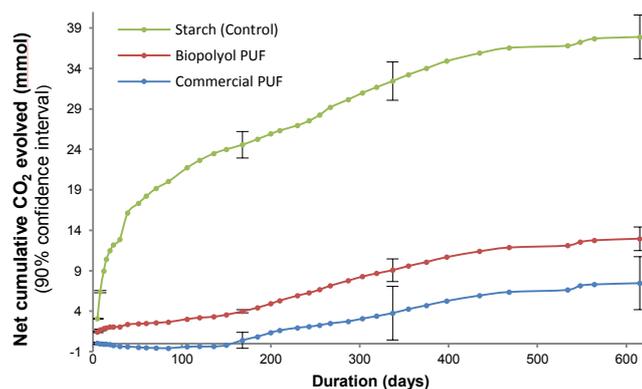


Figure 4.10: Net cumulative CO₂ evolved during soil incubation of biopolyol PUF and commercial petroleum-derived PUF. Starch was used as the control material.

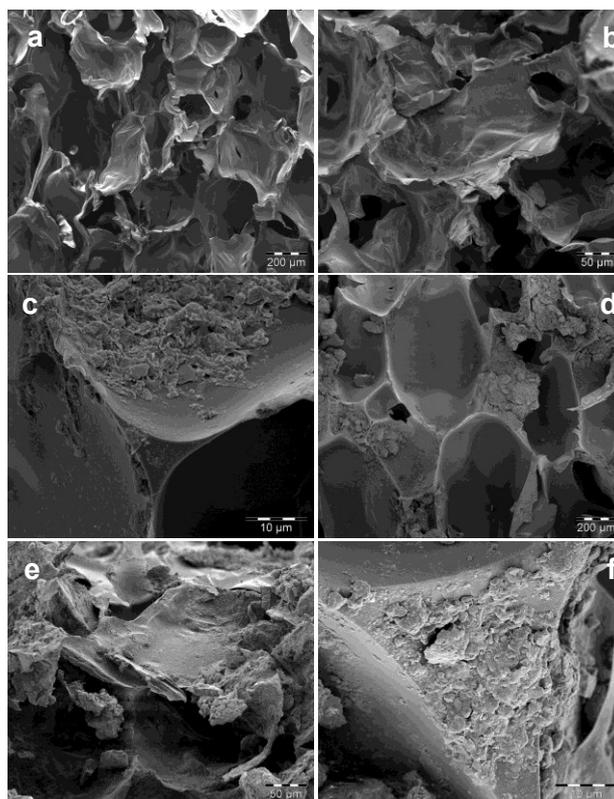


Figure 4.11: Micrographs of the petroleum-derived PUFs incubated in soil for increasing durations. a) Original polyether PUF, b) 2 months (polyether PUF), c) 1 year (polyether PUF), d) 18 months with *Aspergillus* addition (polyester-polyether PUF), e) 31 months (polyether PUF), f) 30 months with *Aspergillus* addition (polyester-polyether PUF).

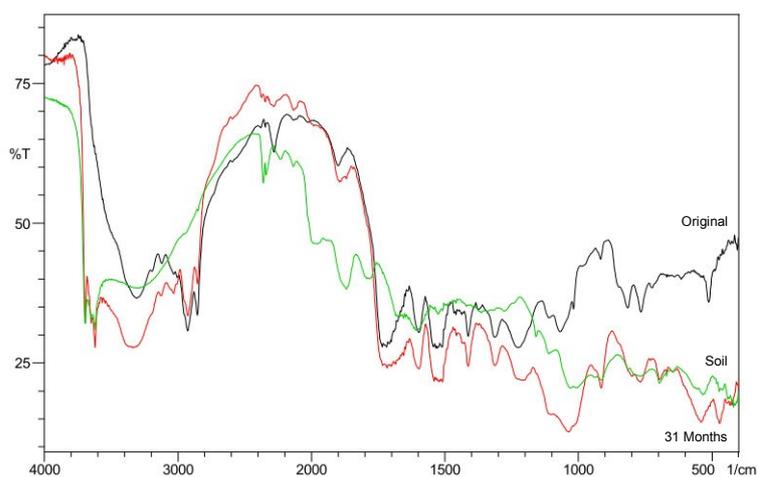


Figure 4.12: FTIR spectra of the biopolyol PUF before and after 31 months incubation compared to the incubation soil's spectra to determine trapped soil interference.

