Valorisation of Technical Lignin in Rigid Polyurethane Foam: A Critical Evaluation on Trends, Guidelines and Future Perspectives

Hima Haridevan[1], *David A.C. Evans*[1], *Arthur J. Ragauskas*[2,3,4], *Darren J. Martin*[1], *Pratheep K. Annamalai**

[1] The University of Queensland, Australian Institute for Bioengineering and Nanotechnology, Brisbane, Queensland 4072, Australia

[2] Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, USA

[3] Center for Bioenergy Innovation, Joint Institute of Biological Sciences, Biosciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

[4] Center for Renewable Carbon, Department of Forestry, Wildlife, and Fisheries, University of Tennessee Institute of Agriculture, Knoxville, TN 37996, USA

Corresponding author E-mail: p.annamalai@uq.edu.au

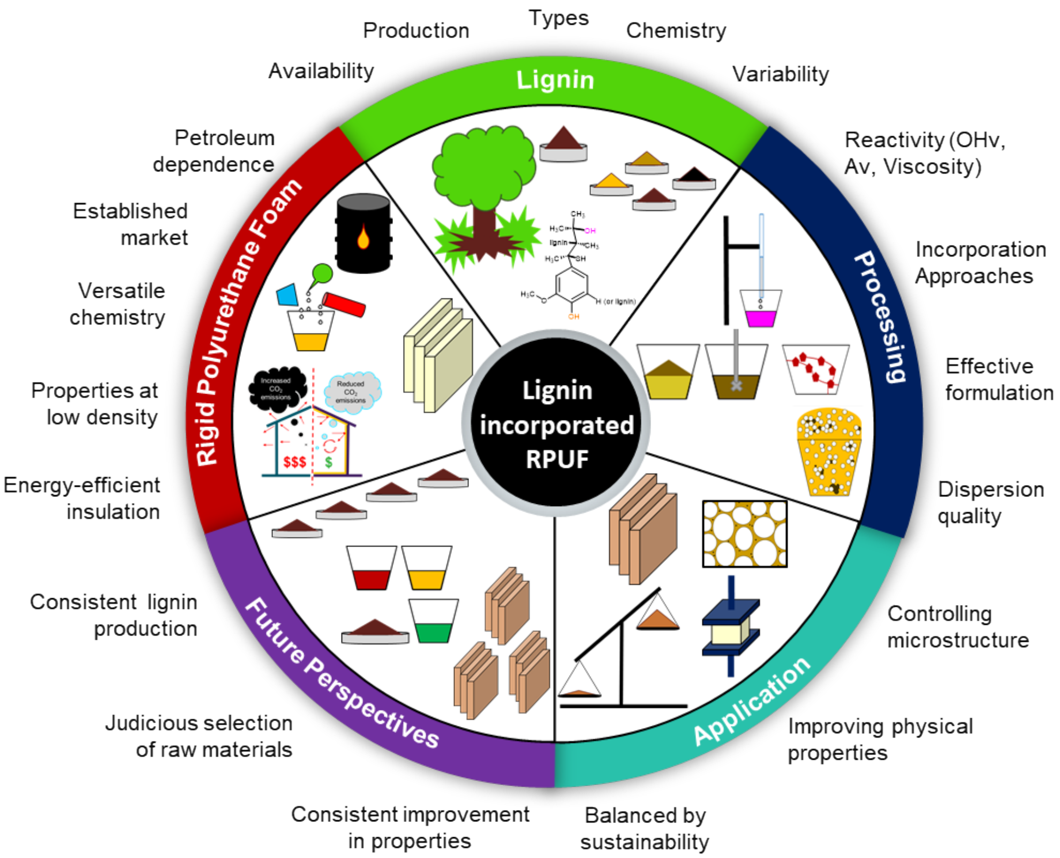
ABSTRACT

Lignin is one of the most abundant aromatic natural polymers. Produced as a by-product from the biomass refinery industries, lignin remains largely underutilised in high-value industrial applications. The incorporation of lignin in rigid polyurethane foam (RPUF) has been the focus of much research, due to its potential to replace fossil fuel-based components of RPUF. However, the overall sustainability of RPUF depends on numerous factors including processability, cost-effectiveness, and retention of performance throughout the service life. To date, the incorporation of lignin has been explored either as filler particles (through direct incorporation) or as a blendable liquid polyol introduced after chemical modifications (such as oxyalkylation, functionalisation, or depolymerisation). However, the production of lignin incorporated foam with high performance through cost-effective processing is still an ongoing challenge. Herein, this review critically appraises the progress on the effective incorporation of lignin in RPUF.

Firstly, this review briefly covers the essential raw materials, formulation, important properties, and sustainability aspects of RPUF for industrial applications. Secondly, it provides insights on the key parameters of lignin of relevance to incorporation into RPUF. Thirdly, it benchmarks the reported studies on incorporation of lignin in RPUF systems by evaluating their important properties and proposes potential strategies for addressing the key challenges in the incorporation of lignin in RPUF. By bridging the gaps that exist in the literature on the utilisation of lignin in RPUF this account will serve as a resource for both beginners and professionals in the polyurethane and biorefinery industries towards the successful development of lignin incorporated RPUF for industrial applications.

Keywords: Lignin, polyurethane foam, polyol, reactivity, microstructure, mechanical properties, thermal insulation

Graphical abstract



Contents

1. Introduction 8

2. Rigid Polyurethane Foam (RPUF) 9

2.1. Physical Properties of RPUF for Insulation 10

2.2. Structural Aspects of Physical Properties 15

2.3. Formulation of RPUF 16

2.4. State of Art in Bio-based Polyols for RPUF 23

2.5. Sustainability of RPUF 26

3. Lignin 30

3.1. Types and Production of Technical Lignin 32

3.2. Properties of Technical Lignin 34

3.3. Characteristics of Technical Lignin Relevant to its Incorporation into RPUF .47

4. The Incorporation of Technical Lignin into RPUF 58

4.1. The Direct Incorporation Approach 61

4.2. The Chemical Modification Approach 66

5. Outlook and Future Perspectives 74

6. Conclusions 77

Acknowledgments 79

Supporting Information 80

References 108

Abbreviations:

PU, polyurethane; RPUF, rigid polyurethane foam; PIR, Polyisocyanurate foams; pMDI, polymeric methylene diphenyl diisocyanate; λ_{TOTAL}, effective thermal conductivity; λ_{SOLID}, thermal conductivity of the solid phase; λ_{GAS}, thermal conductivity of the gas phase; $\lambda_{CONVECTION}$, thermal conductivity through convection; $\lambda_{RADIATIVE}$, thermal conductivity through radiation; f, functionality; Av, Acid value; OHv, hydroxyl value; Mw, weight average molecular weight; Mn, number average molecular weight; w/w, weight by weight; v/v, volume by volume; MDI, diphenylmethane diisocyanate; php, parts per hundred; T_g, glass transition temperature; CFC, chlorofluorocarbons; HCFC, hydrofluorocarbons; HC, hydrocarbons; HFO, hydrofluoroolefins; HCFO, hydrochlorofluoroolefins; DMCHA, dimethylcyclohexylamine; ODP, ozone depletion potential; GWP, global warming potential; H unit, para-coumaryl alcohol; G unit, coniferyl alcohol; S unit, sinapyl alcohol; KL, Kraft lignin; SL, soda lignin; LS, lignosulfonate; OSL, organosolv lignin; HL, hydrolysis lignin; SKL, softwood kraft lignin; HKL, hardwood kraft lignin; SAL, soda/anthraquinone lignin; EPL, ethanol process lignin; GPC, gel permeation chromatography; SEC, size exclusion chromatography, THF, tetrahydrofuran; TnBAH, tetra-n-butyl ammonium hydroxide; DMF, dimethylformamide; NaLS, sodium lignosulfonate; CaLS calcium lignosulfonate; DMSO, Dimethyl sulfoxide; IPDI, isophorone diisocyanate; TDI, toluene diisocyanate; HDI, 1,6-hexamethylene diisocyanate; DEG, diethylene glycol; TEG, diethylene glycol; PPG, polypropylene glycol; MCC, microcrystalline cellulose; CNC, cellulose nanocrystals; TMDP, 2-chloro-4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaphospholane; CV, coefficient of variation; SEM, scanning electron microscopy; FTIR, Fourier transform *infrared spectroscopy; UV, ultra violet spectroscopy; NMR, nuclear magnetic resonance; NR, not reported.*

1. Introduction

Polyurethane (PU) is one of the largest and fastest-growing classes of polymers as it is used in a wide range of applications such as thermoplastics, foams, elastomers, adhesives, coatings, and sealants because it can be easily tailored to obtain specific properties by altering the types and quantities of the constituents [1]. This versatility in chemistry and processing enables wide opportunities for introducing new raw materials into polymer products.

Rigid polyurethane foam (RPUF), is a cellular plastic, largely used as a lightweight insulation material for appliances and buildings, due to its superior physical properties at low density and long-term durability [2-4]. The global market for RPUF is estimated to increase to USD 58 billion by 2021 due to the increasing demand for infrastructure development and energy-saving materials due to climate change regulations and growing population. The production of RPUF and the related polyisocyanurate (PIR) foams with high mechanical performance and long-term thermal resistance currently utilises large amounts of petroleum-based aliphatic polyether polyols, aromatic polyester polyols, and aromatic polyisocyanates. Thus, there has been considerable research over the years regarding the preparation of RPUF based on polyols from biomass (polysaccharides, lignin, and tannin), vegetable oils, industrial residues, and the production through non-isocyanate routes [4-9].

Lignin which is readily available as a by-product from the biorefinery pulping processes is of particular interest as a potential precursor because it has high aromatic content and contains both aromatic and aliphatic hydroxyl groups for incorporation into the RPUF matrix [10-12]. The interest in the use of lignin in polyurethane (**Figure 1**) has been increasing exponentially, however, the commercial use of lignin in RPUF is yet to be realised. Hence, it is worthwhile to review the current status of studies to date on the incorporation of lignin in RPUF.

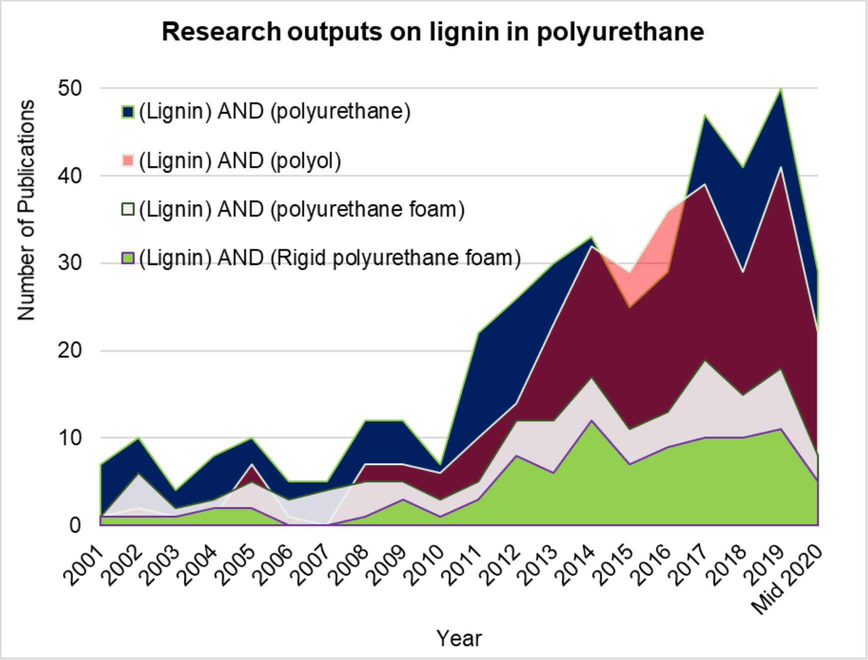


Figure 1 Research trends on the use of lignin in PU and RPUF over the last 20 years based on a search with relevant keyword combinations in the citation database 'Scopus' (accessed in June 2020).

While there are many excellent reviews available on the use of bio-based materials in polyurethanes [4, 5, 13], including lignin in polyurethanes [12, 14, 15] and foamed plastics [2, 14, 16], there is no critical review on the effect of lignin incorporation on the key performance of RPUF for potential thermal insulation applications.

2. Rigid Polyurethane Foam (RPUF)

RPUF is a thermosetting cellular polymer with a high level of cross-linking formed through urethane linkages. It is synthesized by reacting two liquid components;

polymeric diphenylmethane diisocyanate (pMDI), which contains multiple isocyanate (-NCO) groups, with a polyol blend containing polyols with multiple hydroxyl (-OH) groups, flame retardants, crosslinkers, catalysts, blowing agents, and surfactants [13]. By carefully formulating these constituents, choosing the processing method, and controlling the cell microstructure, the mechanical and thermal properties can be tailored to the intended application [17, 18].

RPUF, depending on its density and physical properties is used in a wide range of applications which include building construction, automobiles, acoustics, machinery, floatation modules, and other applications where they can lend structural support (See **Figure A1** in Supporting Information). For example, RPUF with a density of around 500 kg/m^3 is used as simulated wood for structural applications whereas RPUF with a density of around 30 kg/m^3 is used as a lightweight thermal insulation material for buildings and appliances. Further, the incorporation of various nanofillers in RPUF has also been explored for tailoring the properties required for unique applications [19-21] such as membranes, gas barrier applications, and EMI shielding [22]. However, the vast majority of RPUF is used as lightweight insulation material, as it provides high insulation performance at the minimum thickness and low density [23, 24].

2.1. Physical Properties of RPUF for Insulation

The most important properties of RPUF used as insulation in buildings are low density, good dimensional stability, high compressive strength, low thermal conductivity (both initial and aged), resistance to moisture absorption, air-tightness, fire resistance, and durability [1, 2]. There are many different national standard test methods for characterising RPUF and the materials used to manufacture them (See **Table A1** and **Table A2** in Supporting Information). RPUF based insulation material has a low density (~30-40 kg/m^3), a high closed cell content (above 90%), and low thermal conductivity (~≤ 0.017-0.026 W/mK). **Table 1** also compares the reported properties of a typical commercial PIR foam board insulation from Recticel Insulation [25] used to insulate full cavity masonry walls in buildings, against typical values frequently cited in the literature [18].