CHAPTER 5 CONCLUSION AND FUTURE PROSPECTS

5.1 CONCLUSION

By studying the liquefaction of lignins in crude glycerol with ^1H and ^{31}P NMR spectroscopy some of the major underlying reactions were determined and the products could be characterized. The liquefaction products had hydroxyl contents suitable for polyurethane applications and comparable to that of polyols derived from lignocellulose by others. Glycerol was removed in part through formation of monoacylglycerol (MAG) and in part by reaction with lignin. The liquid phase product compositions differed in terms of glycerol, MAG, diacylglycerol and fatty acid ethyl ester (FAEE) content for the respective lignins. The organosolv lignin (OL) and lignosulphonate (LS) liquid products showed the presence of lignin derivatives at low levels. The solid phase product spectra resembled that of the respective lignins with the addition of aliphatic OH and fatty acid chain signals. It was concluded that the respective lignins were functionalised with glycerol, FAEE and MAG to yield solid products which differed in terms of functionality.

Further analysis by size-exclusion chromatography revealed that the lignins and the respective liquefaction products had varying MM. The kraft lignin (KL) had a higher MM attributed to increased condensation during isolation. The solid phase products of OL and LS liquefaction in crude glycerol were found to have higher MM than the respective lignins, while the KL product showed a significantly decreased weight-average MM. The difference in behaviour correlated with the ratio of aliphatic to phenolic hydroxyl groups in the respective lignins. SEC further indicated that the liquid phase products all contained glycerol and MAG, while low levels of higher MM lignin derivatives were also detected in the OL product. That correlated with a higher liquid phase yield obtained for OL liquefaction. The solid product FTIR spectra resembled that of lignin, but modifications could be observed. Aliphatic chains increased, aliphatic ester bonds formed and ether bonds increased significantly. Based on the aforementioned it was concluded that the solid products formed through functionalisation of lignin with glycerol, MAG and FAEE. FTIR spectra of the OL and KL liquid products showed decreases in OH content compared to crude glycerol and ether bond content increased in all liquid products. The SEC analysis in combination with NMR spectroscopy results gave indications that glycerol bound to OL more extensively than LS and conversely MAG bound to LS to a greater extent. Differences in product structure such as the lower MM of the KL solid phase were significant and expected to affect polyurethane properties.

Rigid polyurethane foams were prepared through reaction of the liquefaction products as sole polyol component with diisocyanate. Urethane bond formation was confirmed by FTIR spectroscopy. Final biobased contents ranged 32–55 wt% and the foams exhibited material

properties and thermal characteristics similar to that of petroleum and lignocellulose-based polyurethane foams. Open cell content was however high and should be minimised for insulation applications. Lignin type had a significant influence on foam properties such as microstructure, morphology and compressive strength. In this regard kraft lignin yielded superior foams. The differences in OH contents, functionality and MM of the respective lignins and liquefaction solid phase products were concluded to have caused the observed variation in polyurethane microstructure. MAG and glycerol contents in the liquid phase products then further affected crosslink density and strength. The prepared foams did not exhibit higher levels of biodegradability than the petroleum-derived foams during soil incubation over a 30 month period, even with the addition of *Aspergillus*.

5.2 FUTURE PROSPECTS

Depending on the application, the liquefaction conditions can be adjusted. Less harsh conditions would lower condensation and may yield lower MM solid phase products and increase lignin derivatives in the liquid phase. OH content is expected to be higher. Other catalysts should be considered, such as *p-toluene* sulfonic acid monohydrate (PTSA) which has been shown to lower condensation.⁸⁶

Lignin reaction with glycerol, MAG or fatty acid esters may be favoured at different conditions. The product functionality and MM could possibly be tailored by conducting these reactions sequentially, although that might require processing crude glycerol beforehand.¹²³

The foams were rigid with mostly open cell content. Flexibility could be increased by the incorporation of chain extenders which can result in higher closed cell content. The fatty acid chains of MAG and fatty acid esters, which are bound to lignin may be functionalised with hydroxyl groups at the unsaturated bonds.^{124,228} This could have a similar effect to introducing a chain extender such as PEG, increasing flexibility by utilizing the dangling chains which can otherwise be detrimental to foam strength. Incorporation of ricinoleic acid would have the same effect without the need for further modification.

In this work the liquefaction products were employed without further processing. By separating the solid and liquid fractions and either employing them separately or combining them in different ratios, polyurethane properties could be adjusted. Reducing glycerol content for instance would lower crosslink density.

Where biodegradability is desirable, it would require the incorporation of additional components susceptible to biological breakdown. Ester groups in polyurethane for instance have been shown to be degraded.^{74,76} Fungi such as *Aspergillus* have been reported to degrade polyurethane to some degree and should be further studied.^{76,78} The effect of solar radiation on

degradation was not evaluated in this work, but susceptibility to photodegradation could possibly be enhanced due to the presence of lignin derivatives.²²⁹

Lignosulphonate was reported by Lu et al. to act as a flame retardant in PUF.²³⁰ Mandlekar et al. compared the use of different lignins in polyamide 11 composites and found that lignosulphonate had the greatest effect on enhancing the fire performance of the materials.²³¹ Hejna et al. reported that crude glycerol derived polyols did not have a detrimental effect on fire performance of polyisocyanurate foam when used at levels up to 35 wt% of the polyol fraction.²³² Other important properties of rigid PUF are specified in industry standards and include, but are not limited to the following: density, thermal conductivity, water absorption, water vapour transmission, closed cell content, compressive strength, tensile strength, shear strength, dimensional stability, friability and flexural properties.^{44,189} The relevant material properties depend on the intended application and extensive testing would be required during further development of the subject PUF before a commercially viable product could be obtained.

Much work has been published on the preparation of polyols from lignocellulose and lignin. Studies that evaluate the economic feasibility are however scarce.^{174,233-234} In this regard a comparison of liquefaction solvents and lignin or biomass types would be invaluable. Compared to other lignin-derived products such as vanillin, phenolics or activated carbon, polyols have been indicated as being of lower monetary value. Therefore costs, potential prices and environmental impact could be studied in greater detail to evaluate the viability of taking this route in terms of lignin and lignocellulose valorisation.²³⁵⁻²³⁶

In future biorefineries where lignin cannot be converted to the primary biobased product along with biomass components like cellulose and hemicellulose, maximum value could be extracted from feedstock by designing biomass processing methods to isolate lignin fractions in a manner that would preserve lignin properties required to produce higher value by-products. Only three lignin types were evaluated in this work and with the vast number of biomass types and processing procedures being studied, much further research on lignin valorisation is required.