Table 1 Typical physical properties for RPUF [18] [25]

Property	**Typical values**[a]	**Commercial Example**[b]	**Test standard**
Typical core density (kg/m^3)	24-32	~30	
Thermal conductivity (mW/mK)	17-30	22	EN 13165
Tensile strength (MPa)	0.2-0.28	-	
Compressive strength (MPa)		≥ 0.12	BS EN 826:2013
Parallel to foam rise	0.14- 0.31		
Perpendicular to foam rise	0.10-0.17		
Closed cell content (%)	92-98		

Dimensional stability at (% volume change)	
At 70°C, 14 days	7-15
At 100°C, 14 days	5-10

The lower the *density* of RPUF the more economic it is against other competitive insulation materials [26]. However, it should be within the limit of providing dimensional stability according to an industry-standard (BS EN ISO 844:2014) and load-bearing capacity with a minimum compressive strength of RPUF (100 kPa) [27, 28]. It is generally measured in the direction of foam rise by a standard method, above which the RPUF will be dimensional stable [29].

The *compressive strength* of RPUF, at room temperature, for commercial densities of between 30-45 kg/m^3 is directly proportional to the density [30]. To date, while there is no generally accepted correlation between compressive strength and fundamental parameters, such as cell size, it is generally accepted that the compressive strength of RPUF increases with smaller cell size and narrower cell size distribution [31, 32]. Finally, the compressive strength of RPUF depends on the direction of measurement as RPUF exhibits strong anisotropic behaviour and is stronger in the direction of foam rise [30, 33].

The *thermal conductivity* (denoted by λ or the k-factor) of RPUF [34] is the sum of four parts ($\lambda_{TOTAL} = \lambda_{SOLID} + \lambda_{GAS} + \lambda_{CONVECTION} + \lambda_{RADIATIVE}$) but given that the cells in RPUF are so small $\lambda_{CONVECTION}$ is considered negligible. Given constant conduction for gas phase (λ_{GAS}) and solid phase (λ_{SOLID}), the initial thermal conductivity of RPUF is directly proportional to the radiative conduction ($\lambda_{RADIATIVE}$) which is linearly dependent on the average cell size (as indicated in yellow arrows in **Figure 2a**) of the foam [29, 35, 36]. Hence, the most common strategy for improving the thermal insulation of RPUF is to reduce the average cell size (**Figure 2b** and **Figure 2c**), without a significant change in the density (as it affects λ_{SOLID}) and overall closed-cell content (%) (as it affects cell size and because open cells contain air which has a high thermal conductivity).

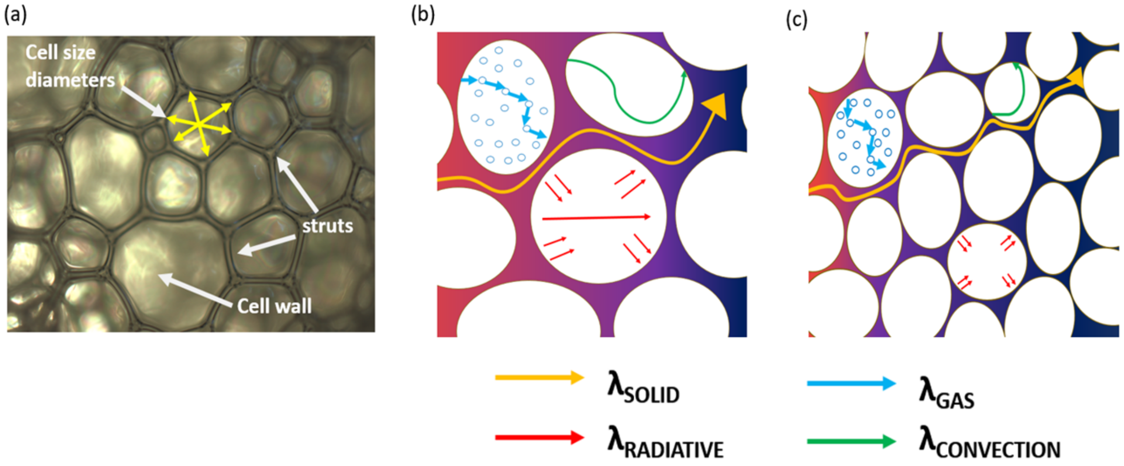


Figure 2 Relationship between overall thermal conductivity and microstructure of RPUF (a) 2D optical micrograph showing different components of cell morphology of RPUF, (b, c) Schematic comparison of influencing factors on total thermal conductivity of RPUF with relatively larger and smaller cells

The *resistance to moisture absorption* is an important property of RPUF, as the thermal conductivity of water ($\lambda = 0.59$ W/mK at 25^{o}C) [37] is significantly higher than that of the common physical blowing agents. Hence, long-term absorption of moisture into the RPUF could increase thermal conductivity. Fortunately, because of its high closed cell content and hydrophobicity RPUF has good water and moisture resistance [38]. Further, this resistance is often enhanced by the use of facers. For example in **Table 1** Eurowall®+ is faced with an impermeable aluminium/plastic foil composite [25].

The *high closed cell content* of RPUF also makes it airtight and this property is enhanced by the presence of facers on the RPUF. The diffusion of air (λ=0.024 W/mK) into RPUF and diffusion of CO_2 (λ= 0.016 W/mK) or other blowing agents (0.009-0.012 W/mK) out of RPUF will occur over time [34] leading to an increased *aged thermal conductivity*. This process is slow and can be retarded by the presence of facers or the use of thicker sections of RPUF. Tests conducted over 15 years on RPUF have shown that the increase in thermal conductivity (about 0.003 W/mK) due to gas diffusion reaches a stable equilibrium at around the first three years [38, 39].

In terms of *fire resistance*, RPUF does not melt or produce burning droplets when exposed to fire due to its thermosetting nature [28]. However, they do require the addition of fire retardants to meet various national standards used in the building industry. The performance of RPUF can also be enhanced by using an aluminium foil or steel facing as used on RPUF board stock or RPUF composite panels respectively [1]. RPUF is also considered low risk in applications where it is covered with drywall (plasterboard), sandwiched between a double brick construction, or covered both sides by concrete as floor insulation.

Over the last few years, there has been a move away from small scale fire tests to large scale fire tests [40] on building elements and this is driving the use of PIR foam at the expense of fire retarded RPUF. While RPUF generally decomposes at around 200 °C leaving a 20% ‘char yield’, PIR foams have higher thermal stability and decompose at around 325 °C leaving a ‘char yield’ of around 50%. PIR foams have superior fire resistance compared to RPUF [41, 42] due to the use of aromatic polyester polyols which increases the overall level of aromatic moieties in PIR foam providing improved high thermal stability and char yield [43].

RPUF is a very *durable* product as it is resistant to common chemicals used on a building site including solvents in adhesives, sealants, primers and bituminous materials. Further, it is resistant to mould caused by moisture and has no detectable odour.

2.2. Structural Aspects of Physical Properties

Polyurethanes are segmented polymers consisting of alternating soft and hard segments. The soft segments, typically polyether or polyester polyols, are flexible and low polarity while the hard segments are polar urethane moieties capable of interaction by hydrogen bonding [18]. In PU elastomers which are based on linear high molecular weight polyols (M_w = 500-5,000) and monomeric diisocyanates (such as methylenebis(phenyl isocyanate) (MDI), toluene diisocyanate (TDI), naphthalene diisocyanate (NDI), isophorone diisocyanate (IPDI), methylene bis-cyclohexylisocyanate (hydrogenated MDI, HMDI,), and hexamethylene diisocyanate (HDI)) with low functionality (f) of 2 (See definitions in section S2 of Supporting Information), the hard segments can phase-separate into domains that influence the mechanical properties [18]. However, since RPUF is based on low molecular weight polyols (M_w = 400-1200) with higher functionality ($f \geq 3$) and polymeric isocyanates with a functionality (such as polymeric diphenylmethane diisocyanate (pMDI), f~2.7) [44], the high cross-link density inhibits such microphase separation. Hence, the physical properties, such as compressive strength, primarily depend on the density of the RPUF. However, for a given density, and cellular structure (cell size and closed-cell content), the mechanical properties of RPUF depends primarily on the cross-link density (from covalent bonds) and the extent of hydrogen bonding between the urethane hard segments. The cross-link density will reflect the functionality of the polyols and pMDI and the isocyanate index [45].

Low-density RPUF has a pentagonal dodecahedron microstructure [46]. The cellular structure (cell size and closed-cell content) of RPUF directly affects the thermal conductivity and indirectly affects the compressive strength of RPUF. The polymer matrix of RPUF at a density of around 30 kg/m^3 only represents about 3% of the volume of these materials [45]. The bulk of the material is closed cells (typically over 90%) filled with blowing agent. While the thickness of the cell walls of RPUF range from around 3 μm (cell windows or faces) to 30 μm (cell edges or struts), the cells themselves are typically around 250-500 μm in size [27] and elongated in the direction of foam rise [46].

2.3. Formulation of RPUF

The production of RPUF with the desired range of physical properties depends on the formulation and the processing conditions. The general definitions and calculations involved in the formulation are discussed in section S2 of the Supporting Information. The formulation and the function of the major ingredients are explained further with corresponding foaming reactions (**Figure 3**) [18, 47, 48] using a model commercial formulation (**Table 2**) without fire retardants or other additives. This formulation is originally from the Dow Chemical Company [49] but slightly modified in our laboratory to accommodate a different blowing agent [29].

Table 2 Typical formulation for RPUF [29, 49]

Material	**Quantity**	**Description**
Part A: Isocyanate (by parts)		
Polymeric methylene diphenyl diisocyanate (pMDI)	103	Isocyanate
Part B: Polyol Blend (by parts)		
Voranol™ 446	100	Polyether polyol
Tegostab® B8460	2.0	Surfactant
HFC-M1	30	Physical blowing agent
Water	1.5	Chemical blowing agent
DMCHA	1.0	Catalyst
Apparent Core Density (kg/m^3)	33.5 ± 0.7	
Reactivity (± 2 s)		
Cream time	40	Nucleation
Gel time	245	Polymerisation
Free rise time	367	Cell expansion

pMDI is the main *isocyanate* used to manufacture RPUF although there are niche applications, such as surfboard foam, which are made from other isocyanates. pMDI is a mixture of aromatic compounds containing an average of 2.7 isocyanate groups per molecule (f= 2.7) which are particularly reactive towards nucleophiles such as amines, alcohols, carboxylic acids, thiols, water, urea, and urethane [50]. The *isocyanate index* for a formulation is a measure of the excess isocyanate used relative to the theoretical amount required to react with all of the *reactive hydrogen* groups in the polyol blend. Typically, RPUF has an index from 90-130 [51], whereas PIR foam (discussed later) has an index above 180 [52, 53] and typically around 300.

Voranol^{TM} 446 is a sucrose-glycerine initiated *polyether polyol* with a functionality of 4.5 (average number of hydroxyl groups per molecule) and a hydroxyl value of 446 mg KOH/g which means it has an average Mw of 566 Da [49]. The polyols used in RPUF are chosen to have a hydroxyl value of 250-1000 mg KOH/g, a functionality of 3.0-8.0, and an Mw of 150-1,200 Da [54]. (Refer section S2 in Supporting Information for a discussion on the relationship between hydroxyl value, acid value, functionality, and molecular weight).

Simplistically, when pMDI is reacted with Voranol^{TM} 446 it forms a highly cross-linked polymer matrix (reaction I, **Figure 3**). As the reaction is exothermic (the centre of the foam can reach temperatures over 150 °C within 200 seconds) it evaporates the *physical blowing agent* while the *surfactant* stabilises the resultant gas bubbles [54] to form a gas-filled cellular structure. In practice, the formation of RPUF is much more complex and the first reaction that occurs is the reaction of pMDI with water. The water acts as a *chemical blowing agent* by generating CO_2 (reaction II, **Figure 3**) which also leads to the formation of urea (reaction III, **Figure 3**). The urea can further react in the presence of excess pMDI to form a biuret (reaction IV, **Figure 3**). This latter reaction although reversible at high temperatures is important in the chemistry of RPUF as it is used to increase the cross-link density and thus the physical properties, such as the compressive strength, of the RPUF [44, 54, 55]. However, it has been reported that RPUF made with physical blowing agents has a smaller cell size than those made of chemical blowing agents [56] which improves the thermal conductivity [57].

The work of Seo et al [58] on a full water-blown polyether RPUF at a pMDI index of 105 provides perspective on the impact of biuret cross-linking in RPUF. When the level of water is increased (0.5 to 3.0 php), the average cell size increases, while the density of the RPUF decreases. Hence, as a result, the compressive strength decreases because the mechanical properties of RPUF depend mainly on density. However, at constant density, the compressive strength of the RPUF increases with increased water content but the associated increase in the compressive strength of the RPUF, due to the increased cross-link density (as seen in the T_g of the RPUF) from the biuret, is an order of magnitude lower than that due to the density decrease.

Similarly, when there is an excess of pMDI in an RPUF formulation it can react with a urethane moiety to afford an allophanate group (reaction V, **Figure 3**), which again is reversible at high temperatures, but again is used to increase the cross-link density and thus the physical properties of the RPUF [59, 60]. Guo et al [61] have reported that the compressive strength of RPUF increases proportionally with the pMDI index between 110 to 130 using both HCFC and water as blowing agents. Fan et al [62] have reported a similar linear relationship between compressive strength and pMDI index between 70 and 110 in full water blown RPUF.

Kim et al [51] studied the effect of increasing the isocyanate index on a polyether-based RPUF blown solely with a physical blowing agent (HFC365mfc). It was found that as the index increased from 90 to 130 the gel time marginally decreased, the density decreased by about 9%, the compressive strength decreased by about 16%, the cell size and closed-cell content were unaffected but the thermal conductivity decreased by around 7%. While the increased cross-linked density due to the allophonate groups was visible in the measured T_g values, the increase due to allophonate cross-linking is again an order of magnitude less than that due to the density change.