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ANNEXURE PREPARATION OF POLYURETHANE FROM LIGNIN AND CRUDE GLYCEROL

ABSTRACT

Polyurethane foam (PUF) was prepared by a novel approach, using a renewable polyol derived from only biofuel production by-products, lignin and crude glycerol. This could potentially be a high value biorefinery application for the two by-products from cellulosic ethanol and biodiesel production, respectively. Renewable polyols were synthesized by the liquefaction of lignin in crude glycerol. Three different technical lignins were individually employed to prepare polyols viz.: kraft lignin, lignosulphonates and organosolv lignin. Water-blown PUF was prepared by reacting the polyols with commercial diphenylmethane-4,4'-diisocyanate (MDI). The PUFs had compressive strength which conforms to industry requirements for thermal insulation.¹⁸⁸ The PUFs had renewable content as high as 44 wt%. A major benefit of these renewable polyols is that PUF could be prepared without the need to add any petroleum-derived polyols. Making use of lignin instead of untreated agricultural residues i.e. lignocellulose, enables the production of both polyols and cellulosic ethanol. The structural differences of technical lignins clearly have a significant influence on the ensuing PUF properties. Biomass pretreatment methods therefore need to be selected with consideration of their effect on lignin properties if the high lignin contents present in many biomass types are to be exploited.

Keywords: biodegradable, biopolymers, bioplastic, polyols

INTRODUCTION

Biofuel needs to be produced profitably and generate sufficient return on investment for it to become a sustainable source of energy. Apart from the revenue from biofuel itself, biorefineries can make use of production by-products to generate further income.

Lignin is a major component of lignocellulosic biomass, which cannot be fermented and is removed during bioethanol production.²³⁷ Crude glycerol is a by-product of biodiesel production. About 1 kg is produced per 10 kg biodiesel and is of low value.²³⁸ Both lignin and crude glycerol have been studied as potential reagents for producing polyurethane which is partly renewable.

Lignin has been used both modified and unmodified as biobased polyol (biopolyol) component in polyurethane formulation.¹⁷ Modification is achieved through liquefaction in polyol solvents such as propylene oxide (PO)²³⁹ and polyethylene glycol (PEG).⁵⁶ More often agricultural residues i.e. lignocellulose, have been used to prepare biopolyols through liquefaction.⁶⁰ The benefit of using lignin instead of lignocellulose during liquefaction is that cellulose and hemicellulose can still be employed for fermentation or any other application if the lignin is isolated beforehand.

A couple of studies have looked at liquefying lignocellulose⁶³⁻⁶⁴ in crude glycerol to yield biopolyols intended for polymer synthesis. The advantage of using crude glycerol is of course its lower price compared to petroleum-derived PO or PEG and the fact that it is renewable. Crude glycerol has recently even been applied successfully as sole biopolyol after modification by Luo *et al.*⁸⁷

Therefore, in this study we investigate the combination of crude glycerol as liquefaction solvent, with technical lignin as a novel preparation route of polyurethane with increased renewable content. The material's biodegradability is also evaluated based on the high biobased content. This is proposed as a potentially feasible route for utilizing biofuel by-products and additionally the importance of biomass and pretreatment method selection are evaluated.

EXPERIMENTAL

Materials

Sugarcane bagasse was obtained from Tsb Sugar RSA (Malalane, RSA). The dried bagasse was milled to pass through a 1.5 mm sieve using a hammer mill. Hardwood calcium lignosulphonates (LS) was supplied by Sappi Saiccor mill (Umkomaas, RSA). Softwood kraft lignin (KL) was purchased from Sigma-Aldrich (Kempton Park, RSA). Sunflower oil (Crispa gold) was purchased from Sime Darby Hudson & Knight (Boksburg, RSA). Diphenylmethane-4,4'-diisocyanate (MDI), Desmodur 44V20L, was supplied by Bayer Material Science (Isando, RSA). Catalysts and surfactants for polyurethane preparation were supplied by Air Products South

Africa (Kempton Park, RSA). PEG of average molar mass 400 g mol^{-1} was also bought from Sigma-Aldrich. All other chemicals used were of reagent grade or purer and used as received.

Crude glycerol preparation

Crude glycerol was prepared from sunflower oil by transesterification. Reaction temperature was $60 \text{ }^{\circ}\text{C}$, duration 120 min, molar ratio of oil:bioethanol was 1:6, 1% potassium hydroxide (oil weight), stirred at 100 rpm.²⁴⁰⁻²⁴² The reaction was conducted in a stainless steel vessel with a fixed impeller and steel tubing for heating by steam. After reaction the mixture was left for 24 h to separate into the glycerol and fatty acid ethyl ester (FAEE) rich phases. The crude glycerol was drawn from the bottom of the reactor.