Catalysts are used in the manufacture of RPUF to promote selective reactions when multiple reactions can occur at the same time [13]. For example, N, N-diamethylcyclohexylamine (DMCHA) used in **Table 2** offers a balanced catalytic reaction in creaming, gelling and foaming reactions (explained below). It has a strong catalytic affinity for the reaction between water and isocyanate and a moderate catalytic affinity for the reaction between polyols and isocyanate [63].

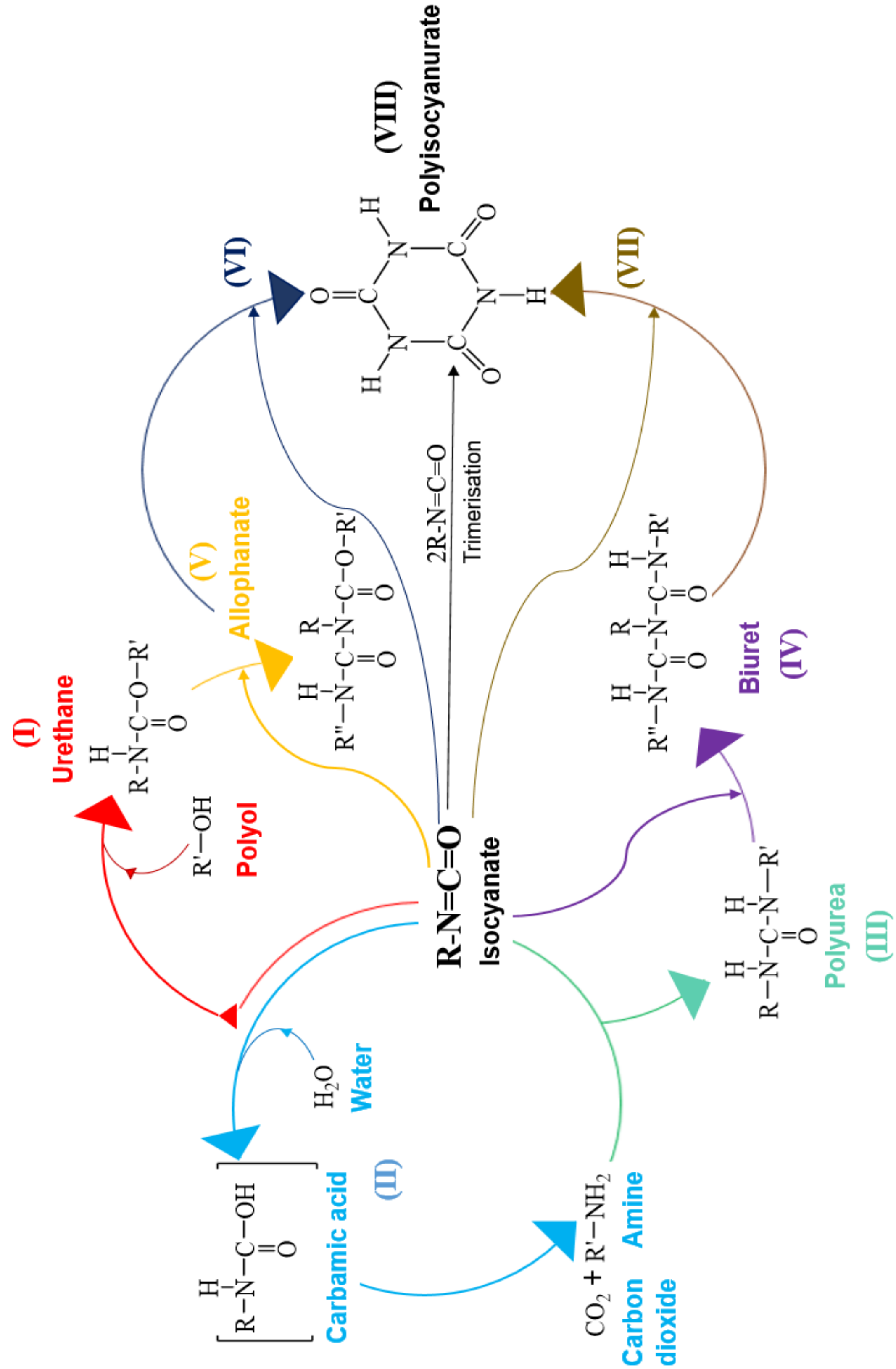


Figure 3 Key chemical reactions involved in polyurethane foam formation [18, 47, 48]

Aside from continuous manufacturing processes (used for the production of PIR foam), discontinuous manufacture of RPUF is normally done by the two-shot method where premixed polyol blend (Part B) containing polyols, blowing agents, catalysts and other components is mixed with pMDI (Part A) [2]. The foaming process can be explained in terms of the reaction profile (**Figure 4**) [64]. The mixture immediately turns cloudy and starts to rise which is called the 'cream time'. The expanding foam then starts to polymerize which is called the 'gel time'. The time taken for the foam to reach its largest volume is called the 'rise time'. Finally, the time taken for the foam to lose its 'stickiness' is known as the 'tack-free time' [64].

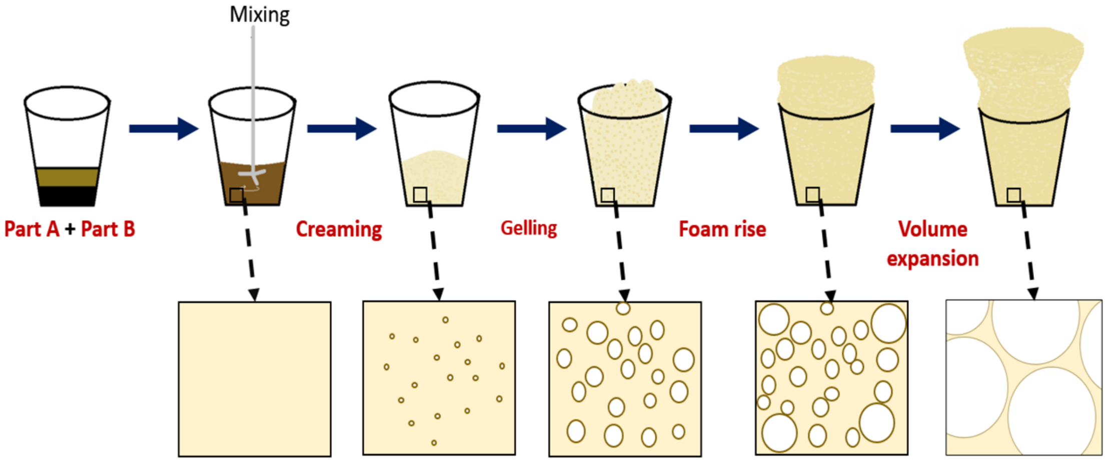


Figure 4 Schematic representation of physical and morphological changes occur at different stages [64].

PIR foam contains both urethane and isocyanurate groups. The latter is generated by the trimerization of an excess of -NCO groups (reaction VI, **Figure 3**) but this will only happen at a later stage when the temperature is high and usually in the presence of trimerisation catalysts such as potassium octoate [18]. The isocyanurate ring formation is also exothermic which causes a secondary rise in the foam. There is no industry agreed isocyanate index above which foam is classified as a PIR foam but an index of 350 is usually the upper limit due to the level of friability of the PIR foam [54]. The isocyanurate groups confer additional crosslinking to the foam which increases the thermal stability, improves fire performance, and reduces smoke generation [1]. While PIR foam can be made using polyether polyols it is normally manufactured using aromatic polyester polyols which are currently manufactured from petrochemical feedstock by condensation of polyhydroxy compounds with an aromatic dicarboxylic acid [41].

2.4. State of Art in Bio-based Polyols for RPUF

The RPUF market is still dominated by petroleum feedstock-based polyols. As a result polyols from alternative renewable resources such as natural products and vegetable oils [6, 15, 24] have been of academic and industrial interest for several years because bio-polyols have the potential to enable a cost-effective improvement in the sustainability of RPUF production [5]. Various natural products in their modified or unmodified state have been investigated for polyol production include seed oils, castor oil [65, 66], palm oil [29], coffee [67, 68], soy [69, 70], rapeseed oil [71], grape seeds [72], corn stalks [73], sugar cane bagasse [74] and wood [75, 76].

However, to date, the substitution of petrochemical polyols with bio-polyols has been limited because high loadings of bio-polyols can have a detrimental effect on the physical properties of the RPUF and/or the production of the bio-polyols involve energy-intensive multi-step chemical modification processes such as liquefaction, esterification, transesterification, epoxidation, and oxypropylation of the natural product [5].

Excessive loadings of bio-polyols to replace petrochemical polyols usually reduces the compressive strength of the RPUF which necessitates increasing the density to maintain the minimum compressive strength (and dimensional stability) making them uneconomic. For example, Septevani et al [29] observed that the mechanical, thermal properties and dimensional stability of RPUF produced by substituting polyether polyols with palm kernel oil-based polyester polyol were only comparable to the pure polyether polyol based foams at a loading of up to 20% w/w in the polyol or 8.4% w/w in the total RPUF.

Fan et al [62] have studied the effect of replacing polyether polyol in RPUF with soy-phosphate polyol at various loadings up to 50% w/w and observed a continuous decrease in compressive strength with an increase in soy phosphate polyol loading. Thus, while soy-based polyols and foams have been commercialised [77] they have only found limited use in spray foam (polyurethane mixture sprayed through a gun to expand on the applied surface) for non-load bearing applications.

The issue can be illustrated by comparing three commercial products (**Table 3**) from Demilec Inc. *[78-80]*. Heatlok®Soy200+ is described as a mixture of polyether, aromatic polyester, and soybean oil derived polyols, and reading between the lines the other two products are similar but with different proportions of the polyol components [74]. In all cases, the proportion of soy-based polyol does not exceed 14% (total foam) which would be consistent with a limit of around 20% in the polyol blend (Part B) as discussed above.

Further, as the blowing agent moves towards the more environmentally friendly HFO (hydrofluorolefin) material the level of renewable (soybean oil polyol) drops significantly presumably due to a compatibility issue with the blowing agent [56]. Finally, we cannot draw any conclusions between compressive strength and soy-based polyol content because every formulation uses a different physical blowing agent. Agrawal et al [7] and Zhang et al [81] have reviewed studies on renewable resources for polyurethane foam production with the perspective of enhancement of properties, including the utilization of natural or synthetic fibers, nano-fillers, and reinforcements.

Table 3 Physical properties of commercial RPUF using biobased polyols [78-80].

Property	**Heatlok® Soy 200+**	**Heatlok® XT (Summer)**	**Heatlok® HFO Pro**	**Test Method**
Core density (kg/m^3)	33.6	35.7	32-38.4	ASTM D1622
Thermal conductivity (W/mK)	0.020	0.022	0.020	ASTM C518
Closed Cell Content (%)	90	93	98	ASTM D2856
Air Leakage at 75Pa 25.4mm (L/s.m^2)	<0.002	<0.002	<0.002	ASTM E283
Water vapour permeance (ng/Pa*s*m^2)	<57.2 36mm	<57.2 28mm	52.5 25mm	ASTM E96
Compressive strength (kPa)	198	124	214	ASTM D1621

Tensile Strength (kPa)	319	261	303	ASTM D1623
Dimensional stability @70C & 97%RH (168hrs without substrate)	(-1.37, -0.42,+0.27% volume change)	-5.5% volume	-3.7% volume	ASTM D2126
VOC Emissions standard	Compliant	Compliant	Compliant	CA 01350
Fungi resistance	No fungal growth	No fungal growth	No fungal growth	ASTM C1338
Fire test:				ASTM E84
Surface Burning Characteristics	Class 1	Class 1	Class 1	
Flame spread Index	20	0-5	12	
Smoke Developed	400	350-400	350-400	
Renewable content	13.5%	8%	6%	
Recycled content	26.5%	37.4%	19%	
Blowing agent	HFC245fa, HFC365mfc & HFC227ea	HFC245fa	HFO-1233zd(E)	

2.5. Sustainability of RPUF

Figure 5 *[1, 5, 18, 28, 41, 82]* summarises the factors for consideration in assessing the sustainability of RPUF including raw materials and long-term performance

[27]. According to an evaluation [82] conducted by the Building Research Establishment (BRE) in the UK on a series of insulation materials for long-term performance, RPUF was found to be the superior insulation choice at the total building level due to the low thermal conductivity achieved at low density without compromising load-bearing capacity. However, when assessed at the raw material level (or manufacturing phase) from environmental impact perspectives [83] there are still several issues and opportunities.

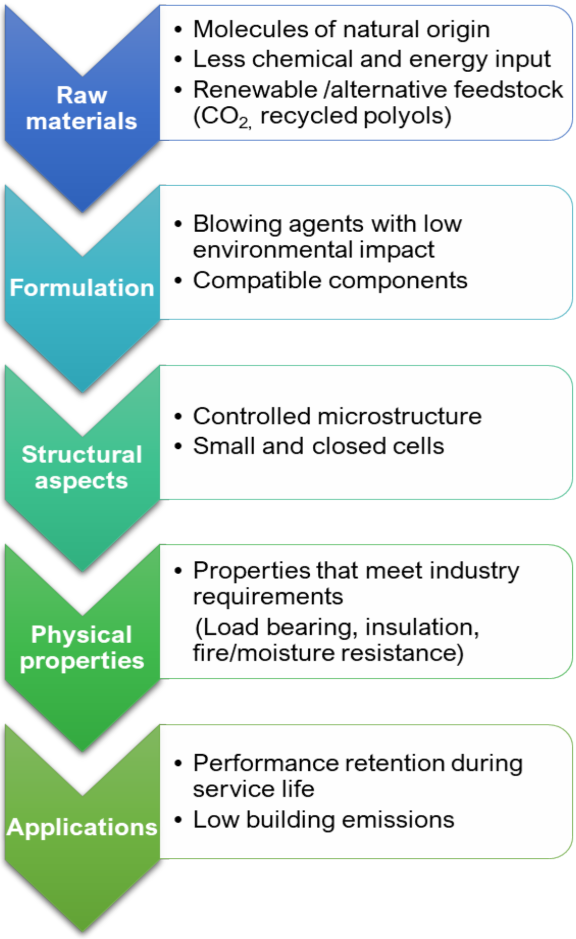


Figure 5 An overview of the various factors influencing the sustainability and performance of RPUF [1, 5, 18, 28, 41, 82]

First, the majority of the raw materials used in *RPUF* production are derived from fossil fuels. For example, polyether polyols for RPUF are manufactured using propylene oxide and efforts to date to manufacture propylene oxide using bio-based materials have been unsuccessful. That this might change in the future, has credence from the fact that Croda International Plc [84] has built a plant to make bio-ethylene oxide, a related chemical used in the manufacture of surfactants and flexible polyurethane foam polyols. Efforts to make a bio-isocyanate have also been unsuccessful to date.

Second, RPUF in the past had utilised *blowing agents* that were reported to contribute to atmospheric ozone depletion. Following the adoption of Montreal Protocol in 1987 the PU industry phased-out chlorofluorocarbons (CFC), because of their high global warming potential (GWP), with hydrochlorofluorocarbons (HCFC) which were subsequently replaced with hydrocarbons (HC) and hydrofluorocarbons (HFC). The industry is now gradually replacing HFC with hydrochlorofluoroolefins (HCFO) which have low thermal conductivity and exhibit both low ozone depletion potential (ODP) and GWP values [85]. **Table 4** [85-87] summarises the physical properties of some of the current and past blowing agents in RPUF.

As a result, the majority of the current research to improve the sustainability of RPUF has been focussed on the replacement of the polyether polyols in RPUF with renewable polyols from biomass resources [5]. In this regard, lignin is an attractive potential bio-feedstock as it is non-toxic, sourced from a non-food-bioresource, and potentially offers high aromatic carbon content.

Table 4 Properties of common current and past blowing agents used in RPUF [85-87]

Blowing Agent Class	Example	IUPAC name	Flash point (^oC)	ODP	GWP	Mw (g/mol)	λ at 25^oC (mW/mK)
CFC	R-11	Trichloro-fluoromethane	0	1	4750	137.3	8.4
HCFC	R-141b	1,1-Dichloro-1-fluoroethane	0	0.12	725	117	9.7
HFC	R-365mfc	1,1,1,3,3-pentafluorobutane	-25	0	782	148.1	10.5
HC	Isopentane	2-methylbutane	-51	0	11	72.1	13.3
HCFO	R-1233zd(E)	1-chloro-3,3,3-trifluoropropene	0	0	1	130.5	10

3. Lignin

Lignin is an abundant aromatic biopolymer derived from plant biomass. It fills the spaces between the cellulose and hemicellulose in plant cell walls where it acts as a gluing matrix that holds the lignocellulose fibrils together [88]. It is well documented that lignin is a heterogeneous polymer without a fundamentally defined structure [89]. The amount of lignin content varies by source [90, 91]; for example, grass contains 17–24% w/w while softwood and hardwood contain 18–25% w/w and 27–33% w/w respectively.

As depicted in **Figure 6** [92, 93], it is an amorphous three-dimensional polymer formed typically from up to three random repeating monomers; paracoumaryl alcohol (H-type), coniferyl alcohol (guaiacyl unit or G-type), and sinapyl alcohol (S-type), connected *in situ* by radical polymerization to form carbon-carbon bonds and carbon-oxygen bonds with the ß-O-4 being the most abundant linkage. [92] The composition of lignin (H/G/S monolignols ratio) varies by source; grasses contain all three monomeric alcohols (5–33/33–80/20–54 %), softwood contain mainly guaiacyl units (0–5/95–100/0 %), while guaiacyl and syringyl units dominate in hardwood (5–33/33–80/20–54 %) [43, 94, 95].

While lignin present naturally in plants is referred to as ‘native or natural lignin’, the extracted lignin from parent lignocellulosic biomass through common industrial-scale production methods (which include chemical pulping of biomass, and recovery/ separation of lignin) is called ‘technical lignin’ [96-98]. As shown in **Figure 6**, the chemical structure and physical properties of these technical lignins vary depending on the specific extraction method [92, 93].

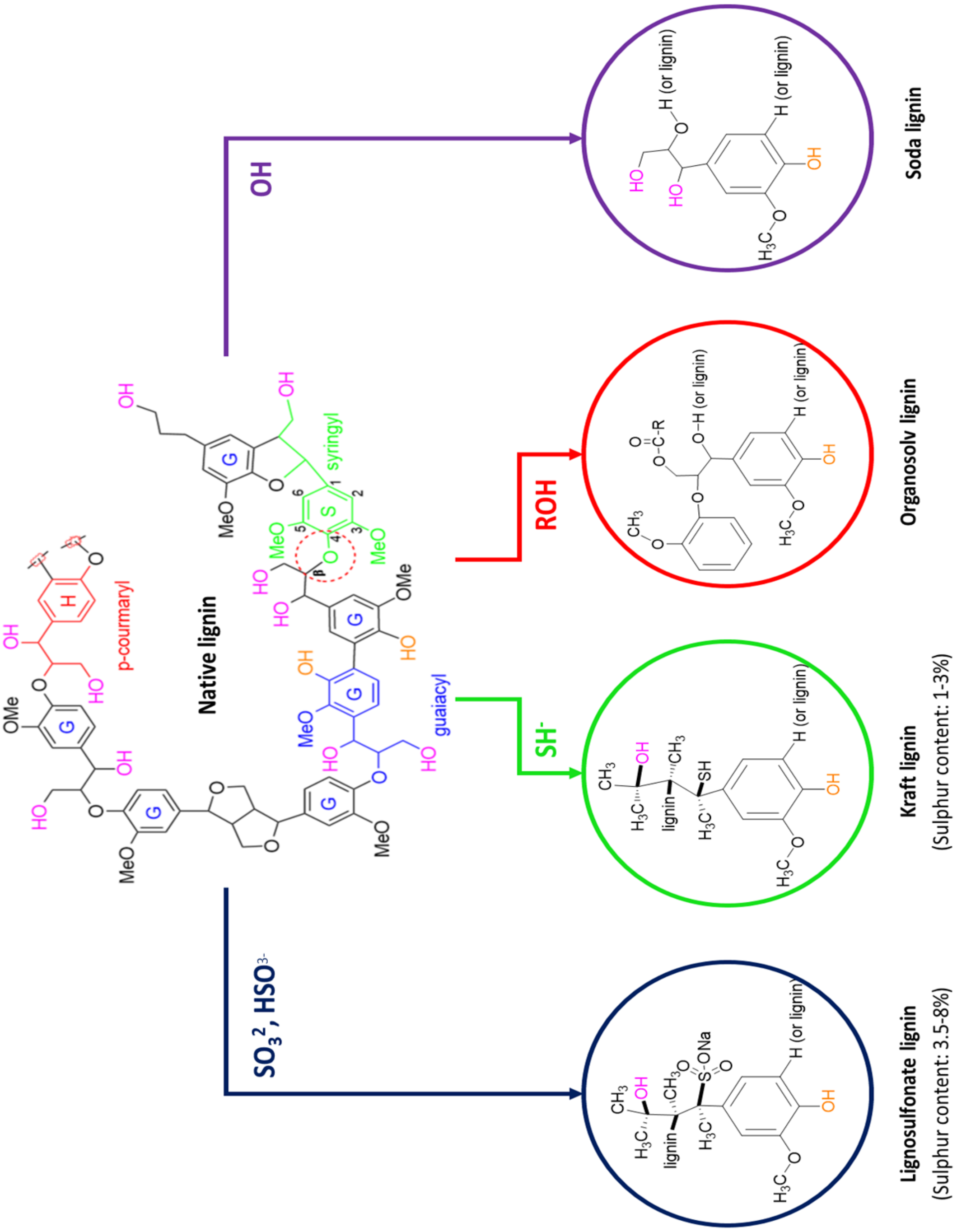


Figure 6 Simplified chemical structure of native lignin (H= p-coumaryl, G= guaiacyl & S= syringyl units and dotted red-circle highlights the ß-O-4 linkage) and lignin extracted

through common technical processes, showing representative functional groups [92, 93, 96].

3.1. Types and Production of Technical Lignin

Numerous processes have been studied for the extraction of technical lignin but as they have been extensively reviewed [90, 96, 98, 99] only the most common industrial methods will be discussed briefly below. Other processes used for the extraction of lignin include ball-milling, milling with or without a catalyst [100, 101], enzymatic degradation, steam explosion, pyrolysis, sequential liquid-lignin recovery and purification (SLRP™), processing with ionic liquids, which are utilized in laboratories or pilot plant reactors [94, 98, 102].

Kraft pulping is a well-established in the pulping industry and commonly used method to remove 85-95% of the lignin and 56-71 % of the hemicellulose from wood biomass [98, 103]. The wood chips are added to a mixture of aqueous sodium hydroxide (NaOH) and sodium sulphide (Na_2S) solutions and heated at temperatures between 150˚C and 180˚C for about 2 hours [94]. The majority of the cooking liquor or black liquor is typically concentrated (to 70-80 %) and supplied for energy needs to operate the mills and recaustisation (recovery of cooking chemicals) [97]. The sodium salt of Kraft lignin (KL) is recovered from the remaining amount of black liquor through acidification (neutralisation) using carbon dioxide and sulphuric acid, followed by hot filtration to afford the sodium salt. The sodium salt is suspended in water and further acidified to a pH around 2.0, filtered, washed, and dried to obtain purified KL (also called alkali lignin) [2, 92, 94, 99]. The final KL is dark in colour, and has a sulphur content up to 3% [96]. It is soluble in ethylene glycol, partially soluble in methyl formate and methanol, and insoluble in in water (unless alkaline) and most other common solvents [104, 105].

Overall, KL is the largest commercially produced technical lignin with over 13 million tonnes [96] produced annually by the paper and pulp industry [106].

Lignosulfonates (LS), also known as 'sulphate lignin', the second most common commercial form of technical lignin, has a global production of only around 1.06 million tonnes per annum [107]. The sulphate process produces wood pulp (cellulose) in an acidic medium (pH 1.5-5.0) by using various salts of sulphurous acid to extract lignin. The salts are either sulfate (SO_3^{2-}) or bisulfites (HSO_3^-) depending on the pH. The counterions can be either sodium, ammonium, magnesium, or calcium [108]. The wood chips are mixed with the pulping chemicals for 4 to 14 hours at temperatures between 120 and 180 °C depending on the chemicals used [93, 98]. The LS extracted from the "brown liquor" is commercially available in the form of sodium or calcium salts or as the free neutralised sulphonic acid [99].

The *organosolv process* involves the treatment of biomass in an organic or aqueous-organic polar solvent mixture with hydrochloric or sulphuric acid (typically) at temperatures from 170°C to 190°C to simultaneously isolate individual streams of hemicellulose, cellulose, and organosolv lignin (OSL) [92, 105, 108]. The OSL is recovered from the organic phase so the specific solvent used in the process influences the properties, polarity, and structure of the OSL. The most common process is based on aqueous-ethanol however acetic acid and formic acid solutions are also used [109]. As a result, OSL is highly soluble in organic solvents but insoluble in water [73]. Second-generation biofuel production in the USA alone is expected to produce around 62 million tons of OSL by 2023 [110].

The *soda process* is generally used for chemical pulping of non-woody biomass sources such as sugar cane or flax. The feedstock is mixed into an aqueous solution of sodium hydroxide (13-16% w/w) at a temperature of 140 to 170 °C [105]. The soda lignin (SL) is isolated by acidification and precipitation [94]. SL is closer to native lignin in structure due to its relatively gentle pulping conditions and absence of sulphur [106].

Hydrolysis lignin (HL), a solid byproduct from the pretreatment process in bioethanol plants, is soluble in solvents like acetone but it is a mixture of lignin and carbohydrates [2]. For example, FP Innovations LignoForce^{TM} hydrolysis lignin contains by weight 56.7% lignin, 29.8% carbohydrates, 1.2% ash, and 12.3% '*other*' [107].

3.2. Properties of Technical Lignin

Recent developments in analytical methods (including structure, monomer composition and purity) for technical lignin has been comprehensively reviewed elsewhere [111]. Since most of the products are not available in large quantities with consistent quality and an attractive price, non-commercial technical lignin is not considered as a credible feedstock for a bio-chemical industry. Therefore, from this point onwards we will use compiled data on typical characteristics, as best we can, from the recent literature on various technical lignin.

3.2.1. Purity

The total ash content of technical lignin varies with the biomass source and the delignification method. Grass and softwood derived technical lignin contains more ash than that from hardwood due to their high silicon content, while certain delignification methods produce salts which contribute to the total ash content [112, 113]. In terms of the most readily available commercial technical lignin, softwood kraft lignin (SKL), it appears that it can be refined to a level of around 3% (**Table 5**) [112, 114-117] but there has been no known reported work examining if an upper level of ash or carbohydrate at 3% and 2% respectively is satisfactory for use in RPUF. Excessive ash content could introduce errors due to incorrect isocyanate index calculation or interfere with the formation of the cellular structure.

Table 5 Ash and carbohydrate content in commercial technical lignins in % w/w [102, 112, 114-120]

Property	**Ash**	**Carbohydrate**	**Nitrogen**	**Moisture**
Softwood kraft lignin (SKL)				
Indulin AT	3.06	2		
Indulin AT	3.59	1	NR	
Sigma Aldrich 370959	2.1	NR		
Curan 27-11P	17	2		
Aldrich 471003	66.19			3.7
Biochoice™ (LignoBoost)	0.02-1	2.2	0.2	32.3
LignoForce™ (FP Innovations)	0.10-1.5	1.2-2.4	NR	NR
SLRP™ (Liquid Lignin company)	1-3	NR	NR	32-48[a]

Soda lignin (SL)				
Sarkanda	3.26	5		
Protobind 2400 (wheat straw)	1.61	1.3	NR	
Organosolv lignin (OSL)				
Alcell®	0.05	0.2		
Alcell®	0.1	0.32	0.14	
Aldrich 371017 (hardwood)	0.11			2.4
Lignosulphonate (LS)				
Aldrich 471038 (softwood)	20.02			6.81

Footnotes: NR = not reported; ^{a} liquid-phase

3.2.2. Elemental Composition

The complex structure of lignin is typically represented by an empirical formula (C9 formula) representing average repeating lignin monomers [121]. The C9 formulae provide structural information on technical lignins, but it does not provide information on molecular weights or the monomer ratio (H/G/S) or functional group composition [95].