Organosolv lignin isolation

Lignin was extracted from the sugarcane bagasse by an organosolv method described by Xu *et al.*⁹² Briefly: Bagasse was dewaxed with toluene/ethanol (2:1 v/v) at 9 mL g^{-1} bagasse, $73 \text{ }^{\circ}\text{C}$ for 6 hours under reflux. Bagasse was extracted with solvent: formic acid/acetic acid/water of 3:6:1 (v/v/v) at a ratio of 10 mL g^{-1} bagasse with HCl as catalyst (0.1 wt% of bagasse). The mixture was stirred at $85 \text{ }^{\circ}\text{C}$ for 4 hours. The filtrate was reduced under vacuum and hemicellulose precipitated in three volumes 95 v% ethanol. The solubilized lignin was obtained by evaporating the solvents and isolated in pH 2 water by centrifugation at 4000 rpm for 15 min. This acid insoluble lignin was freeze dried.

Liquefaction

Liquefaction was conducted in a temperature-controlled glass reactor under atmospheric pressure. Catalyst, H_2SO_4 , was first added to crude glycerol until pH 8 was measured. The mixture was heated to $160 \text{ }^{\circ}\text{C}$, lignin was then added at 9:1 (crude glycerol:lignin wt/wt). The reaction ran 90 min under magnetic stirring whereafter it was immediately cooled.

Polyurethane foam preparation

Rigid PUF was prepared by weighing the polyol, catalysts, surfactant and blowing agent into a cylindrical beaker and mixed at 6000 rpm for 15 s. MDI was then measured into the beaker and mixed at 6000 rpm for 10–15 s. The foam was left to rise and cure for at least 24 h. Table A1 gives the KL PUF formulation. Isocyanate index of 1.05 was employed.

Biodegradability test

Both petroleum-derived PUF, (PEG/glycerol made up the polyol), and the KL PUF were cut into discs of 2–3 mm and buried in fertile soil samples taken from the local area and stored at ambient temperatures away from direct sunlight.

Table A1: KL PUF formulation.

Reagent	Parts (weight)
KL derived biopolyol	100
Gelling catalyst	0.86
Blowing catalyst	0.67
Surfactant	2.50
Water	1.25
MDI	126.6

Characterization

Lignins were characterized by FTIR recording diffuse reflectance spectra of samples in a potassium bromide matrix.

The hydroxyl numbers of the biopolyols were determined according to ASTM D4274-11 Method D.⁹⁷ Viscosity of the same was measured according to ASTM D4878-08.²⁴³

The compressive strength of the PUF was measured according to the method described in ASTM D1621-10.¹⁷⁵ Density was determined according to SANS 1383:2008.¹⁷⁶ PUF samples, prepared from KL biopolyol and PEG/glycerol respectively, were further aged in soil and the microstructure analysed over time by scanning electron microscopy (SEM) on a FEI Quanta 250 FEG. Foam samples were sputter coated with gold/palladium and micrographs captured under high vacuum mode using the secondary electron detector and an accelerating voltage of 5kV. Thermogravimetry (TG) was conducted according to literature.²⁴⁴ About 7 mg samples of PUF were used. The heating rate was 20 °C min⁻¹, nitrogen flow was 100 cm³ min⁻¹. Heating range was 25–600 °C.

RESULTS AND DISCUSSION

By-products

Figure 2.7 and Table 2.8 in Chapter 2 show the composition of the crude glycerol.

Figure A1 shows the FTIR spectra of the three lignin types. The spectra of the organosolv lignin and liginosulphonates are similar to that of the synthetically isolated kraft lignin. There is however variation of the peaks in some areas of the spectra which would be due to the differences in plant species and extraction methods.¹⁴⁸

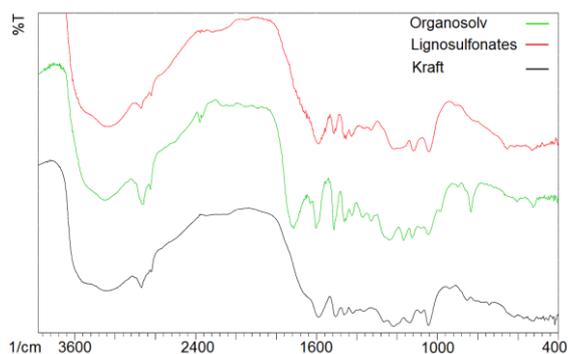


Figure A1: FTIR comparison of the three lignins.

Biopolyols

Table A2 shows the liquefaction results. The OL gave a higher yield than the other lignins. The difference in yields indicates that lignin did react with the crude glycerol constituents because if there was no reaction, the three lignins should have given similar yields. The hydroxyl numbers of the biopolyols in Table A2 are similar to those of commercial petroleum-derived polyols,¹⁶⁸ which include polyols with a range of values for properties such as hydroxyl number and viscosity. It is also clear that a wide range of hydroxyl numbers can be obtained by liquefying different lignin types. The three lignin type biopolyols had differing viscosities. The values are low but still comparable to a certain class of “low viscosity” commercial products.¹⁶⁸

Table A2: Liquefaction yield and biopolyol properties.

Lignin	KL	OL	LS
Biopolyol yield (g polyol [g crude glycerol] ⁻¹)	0.62±0.16	0.73±0.06	0.61±0.07
Hydroxyl number (mg KOH g ⁻¹)	412±27	224±10	592±18
Viscosity (mPa s)	610±10	80	210±30

Polyurethane foam

The properties of the polyurethane foams prepared from the biopolyols are given in Table A3. The compressive strength values of the PUF do fall within the usual range for PUF used as thermal insulation and packaging material, which can be as low as 110 kPa, depending on the application.¹⁶⁸ The KL PUF value lies at the higher end of the range, which of course is encouraging. Figure A2 shows photographs of the three lignin foams.

Table A3: Polyurethane foam properties.

Foam type	KL PUF	LS PUF
Compressive strength (kPa)	345±63	215±58
Density (kg m ⁻³)	78±26	160±24
Renewable content (wt%)	44	38



Figure A2: KL PUF (left), LS PUF (middle), OL PUF (right).

The renewable content of PUF prepared from polyols obtained through liquefaction of lignocellulose or lignin in petroleum-derived solvents has generally been below 20 wt%.^{48,132,167} As can be seen in Table A3 the renewable content can be substantially increased if a “green” solvent such as crude glycerol is used.

The results of the TG analysis are shown in Figure A3. The foams display initial mass loss between 150–200 °C. There is a second stage of weight loss visible in the KL PUF above 300 °C. The urethane bonds in polyurethane normally break at 150–220 °C.⁴⁷ As mentioned the KL PUF exhibits a curve with a unique shape and onset of mass loss occurs at a higher temperature. The higher thermal stability of the KL PUF in some areas, corresponds to the higher compressive strength measured for the same. An increased degree of cross linking in the KL PUF could possibly cause the higher thermal stability.¹⁶⁷

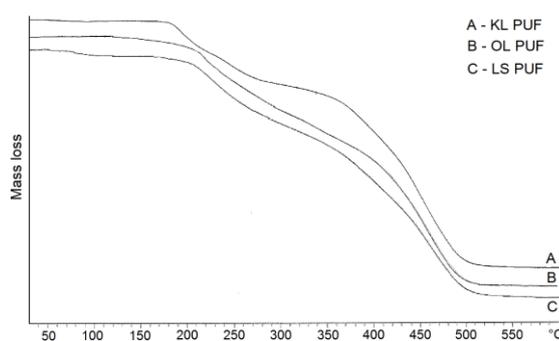


Figure A3: TG curves of the by-product-derived PUF.