Table 6 [114, 115, 122-129] summarises the elemental composition of various commercial technical lignins (% w/w) together with the corresponding C_5 or C_9 formulae [121]. The methoxyl content of technical lignin is generally determined by ^{13}C-NMR spectroscopy on their non-acetylated samples. It appears that there are some inconsistent results for SKL, presumably reflecting analytic errors or batch variations.

Table 6 Elemental composition (% w/w) and C9 formulae of various commercial technical lignin

Lignin	%C	%H	%N	%S	%O	% OCH_3	C_9 or C_5 formulae
Softwood kraft lignin (SKL)							
Curan 27-11P [115]	50.13	4.88	<0.30	2.30	25.69	13.1	$C_9H_{8.99}O_{2.95}S_{0.17}(OCH_3)_{0.83}$
Indulin AT [114]	63.9	5.6	0.39	2.1	24.4	11.2	$C_9H_{8.13}O_{2.1}N_{0.05}S_{0.11}(OCH_3)_{0.66}$
Indulin AT [122]	66.10	6.37	0.67	1.57	25.30	NR	$C_{5.51}H_{6.37}O_{0.049}N_{0.048}S_{0.049}$
Indulin AT [115]	61.64	5.81	0.48	1.05	27.97	12.9	$C_9H_{8.74}O_{2.56}N_{0.064}S_{0.062}(OCH_3)_{0.77}$
Indulin AT [123]	65.5	5.6	0.4	3.3	25.2	13.6	$C_9H_{8.5}O_{1.9}S_{0.19}(OCH_3)_{0.80}$
BioChoice [123] (LignoBoost)	65.0	6.7	0.2	1.6	26.5	12.8	$C_9H_{9.8}O_{2.0}S_{0.09}(OCH_3)_{0.74}$
Sigma Aldrich 370959 [124]	62.24	5.69	0.73	1.54	29.78	NR	$C_{5.18}H_{5.64}O_{1.86}S_{0.048}$

FPInnovations [125](LignoForce^{TM})	63.8	5.4	0.02	5.2	25.6	NR	NR
Soda lignin (SL)							
Sarkanda [115]	58.84	5.86	1.14	1.01	29.89	15.6	$C_9H_{8.99}O_{2.82}N_{0.16}(OCH_3)_{0.98}$
Protobind [122]	65.41	6.53	0.59	0.38	27.09	NR	$C_{5.45}H_{6.53}O_{1.69}N_{0.042}S_{0.012}$
Protobind 2400 [114, 126]	61.2	6.3	0.93	2.0	28.0	14.8	$C_9H_{9.42}O_{2.5}N_{0.11}S_{0.12}(OCH_3)_{0.93}$
Lignosulfonate (LS)							
Sappi Saicor[a] [127]	42.8	4.0	0.2	4.5	40.2	7.54	$C_9H_9O_{6.2}S_{0.4}(OCH_3)_{0.6}$
Organosolv lignin (OSL)							
Alcell® [115]	65.88	5.82	<0.30	<0.20	27.69	18.6	$C_9H_{7.39}O_{2.08}(OCH_3)_{1.1}$
Pine lignin [128]	61.9	6.0	-	-	29.6	16.2	$C_9H_{8.5}O_{2.6}(OCH_3)_{1.0}$
Eucalytus lignin [129]	58.8	5.4	0.01	-	35.8	17.4	$C_9H_{7.7}O_{3.5}(OCH_3)_{1.16}$

Footnotes: NR = not reported; [a]The LS was the Ca salt (6.6% w/w) with an ash content of 17% w/w. The Alcell® was from hardwood using aqueous-ethanol extraction.

3.2.3. Molecular Weight and Distribution

The determination of the molecular weight of technical lignin is difficult due to the poor solubility of lignin in most organic solvents or water, and their affinity to associate via hydrogen bonds and other secondary forces [112]. **Table 7** [2, 114, 116, 117, 122-125, 130-139] summarises reported molecular weights and polydispersity of various commercially available technical lignin's from the recent literature. However, in addition to variation by source [89], there appears to be a lot of variation between different commercial suppliers, presumably due to variation in processing or analytical method, and between batches at the same company (see Curan 100 entry in **Table 7**).

Size exclusion chromatography (SEC) has several limitations when applied to technical lignin. Glasser et al [140] have reported that the hydrodynamic volume and the intrinsic viscosity of the lignin acetates do not increase proportionately with Mw as it would for a linear coil molecule, signifying lignin acetates are highly spherical molecules in tetrahydrofuran (THF) solution. Gosselink et al [116] have reported that the SEC of technical lignins is affected by the choice of solvent and column due to the adsorption of lignin molecules onto the stationary phase. For example, Alcell™ Mw was determined at 6,820 Da in THF, 9,060 Da in dimethylformamide (DMF) on one column, and 11,100 Da in DMF on a different column (entry denoted with * in **Table 7**). However, in broad terms, it appears that the Mw decreases in the order LS > KL > SL~ OSL.

Table 7 Reported molecular weights and polydispersity for various commercial technical lignins

Source or Trade Name	M_w (g/mol)	M_n (g/mol)	M_w/M_n	Reference

Hardwood kraft lignin (HKL)				
Westvaco[a]	2,400	1,330	1.8	[130]
Softwood kraft lignin (SKL)				
Curan 100 (batch 1)	5800	2760	2.1	[131]
Curan 100 (batch 2)	7120	3000	2.4	[131]
Indulin AT	7600	1100	7.0	[132]
Indulin AT	6096	1191	5.12	[122]
Indulin AT*	4549	1248	3.65	[114]
Indulin AT	4290	530	8.1	[133]
Indulin AT	6549	656	9.9	[123]
Indulin AT	4680	1980	2.4	[134]
Sigma Aldrich 370959	3980	2211	1.8	[117]
Sigma Aldrich 370959	4600	2300	2.0	[135]
Sigma Aldrich 370959	9500	3000	3.21	[124]
FPInnovations (LignoForce™)	10000	5000	2.0	[2, 125]
BioChoice™ (LignoBoost™)	6772	949	7.1	[123]
Lignosulfonates (LS)				

Sigma Aldrich 471038 (Na salt)	52000	7000	7.4	[136]
Soda lignin (SL)				
Protobind 1000 (Non-wood)	3270	620	5.2	[133]
Protobind (Non- wood)	5008	1084	4.62	[122]
Protobind 2400 (Non-wood)	2802	838	3.34	[114]
Organosolv lignin (OSL)				
Lignol Innovation (Hardwood)	2600	1600	1.62	[130]
Biolignin ™	17800	900	19.8	[137]
Alcell® (Softwood)	2650	1850	1.4	[131]
Alcell® (Hardwood)	2580	600	4.3	[133]
Alcell® (Hardwood)	2000	900	2.22	[138, 139]
Alcell®* (Hardwood)	9060	1320	6.86	[116]
Alcell®* (Hardwood)	11100	2500	4.44	[116]
Alcell®* (Hardwood)	6820	1900	3.59	[116]

Footnotes: [a] discontinued

3.2.4. Functional Group Content

The variation in functional group content (aliphatic, phenolic and benzylic hydroxyl alcohols, methoxy groups, thiol groups, carbonyl groups, etc.) in technical lignin affects the reactivity in chemical reactions with other reagents including pMDI [141, 142]. This section introduces the methods used to quantify the main functional groups in technical lignin and discusses their relative reactivity with pMDI. **Table 8** [73, 115-117, 122, 130-134, 143-145] summarises the functional groups present in several commercially available technical lignins from the recent literature.

Ignoring HKL and HL results, as there is only one example for each product, in general, technical lignins appear to contain more phenolic than aliphatic hydroxyl groups and the levels of both carboxylic acid and thiol groups should not be ignored in calculating the stoichiometric quantity of pMDI required to achieve the desired isocyanate index. Part of the variation in functional group content could also reflect the issue that the analysis is subject to variation between different analytic methods [121, 146]. For example, a comparison of aminolysis, non-aqueous potentiometry, ^{1}H-NMR, ^{13}C-NMR, and UV-spectroscopy methods for determining the phenolic hydroxyl content of different types of technical lignin showed a poor correspondence between the aminolysis, ^{13}C-NMR, and UV spectroscopy tests and the non-aqueous potentiometry and ^{1}H NMR tests at the 0.05 significance level [146].

Gosselink et al [116] recommend non-aqueous titration in DMF using TnBAH (tetra-n-butylammonium hydroxide) as the preferred method for the determination of phenolic hydroxyl content as the FTIR method is affected by the fact that the acetylation of phenolic hydroxyls in lignin can be incomplete due to steric hindrance by the methoxy groups. For the same reason, the determination of the total hydroxyl content can also be dependent on the acetylation method. However, non-aqueous titration in DMF using TnBAH for the carboxylic acid group content is recommended [116].

Table 8 Functional group composition of commercial technical lignin's

Source or Trade Name	**Aliphatic-OH (mmol/g)**	**Phenolic-OH (mmol/g)**	**Carboxylic-OH (mmol/g)**	**Methoxy (mmol/g)**	**Thiol (mmol/g)**	**Ref**
Hardwood kraft lignin (HKL)						
Westvaco[a]	4.12	4.29	NR	5.81	NR	[130]
Softwood kraft lignin (SKL)						
Curan 100	1.0	3.4	1.0	12.05	NR	[131]
Curan 27-11P	2.16	3.63	0.47	0.2	0.7	[115]
Indulin AT	1.95	3.24	0.43	NR	NR	[132]
Indulin AT	2.59	4.00	0.20	NR	0.4	[122]
Indulin AT	2.34	3.95	0.39	0.2	0.33	[115]
Indulin AT	1.79	2.77	0.33	NR	NR	[133]

Indulin AT	5.22	3.75	NR	NR	NR	[134]
Sigma Aldrich 370959	2.62	3.43	0.48	1.9	0.4	[117]
Sigma Aldrich 370959	1.39	1.55	0.50	NR	1.00	[143]
LignoBoost	1.78	3.64	0.41	NR	0.94	[143]
Soda lignin (SL)						
Protobind (non- wood)	2.47	2.28	0.22	NR	0.1	[122]
Protobind 1000 (non-wood)	1.26	2.86	0.80	NR	NR	[133]
Sarkanda (non-wood)	1.89	2.41	0.62	0.3	0.3	[115]
Organosolv lignin (OSL)						
Lignol Innovation (Hardwood)	2.88	2.76	NR	6.16	NR	[144]

Alcell® (Hardwood)	2.16	3.81	0.47	0.3	0	[115]
Alcell® (Hardwood)	1.04	3.30	0.22	NR	NR	[133]
Alcell® (Hardwood)	4.17	2.24	0.71	NR	NR	[116]
Biolignin™	6.0	1.1	1.3	3.1	NR	[145]
Hydrolysis lignin (HL)						
Cofco (non-wood)	7.78	14.30	0.59	NR	NR	[73]

Footnotes: NR = not reported; [a] discontinued

3.3. Characteristics of Technical Lignin Relevant to its Incorporation into RPUF

3.3.1. "Solubility" of Lignin

Several groups have studied the dissolution of technical lignin in common organic solvents [147-149]. For example, Giummarella et al [150] reported that while highly polar solvents and non-polar solvents were poor solvents for technical lignin better dissolution could be achieved in semi-polar solvents, such as ethanol, acetic acid, methanol, and furfuryl alcohol. The latter was postulated due to the interaction of the aromatic furan ring with the aromatic structures in lignin. However, given that dissolution was defined as technical lignin in liquid supernatant after centrifugation there was no clear distinction between a true solution and a dispersion. Similarly, Ni et al [151] and Sameni et al [122] have studied the solubility of lignin in organic solvents from the perspective of the Hildebrand and Hansen solubility parameters.

The morphology of lignin is the result of hydrogen bonding between hydroxyl groups [122] and π-π interactions [152] between phenyl rings. Vainio et al [131] have examined the morphology of KL dry and in aqueous alkaline solution and found when in "solution" the KL is still present as rods/fractals with a thickness of around 1-3 nm and a length of 5-9 nm depending on the KL concentration. Vainio et al [153] have also looked at the morphology of sodium lignosulphonate (NaLS) in aqueous (alkaline) solution and found it to be a flat ellipsoid the same as for kraft lignin [35].

Zhao et al [148] and Cheng et al [149] have reviewed technical lignin association to form nano/micro-particles in solution. Yang et al [135] has reported that KL in ethylene glycol or DMSO exists in two forms; lignin nano-particles and lignin nanoparticle agglomerates and that it can take up to a week for them to reach a state of dynamic equilibrium which can complicate the reproducible characterisation of technical lignin's properties such as the molecular weight by GPC. The interparticle-association of technical lignin is a common phenomenon that occurs in the solid matrix as well as aqueous and organic dispersions. Aggregation and disaggregation of technical lignin have been well documented for KL [39, 154-160], SL [152], solvolysis lignin [161, 162], and enzymatic mild acidolysis lignin [163-165].

Thus, there is no such thing as a true solution of technical lignin [131]. They are dispersions of technical lignin particles ranging in size from the nano-scale to the micro-scale and as such, this has three consequences in terms of incorporation into RPUF. Firstly, the presence of micro-scale agglomerates can negatively affect the cellular morphology (discussed further below) and thus the physical properties of the RPUF. Secondly, the presence of both nano-scale and micro-scale particles restricts the potential cross-linking between the technical lignin and pMDI due to the steric hindrance of the tightly hydrogen-bonded structure (also discussed further below). Thirdly, the presence of high loadings of technical lignin can increase the viscosity of the lignin-polyol dispersion so it is too viscous for effective mixing with pMDI resulting in a non-homogenous RPUF. It also explains part of the variation observed in the experimental determined molecular weights and functional group analysis of technical lignin.

3.3.2. Reactivity of Lignin with pMDI

The reactivity of pMDI with technical lignin would be expected to be slower than with polyether polyols because of the high content of aromatic hydroxyl groups given the order of reactivity with isocyanate is primary aliphatic amines > aromatic amines > primary alcohol > aromatic alcohol > thiol [166]. **Table 9** [47] provides a general ranking of active hydrogen group reactivity with isocyanate. However, two other nuances need to be acknowledged; first, phenolic groups with an α-methoxy group (single methoxy in the salicylic group and double methoxy in a syringylic group) will be even more inactive because of the steric hindrance of the methoxy group [167]. Thus, it can be expected that SKL would be more reactive than HKL but this is probably mute as the second point dominates in that if the lignin is present as a solid particle a lot of the active hydrogen-containing groups (aliphatic and phenolic hydroxyl groups, thiols, carboxylic acid groups) will be inaccessible due to steric hindrance [168] as a result of agglomeration.

Table 9 Relative rate of reaction of active hydrogen groups with isocyanate [47]

Reaction	**The relative rate of reaction**
Reaction with an amine to give urea: R-NCO + H_2N-R’ -> R-NH-CO-NH- R’	Primary aliphatic amine: 100,000 Secondary aliphatic amine: 20,000-50,000 Primary aromatic amine: 200-300
Reaction with water to give an amine: R-NCO + H_20 -> RNH_2 + CO_2	Water: 100
Reaction with a hydroxyl group to give a urethane: R-NCO + HO-R’ -> R-NH-CO-O-R’	Primary hydroxyl: 100 Secondary hydroxyl: 30 Tertiary hydroxyl: 0.5
Reaction with carboxylic acid: R-NCO + R’-CO_2H ->	40
Reaction with urea: R-NCO + R’-NH-CO-NH-R” ->	15
Reaction with urethane: R-NCO + R’-NH-CO-OR” ->	0.3
Reaction with amide: R-NCO + H_2NCO-R’ ->	0.1

To the authors' knowledge, no one has reported on the kinetics of the reaction between pMDI and technical lignin. However, Cateto et al [169] have studied the kinetics of the formation of a polyurethane elastomer based on pure MDI (f = 2) and a series of different polycaprolactone polyesters (f = 2) containing SKL (Indulin AT) and OSL (Alcell®) at various loadings (10, 15, 20 & 25% w/w) at a NCO/OH ratio of 1.0. It was reported that the polymerisation goes from a global second-order model to diffusion control as the lignin content increases or the polycaprolactone molecular weight increases. The point of change is also dependant on the type of lignin and the isocyanate conversion was not significantly affected by the presence of lignin indicating that the reaction occurred mainly with the polycaprolactone polyol rather than the lignin.

However, reported research with KL in polyols [124] would suggest Cateto et al [169] were working with a dispersion of nano-KL and micro-scale KL agglomerates rather than a true solution. Working from that premise, it would be expected that the pure MDI would largely react with the polycaprolactone polyol rather than the lignin due to the steric hindrance of the hydroxyl group's in the KL in both the nano-particles and the agglomerates. This view is supported by their observation of free NCO groups in the reaction mixture after 30 minutes and by the fact that the conversion rate was observed to decrease with increasing lignin loading and increased polycaprolactone molecular weight, which would both lead to increased KL agglomerate size and thus a higher content of inaccessible hydroxyls on the KL.

The key unanswered question in the work of Cateto et al [169] is what proportion of the hydroxyl groups on the KL are accessible?. It would be expected to be low as it has been observed in an analogous situation that isophorone diisocyanate (IPDI) when reacted with cellulose nanocrystal (CNC) under a nitrogen atmosphere in DMSO (a swelling solvent) at 60°C overnight at an NCO index of 72 afforded only a 0.17 *degree of substitution* [170]. Similarly, 1,6-hexamethylene diisocyanate (HDI) when reacted with CNC under a nitrogen atmosphere in DMF (a swelling solvent) at 80°C for 24 hours with an NCO index of 1 afforded only a 0.20 *degree of substitution* [171]. Similarly, toluene diisocyanate (TDI) when reacted with CNC under a nitrogen atmosphere in DMF (a swelling solvent) at 70°C for 24 hours with an NCO index of 2 afforded only a 0.12 *degree of substitution* [172]. However, more importantly, Squeira et al, [173] found that the *degree of substitution* of CNC using n-octadecyl isocyanate was only about 2.5% of the total hydroxyl groups in the CNC after treatment with 10 equivalents of the isocyanate in boiling toluene (a non-swelling solvent) for 30 minutes!

Finally, concerning the use of pMDI and technical lignin in RPUF there has never been a study to examine the degree of substitution, to our knowledge. However, it is likely to be very low because the pMDI has very limited time to cross-link with the accessible (surface) hydroxyl groups of the technical lignin within the RPUF gel time window, which is measured in seconds. Further, the degree of substitution will be dependent on the technical lignin loading as it affects the level of self-agglomerate of the nano-lignin and care will need to be exercised in the determination given that it can take up to a week for an equilibrium to be established between the nano-lignin and the agglomerates [135].

3.3.3. Determination of Important Parameters

In terms of determining the key properties needed for using technical lignin in RPUF the hydroxyl value (OHv), acid value (Av) and the water content are critical to calculating the correct loading of pMDI [174] to ensure that all samples are produced at a constant pMDI index. There are several points to be made about each of these critical parameters.

First, the OHv should include all active hydrogen-containing species in the technical lignin (aliphatic hydroxyl, aromatic hydroxyl, primary amines, and thiol) and not just the hydroxyl groups as we have implied in this document so far for simplicity. Given that Sigma Aldrich 370959 KL, for example, contains around 0.4 mol/g of thiol (**Table 8**) this would be equivalent to an increased OHv of around 22 [124]. However, many of the articles to be discussed latter who have used NMR techniques to determine the total OHv of technical lignin may have incorrectly calculated the required pMDI loading needed by excluding thiols in their calculations.

Second, the Av should also be included if it exceeds 1 mg KOH/g. Given that the Av of KL, for example, ranges from 6 mg KOH/g to 95 mg KOH/g many of the papers to be discussed later have incorrectly calculated the required pMDI loading needed by excluding the Av in their calculations.

Third, all technical lignins contain moisture, and several of the papers to be discussed latter do not dry the technical lignin before use or dry them but do not test the actual water content before use. An exception is the work of Paberza et al [175], who specifically dried and tested for water content. They found their OSL as received contained 10% w/w water (consistent with the specification for Sigma Aldrich 370959 KL), which after drying at 40°C for 24h was reduced to 2% w/w. Measuring the water content after drying allowed them to reduce the water added as a blowing agent to keep the pMDI index constant.

Determination of the OHv

Cateto et al [115] have studied different methods used to determine the hydroxyl value on four technical lignin's (Indulin AT, Alcell®, Curan 27-11P, and Sarkanda) and reported that the values determined by titration, ^{13}C-NMR, and ^{31}P-NMR techniques (**Table 10**) [115] were in close agreement. However, as an example, there is a 7% difference in OHv determined by ^{31}P-NMR spectroscopy and titration for Indulin AT. Given that Cateto et al [115] did not explicitly state that the thiol region was measured (integrated) in the ^{31}P-NMR analysis an alternative interpretation of **Table 10** follows.

First, the ^{31}P-NMR spectroscopy and titration results for the Alcell® OHv are identical, as Alcell® contains no thiol groups. Second, the OHv determined using ^{31}P-NMR spectroscopy for Indulin AT is about 26 mg KOH/g lower than the titration result because Indulin AT contains around 0.4 mmol/g of thiol which has not been quantified. Third, the OHv predicted using ^{31}P-NMR spectroscopy for Curan-27-11P is about 148 mg KOH/g lower than the titration result because Curan-27-11P contains 0.7 mmol/g of thiol (almost double that of Indulin AT) and high levels of ash (at 17% w/w it is three times the level of Indulin AT). Finally, the titration OHv of Sarkanda is 8 mg KOH/g lower than the OHv predicted using ^{31}P-NMR spectroscopy possibly because the Sarkanda contains twice the sugar (aliphatic hydroxyls) and nitrogen (amine) content of Indulin AT.

Table 10 OHv (mmol/g) of selected commercial technical lignin's [115]

Lignin	**Technique** (mmol/g)						**OHv** (mg KOH/g)
	^{13}C-NMR[a]	**^{13}C-NMR[b]**	**^{31}P-NMR**	**Titration**	**Average**	**CV** (%)[c]	

Alcell®	5.24	5.68	5.07	5.04	5.26	5.6	295
Indulin AT	6.89	6.89	6.85	7.32	6.99	3.2	392
Sarkanda	5.39	5.29	5.25	5.10	5.26	2.3	295
Curan-27-11P	5.99	5.99	6.65	(9.3)	6.21	6.2	348

Footnotes: a) acetylation according to ISO 14900:2001 (E), b) acetylation according to the method of Manson, c) coefficient of variation.

In conclusion, the titration, ^{1}H-NMR, and ^{13}C-NMR methods of determining the OHv of technical lignins involve acetylation of active hydrogen groups so titration automatically includes the thiol groups as well as the hydroxyl groups. Similarly given that the acetoxy groups in thioester are typically found around $\delta = 2.30$ ppm which straddles the resonance range $\delta = 1.58 - 2.70$ ppm for acetoxy groups for aliphatic and phenolic integration of this range using the ^{1}H-NMR spectroscopy will also give a good estimate of total OHv including thiols.

While the use of ^{13}C-NMR spectroscopy can in principle do the same, unfortunately, many studies discussed below only integrated the primary hydroxyl ($\delta = 170.4 - 169.4$ ppm), secondary hydroxyl ($\delta = 169.4 - 168.5$ ppm) and the phenolic region ($\delta = 168.5 - 165.8$ ppm) and neglected the thioester region ($\sim\delta = 196$ ppm). Similarly, for ^{31}P-NMR spectroscopy, all of the papers discussed below have only integrated the aliphatic hydroxyl ($\delta = 149 - 146$ ppm), phenolic hydroxyl ($\delta = 143 - 137$ ppm) and carboxylic acid ($\delta = 134 - 136$ ppm) regions and again ignored the thiol region at 210 - 220 ppm. Thus, in many articles discussed latter in this review use of both the ^{13}C and

^{31}P-NMR methodologies have underestimated the total OHv by neglecting the thiol content.

Ideally, the total OHv should be utilised and adjusted with an experimentally determined degree of substitution factor, but as discussed above, no one has determined the latter factor for pMDI and technical lignin to date. Thus the use of the total OHv of the technical lignin alone to calculate the pMDI loading, as in many of the papers to be discussed latter, will mean that the pMDI to accessible OHv index will increase as the lignin loading is increased. Furthermore, the excess pMDI, over the OHv (accessible) value, will preferentially react with the RPUF matrix and increase the cross-link density through the formation of biuret or allophonate groups independently of the presence of the lignin. Likewise, the unreacted isocyanate groups can react with water/moisture to release CO_2 thus reducing foam density.

These phenomena are often misunderstood as an effect of the incorporated lignin in RPUF. Therefore, a reasonable approach for evaluation of hydroxyl groups is using the ASTM D-4274-99 / ISO 14900:2001 acetylation method on the complete polyol blend (part B) including the particulate lignin, as it will be closer to the "accessible OHv" given that the pMDI must react with the hydroxyl groups within the gel-time of the RPUF, which is measured in seconds.

As this inaccessibility of active hydrogen moieties (both OH groups and SH groups) in lignin is caused by the steric hindrance by the two methoxyl groups in the syringyl unit and/or aggregation, all methods utilising the acetylation process can cause variation in OHv [116]. **Table 11** [2, 115, 117, 124, 132, 137, 143, 145, 176-178] summarises the OHv, Av, and calculated functionality (f) of several commercially available technical lignin's reported in the recent literature and indeed there is significant variation in the OHv whereas Av is relatively consistent.

Table 11 OHv, Av and functionality of selected commercial technical lignin

Lignin	**OHv (mg KOH/g)**	**Av (mg KOH/g)**	**Functionality (f)**	**Ref**
Hardwood kraft lignin (HKL)				
Suzano	307	NR	NR	[176]
Softwood kraft lignin (SKL)				
Indulin AT	291	24	43	[132]
Indulin AT	392	22	7.5	[115, 177]
Curan-27-11P	348	26		[115]
Sigma Aldrich 370959	339	27	26	[117]
Sigma Aldrich 370959	356	NR	60	[124]
Sigma Aldrich 370959	165	28	~34	[143]
LignoBoost^{TM}	304	23	>28	[143]
FPInnovations (LignoForce^{TM})	275	NR	NR	[2, 178]

Soda lignin (SL)				
Sarkanda	295	35		[115]
Organosolv lignin (OSL)				
Alcell®	295	13	4	[115, 177]
Biolignin™	398	73	NR (7.6)	[145]

Footnote: The f = 7.6 for BioLignin™ was reported by Jablonski et al [137].

Finally, the nominal functionality (f) of Sigma Aldrich 370959 was reported by Hayati et al [124] at 60 which is significantly different from that reported by Cateto et al [115] of 7.5 for a similar SKL (Indulin AT). However, such figures should not be considered precise as it was calculated, according to the formula I given in section S2 of Supporting Information, from the M_w estimation from GPC and a measured hydroxyl value based on acetylation of lignin which can be underestimated due to incomplete acetylation of the sterically hindered hydroxyl groups on lignin [116].

4. The Incorporation of Technical Lignin into RPUF

There are no mainstream commercial RPUF insulation products incorporating technical lignin on the market to date. In principle, technical lignin can be incorporated into RPUF by two routes; inclusion in the pMDI (A-side), or inclusion in the polyol blend component (B-side). The former is usually not practical however for two reasons. First, simple mixing of pMDI with SL at a 10% w/w loading, for example, increases the viscosity from 150 cps at 25°C to over 490,000 cps [179] which is too viscous for effective mixing with the polyol blend (B-side) [180, 181].

Second, a mixture of SL, for example, and pMDI will not react at room temperature to afford a pre-polymer as heating at high temperatures in a suitable solvent is required. For example, Zhang et al [182] reported a 'prepolymer approach' that '*compatibilises*' SKL by pre-reacting with pMDI to form a pre-polymer which was subsequently mixed with an unknown polyester polyol and further reacted with additional pMDI to form a RPUF. Such an approach involves a considerable number of additional steps for a minor improvement (3%) in thermal conductivity and an insignificant increase in compressive strength (after normalisation for density). As a result, this article will focus on the most common approach for incorporation of technical lignin in RPUF; inclusion in the polyol blend component.