Biodegradability

Figures A4 and A5 show SEM micrographs of the foams before and after aging in soil. The KL PUF structure appeared different after 6 months. The surface of the foam showed perforations in certain areas (Figure A4). The number of pores visible in the cross section of the cell walls increased substantially (Figure A5). The PEG/glycerol PUF appeared unchanged after 6 months (Figure A4). From the above alone it cannot be concluded that the foam was broken down by microorganisms, but Amaral *et al.*⁷⁵ found similar results and in combination with respirometry tests concluded that PUF, prepared with oxypropylated lignin, showed improved biodegradability.

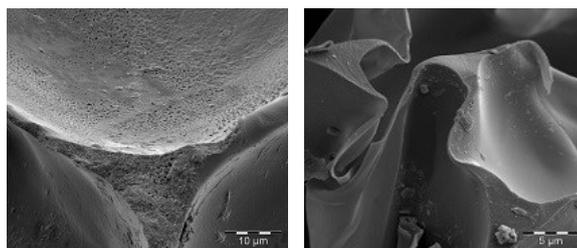


Figure A4: KL PUF (left) and PEG/glycerol PUF (right) after 6 months aging in soil.

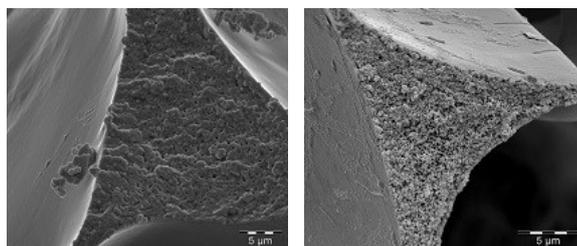


Figure A5: KL PUF before (left) and after (right) 6 months aging in soil.

Polyol cost comparison

Table A4 displays a very basic cost comparison between petroleum-derived polyols and the biopolyols derived from crude glycerol and lignin. Clearly the biopolyols concerned possess a potential cost advantage due to the low cost of crude glycerol and a further, more comprehensive economic feasibility study is therefore warranted.

CONCLUSIONS

The liquefaction of technical lignin in crude glycerol yielded polyols which were successfully reacted with MDI to prepare rigid polyurethane foam. The polyols had hydroxyl numbers and viscosities comparable to those of commercial petroleum-derived polyols. By employing crude glycerol as solvent, renewable content of up to 44 wt% was achieved in the PUF.

Table A4: Polyol cost comparison.

Description	Cost (€ ton ⁻¹)	Ref. / Note
Polyols:		
Petroleum-derived	1760–2050	^{233,245} / (1)
PO/biomass	1000–1500	²³³
Lignin	50–1200	¹⁷
Crude glycerol	190–365	²⁴⁶⁻²⁴⁷ / (2)
KL polyol	724	(3, 4)

The KL PUF structure appeared damaged after a period of soil incubation. Petroleum-derived PUF did not show any signs of damage. The by-product derived PUF might therefore present improved degradability.

A very basic cost comparison revealed that the raw materials to prepare the concerned renewable polyols would be roughly €724 ton⁻¹ which would be lower than the selling price of commercial polyols.

It was found that different technical lignins significantly influence the final PUF properties. Pretreatment method and species selection in the biorefinery context should therefore take into consideration the specific intended use of lignin by-products to maximize profitability.

NOTES

(1) Exchange rate of \$1.10/€ was assumed. (2) Refined crude glycerol: 80 wt% glycerol. (3) 9:1 Crude glycerol/lignin (wt/wt). Liquefaction polyol yield as per Table A2. (4) Based on €1200 ton⁻¹ lignin and €365 ton⁻¹ crude glycerol.

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