In terms of inclusion in the polyol blend (B-side) there are two approaches (**Figure 7**);

- the direct incorporation of technical lignin without any chemical modification [73, 77, 124, 126, 144, 175, 176, 183-189], or
- the incorporation of modified technical lignin with improved solubility and reactivity by making hydroxyl groups more readily available through, hydroxyl-terminated functionalisation [127, 132, 137, 145, 188, 190-202] and the introduction of new functional groups [197, 203] and depolymerisation [73, 76, 107, 127, 178, 204-208].

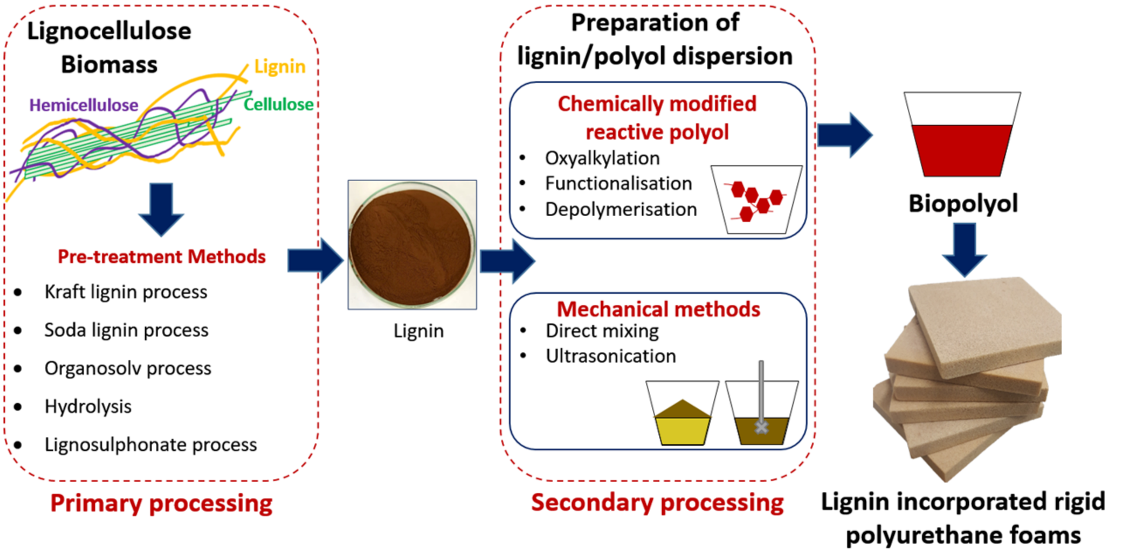
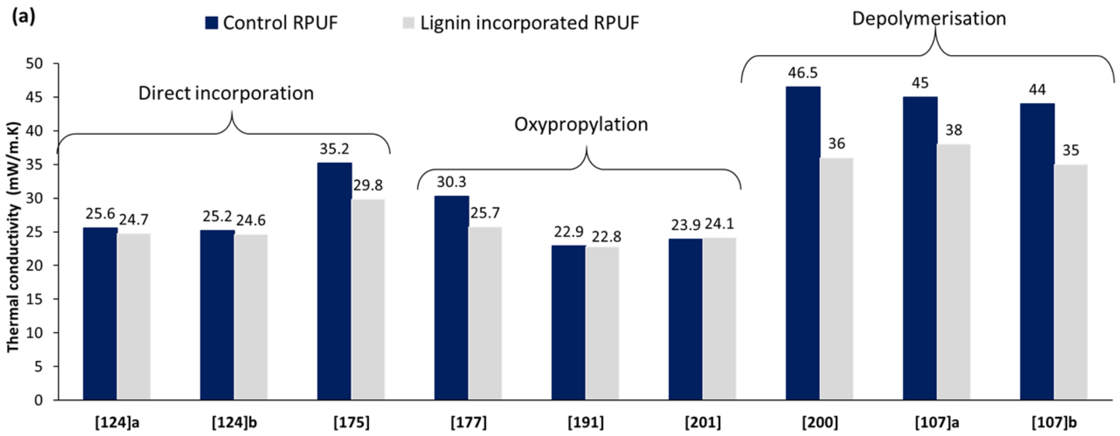


Figure 7 Contemporary approaches of lignin incorporation in RPUF through the polyol-route

The physical properties reported to date for the lignin incorporated in RPUF through both the polyol-routes are summarised in **Table A3** (Supporting Information). The influence of the lignin on thermal conductivity and compressive strength (as a function of density) on RPUF from the reported examples is summarised in **Figure 8**.



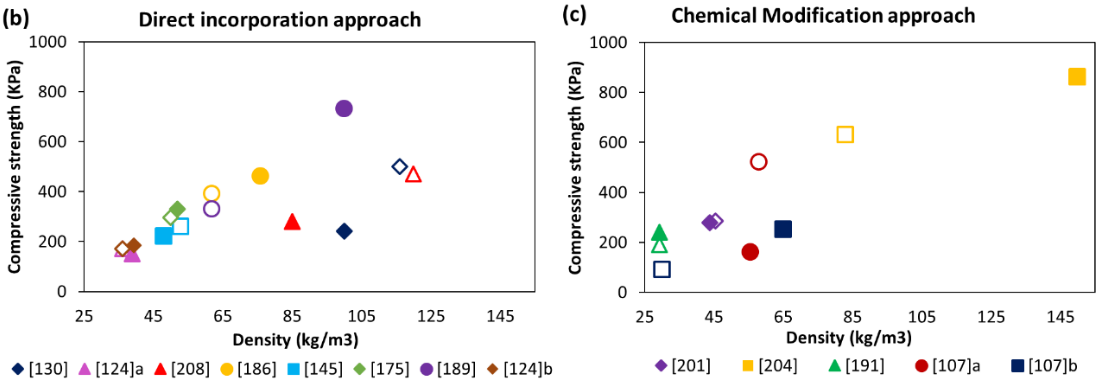


Figure 8 Influence of technical lignin on the physical properties of RPUF (a) thermal conductivity and (b, c) compressive strength. The control (without lignin) and RPUF incorporating technical lignin are represented in (b) and (c) as empty and filled symbols respectively.

4.1. The Direct Incorporation Approach

The direct incorporation approach is an energy-efficient, scalable, and cost-effective strategy for incorporating technical lignin into RPUF [27, 209, 210]. It involves the mechanical blending of lignin into polyols used for RPUF preparation [124]. Owing to its multi-functionality and aromaticity, the expectation is that the lignin will react with the isocyanate to improve the crosslink density in the RPUF matrix [211] and enhance physical properties [144, 175].

In principle this is plausible, in practice many factors such as particle size, degree of dispersion, and the viscosity of the polyol blend [124] can affect the outcome. For example, poor dispersion of lignin particles in the polyol blend (part B) will limit the reaction of pMDI to the accessible hydroxyl groups of the lignin, leaving free pMDI which may further react with urethane groups to form allophonate or urea bonds [73, 144]. The effect of these side reactions, which also enhance the cross-link density, on the physical properties of RPUF [18], can be confused with true cross-linking of the lignin. Hence, this section discusses the effect of processing conditions such as loading levels and miscibility of technical lignin in polyol on the properties of the resultant RPUF.

4.1.1. Influence of Loading Levels

Direct incorporation of technical lignin in RPUF has been studied at loadings from 2.5% w/w [124] up to 64% w/w in polyol [144] and it has been found that the degree of dispersion/miscibility of lignin is directly influenced by the loading level and the compatibility with the polyol [122, 150].

In the extreme, an excessive loading of lignin can make the polyol blend just too viscous to effectively mix with pMDI to afford a homogenous RPUF [175]. While, at intermediate loadings [77, 124, 144, 186, 187, 189] agglomeration of the technical lignin particles can adversely affected the cellular structure and thus the thermal conductivity and mechanical properties of the RPUF. So it is important to identify the optimum loading at which agglomeration of the lignin is minimised and the physical properties are maximised. Prior to illustrating this point further, it should be noted that some properties of RPUF, such as compressive strength, are directly correlated to density.

For example, Zhu et al [73] reported that the density of RPUF doubled from a loading of 2.5% to 15% w/w, so without normalisation for density, it is difficult to judge the true cause for their reported dramatic increase in compressive strength. Parbeza et al [175] avoided this complication in their study by adjusting the level of water (blowing agent) in their formulation to bring all RPUF samples into a density range of 49.5 ± 1.8 kg/m^3. After eliminating the effect of density, they found that the compressive strength of RPUF increased to a maximum (0.35 MPa) at a 1.2% w/w loading before deteriorating.

The importance of selecting the optimum loading of technical lignin was further illustrated in the paper by Hayati et al [124] who studied the incorporation of KL into a low density (~40 kg/m^3) polyether polyol/glycerol-based RPUF. It was found that KL was poorly soluble (~0.9% w/w) in the mixture of polyether polyol and glycerol (91:4% w/w) and the resultant dispersions contained dark-coloured lignin micro-particles measured at 22 ± 18 µm in size. As a result, while the thermal conductivity of the resultant RPUF was reduced by 4% (improved) the compressive strength was also reduced by 17% (declined) [124].

The reality is that KL polyol dispersions are complex heterogeneous systems containing a mixture of particles of nano to micro-scales that can have distinctly different effects on the resultant RPUF and the optimum level of loading is typically no more than 1% w/w [27, 209, 210]. The presence of low volume fractions of well-dispersed nanoparticles can serve as a nucleating agent [210], which can decrease the average cell size of the resultant RPUF leading to improved thermal conductivity and enhanced mechanical properties such as compressive strength [32]. However, while micro-particles can also act as nucleating agents, they are much less efficient and often have a detrimental effect on the mechanical properties because if they get too large, they can disrupt the cellular structure of the resultant RPUF [27, 189, 212].

4.1.2. Influence of Polyol Compatibility

The optimum loading level of technical lignin can be increased by either the method of incorporation or the judicious choice of polyol for the RPUF. For example, in the paper by Hayati et al [124], previously discussed above, they also described the incorporation of KL into the same polyol mixture at the 'softening point' of lignin (120°C) to afford a much more homogenous blend with significantly smaller micro-particles (8.8 µm) at a slightly higher 1.1% w/w loading (**Figure 9**). The improved dispersion/miscibility resulted in an improved (reduced) thermal conductivity (5%) and an improved (increased) compressive strength (4% parallel to foam rise). However, beyond a loading of about 2.5% w/w lignin, the lignin-polyol dispersion becomes too viscous for effective mixing with pMDI so ultimately the approach is limited despite the fact that there is improved dispersion/miscibility at higher loadings up to 10% w/w (**Figure 9**).

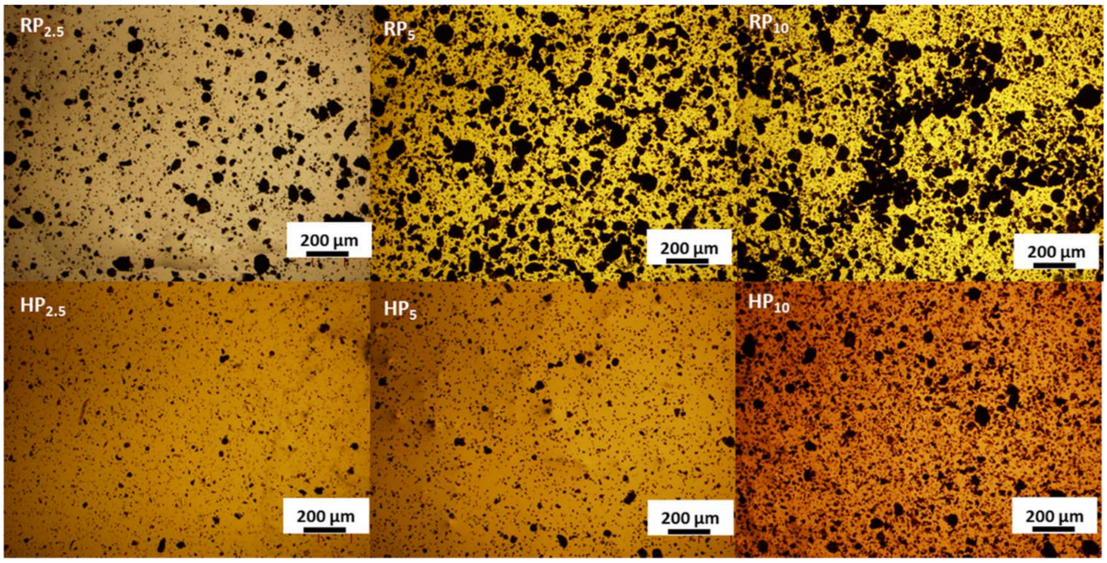


Figure 9 Comparison of lignin dispersed in polyether polyol at room temperature (above) and 120°C indicating the different degrees of dispersion of lignin. (Reproduced from Hayati et al [124])

An alternative approach for enhancing dispersion and miscibility of lignin in polyols is through the judicious selection of compatible polyols. Asano et al [183] and Hatakayama [185] replaced the standard propylene oxide-based polyols used in RPUF with low molecular weight polyethylene glycols which, because of their higher number of hydrogen donor sites and low viscosity, provide much higher lignin dispersion (up to 70% w/w in the case of ethylene glycol) than other alcoholic solvents [147, 213]. While not explicitly stated, this study was an attempt to enhance the solubility of NaLS by adjusting the Hildebrand solubility parameter for the polyol blend (part B) to be closer to that reported for NaLS (~11 $(cal/m^3)^{1/2}$) while simultaneously favouring a 'polyol' with hydrogen bonding capacity ($\Delta\mu \geq 14$) [104].

However, the use of DEG, TEG, or PEG, with a functionality of 2, in an RPUF formulation, will negatively affect the cross-link density and thus compressive strength. They will also accelerate the rate of gelation of the RPUF due to the primary hydroxyl groups (**Table 9**) [47], which would reduce the cell size and increase the density and thus the compressive strength of the resultant RPUF [29]. Further, RPUF based on polyethylene glycols would need to be evaluated for moisture absorption properties as polyethylene glycols are hydrophilic in contrast to propylene oxide-based polyether polyols which are hydrophobic.

Finally, the improved compressive strength properties reported with these polyethylene glycol based RPUF would likely be the combined effect of increased RPUF density and increased crosslink density due to the excess pMDI reacting preferentially with the RPUF matrix rather than the lignin [183-185] as Hatakeyama [183, 184] reported only a slow increase of T_g for the RPUF based on PEG200 with increasing NaLS loading implying minimal interaction between the pMDI and the NaLS.

In conclusion, the direct addition of technical lignin into a standard polyether polyol blend (Part B) is limited due to the low polarity of polyether polyols and the dispersions are a complex mixture of nano-scale lignin and macro-scale lignin agglomerates [124]. However, the compatibility of the technical lignin with the polyol can be enhanced by judicious selection of polyols and/or processing conditions.

The presence of well-dispersed nanoparticles at optimum loading levels act as nucleating agents in RPUF [27, 209, 210], providing smaller cell sizes and thus reduced thermal conductivity and compressive strength. Whereas, loadings above this level usually cause lignin agglomeration, which disrupts the cellular structure of RPUF increasing the cell size and decreasing the close cell content which has a negative effect on the thermal conductivity and mechanical properties [27, 210].

Unfortunately, many earlier papers in the field have reported insignificant or inferior thermal and mechanical properties of RPUF incorporating technical lignin [77, 124, 144, 175, 187, 207] predominately due to processing outside of the optimum loading range resulting in poor dispersion.

4.2. The Chemical Modification Approach

Chemical modification of technical lignin for use as polyols has attracted considerable research interest over the last two decades (**Figure 1**) due to their low molecular weight, high reactivity, and homogeneity [93]. There have been three main approaches for the chemical modification of technical lignin (**Figure 10**); oxyalkylation (or alkoxylation); functionalisation (i.e. introduction of new functionality); and depolymerisation of lignin (or biomass) [2, 93, 214-216].

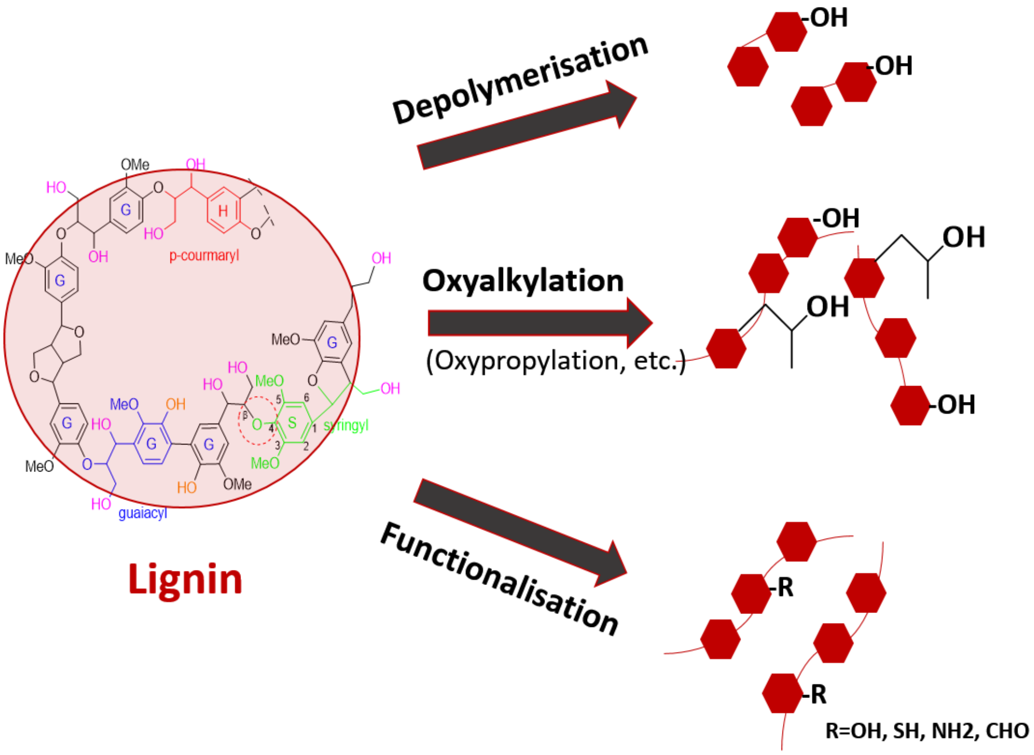


Figure 10 Contemporary approaches for chemical modification of technical lignin for use as polyols [2, 93, 214].

4.2.1. Oxyalkylation of Lignin

Propoxylation or oxypropylation of lignin with propylene oxide has been the most extensively studied [93, 194, 195] modification on lignin. It converts aromatic hydroxyl, thiol groups and alkyl hydroxyl groups into secondary aliphatic hydroxyl groups, breaks up the lignin morphology freeing the phenolic OH groups from electronic or steric hindrance [2]. It also transforms solid lignin into a liquid which is soluble in polyether polyol [93]. Unfortunately, it also generates low functionality by-products, referred to as homo-polymer in the work by Cateto et al [177] as example, at levels significantly higher than would be generated in the production of commercial rigid polyether polyols [34].

Cateto et al [177] has examined the influence of composition and reactivity of oxypropylated lignin polyols on the properties of RPUF. **Table 12** compares the two polyols produced by varying the lignin/propylene oxide/KOH ratio (L/PO/C) with the commercial polyether polyol Lupranol® 3323. The Mw of the oxypropylated polyols were much higher than the commercial RPUF polyol and were comparable to that of polyols used ~~to~~ for the production of flexible polyurethane foams (typically ranging between 1000 - 6000 g/mol) [217]. Furthermore, the presence of the large amount of homopolymer content suggests that the presence of monols, diols and triols potentially increasing the reactivity [218] and flexibility in polymer chains [201].

The oxypropylated polyols were tested in a RPUF formulation based on a mixture of Lupranol® 3323 and glycerol (90/10) at a constant pMDI index of 110. At 100% w/w replacement of the Lupranol® 3323 with polyol 20/80/5 there was a 12% improvement in thermal conductivity but a decrease in the compressive modulus (after normalising their data for density). Whereas, at 50% w/w replacement there was a 9% decrease in thermal conductivity and an even larger decrease in compressive modulus.

In contrast, replacing the Lupranol® 3323 with polyol 30/70/2 (reportedly higher functionality) at 100% and 50% w/w, consistently reduced the thermal conductivity and increased the compressive modulus perhaps reflecting the increased cross-link density due to a higher functionality. Typically, the improved reactivity of polyol could increase the viscosity of polyols resulting in reduced cell size and improved thermal insulation performance. However, the reported cell size reduction was insignificant, thus, the decrease in thermal conductivity could be an effect of the solid polymer matrix.

Table 12 Oxypropylated polyols produced from SKL (Indulin AT) by Cateto et al [177] compared to a typical RPUF polyol (Lupranol ® 3323).

Polyol	**20/80/5**	**30/70/2**	**Lupranol® 3323**
Viscosity (Pa s)	4.34	66.5	3.5
OHv (mg KOH/g)	326	348	340
Homo-polymer Content (% w/w)	36.7	24.2	NR
Mn (g/mol)	1224	1453	NR
Mw (g/mol)	3829	5331	780
Mw/Mn	3.1	3.7	NR
Functionality*	~22	~33	NR

Footnote: * calculated using the formula (I) in section S2 of supporting information neglecting Av; NR = not reported

Cateto et al [192] and Nadji et al [195] also investigated the effect of oxypropylation of lignin in RPUF by varying the type of technical lignin. Cateto et al [192] found that Sarkanda based lignin polyols were too heterogeneous for RPUF whereas Curan based RPUF were too brittle. This could be possibly due to the high ash content observed in **Table 5**.

Nadji et al [195] oxypropylated SKL, hardwood OSL, SL, and oxidised OSL and the polyols, which had hydroxyl values in the range of 150 - 250 mg KOH/g after a separate process to remove the homopolymer polyol PPG, were tested in a RPUF formulation. The oxypropylated SL based RPUF (30 kg/m^3) had a thermal conductivity (0.024 W/m.K) close to a cutting edge value (**Table 1)** while other RPUF samples were not dimensionally stable due to low density.

Oxypropylated lignin has been used to substitute from 10% to 100% w/w of petrochemical polyols in RPUF [132, 145, 201] with mixed results. Li and Ragauskas [132] oxypropylated SKL and tested it in a RPUF, based on a mixture of sucrose and glycerol-based polyether (85:15% w/w) polyols by substituting the sucrose-based polyether polyol at 10, 30, 60, and 100 % w/w, as well as one sample, substituting 100% of both the sucrose and glycerol polyether polyols. All RPUF samples including the control formulation were around 30 kg/m^3 and the compressive strength of all samples was similar to the control formulation except for the RPUF based on 100% bio-polyol that exhibited a 44% increase in compressive strength.

However, Kuranska et al [201] followed the oxypropylation procedure recommended by Cateto et al [177] to prepare an oxypropylated Alcell lignin polyol (at 30/70/3% w/w lignin/ propylene oxide/ catalyst ratio) which was incorporated into a control RPUF based on a polyether polyol formulation. The RPUF samples incorporating oxypropylated lignin polyol were prepared by replacing the polyether polyol at 10, 20, and 30% w/w to afford a low density (~41- 45 kg/m^3) RPUF. The oxypropylated lignin increased the overall reactivity but did not show any improvement on the thermal and mechanical properties of the resultant RPUF.

Arshanitsa et al [145] oxypropylated OSL (BIOLIGNIN™) to produce a liquid oxypropylated OSL polyol (lignopolyol) which was then tested in a RPUF control formulation based on a mixture of Lupranol® 3330 and Lupranol® 3422 (70/30) by substituting the *Lupranol® 3300* (a glycerol-based trifunctional polyether polyol) at a constant pMDI index of 120. As the lignopolyol content increased the density decreased (from 53 kg/m^3 to 40 kg/m^3 at 100% substitution) due to the reduced gel times. After normalisation for density, it was found that lignopolyol enhanced the compressive strength by about 20% at a total lignin content of 8% (corresponds to 10% substitution of the *Lupranol® 3300*).

While there is general evidence that incorporation of propoxylated lignin into RPUF can, under certain circumstances, improve the mechanical properties of the RPUF [132, 145] unfortunately it increases the cost of production and reduces the "lignin" content in the final polyol and RPUF so from a sustainability point of view has no advantage over standard glycerol or sucrose initiated polyether polyol i.e. the use of propylene oxide to modify the lignin negates the whole purpose!

Other reported chemical modification methods of lignin include glycerolation [188], epichlorohydrination [190] for incorporation in RPUF, however the RPUF samples were found to have very high density. One exception being the work of Rogers et al [191] who have reported on the use of KL as a reactive additive in the manufacture of aromatic polyester polyols through glycolysis. They were subsequently tested in a low-density (~30 kg/m^3) PIR formulation (NCO index 260) using pentane and water as blowing agents. At the optimum loading of around 2.5% w/w KL the RPUF exhibited a faster gel time, ~~and~~ improved compressive strength (~14%), a statistically insignificant difference in thermal conductivity (~0.0239 W/(mK) but a reduced (~16%) peak heat release rate in cone calorimeter tests compared to the control RPUF.

Other oxyalkylation methods that have also been explored for polyol synthesis, but to be investigated for RPUF yet. Oxyalkylation of lignin using alkene-carbonates with alkaline catalysts (K_2CO_3, $LiCO_3$, or KOH) is an efficient alternative to propylene oxide for the preparation of lignin-isocyanate pre-polymers [197] or lignin-polymers [219].

Kuhnel et al [219] and Duval et al [220] have explored the reactivity of carbonate-oxyalkylation of lignin for application as polyols.

4.2.2. Depolymerisation of Lignin or Biomass

Depolymerisation of lignin reduces the molecular weight (and the polydispersity) and enhances the reactivity, thus allowing increased substitution levels in RPUF. Demethylation of the ß-O-4 ether bond increases the phenolic hydroxyl content [2] and the accessibility of reactive sites due to the reduced steric hindrance [94]. However, the incorporation of depolymerised lignin polyol in RPUF is challenged by many processing limitations [107, 178]. First, all the modified lignin polyols were solids. Second, acetone had to be used to pre-dissolve the bio-polyol. Third, the morphological form of bio-polyol in the polyol blend (fully dissolved or dispersion) is not identified yet. If it was present as a particle dispersion, then, the OHv determined by ^{1}H-NMR spectroscopy will result in a pMDI loading that will exceed the level of accessible hydroxyl groups on the modified lignin polyol. Following this, the excess pMDI will react with the urethane groups increasing the RPUF matrix cross-link density and improving the mechanical properties of the RPUF. As such, it is difficult to judge if the chemical modification of the depolymerised lignin and subsequent inclusion in RPUF made a positive effect *per se* on the compressive strength.

Depolymerisation of lignin can be achieved through multiple routes such as oxidation, acid catalysis, metallic catalysis, base catalysis, ionic liquid assisted depolymerisation, and sub- or supercritical fluids-assisted depolymerisation. The utilization of these methods for the preparation of bio-polyols in RPUF has been reviewed in-depth by Mahmood et al [2]. The few studies that have incorporated depolymerized bio-polyol into RPUF are discussed below.

Mahmood et al [107] have studied the depolymerization of hydrolysis lignin (HL) in a 50/50 (v/v) water-ethanol mixture under a N_2 atmosphere at 250°C. The solid bio-polyol was produced at a yield of 70% accompanied by 8% w/w of solid char. When tested in a RPUF formulation based on a sucrose polyether polyol which was replaced with 30% w/w of the bio-polyol it was found that the density of the RPUF increased (30 to 35 kg/m^3), the thermal conductivity decreased (0.044 to 0.035 W/m.K) and the compressive strength increased (85 to 185 kPa). However, in a separate study when the substitution of the sucrose polyether polyol [178] was increased to 50% w/w it was found that the density of the RPUF increased (54 to 104 kg/m^3), the thermal conductivity was unchanged (~0.033 W/mK) and the specific compressive strength decreased. The same solid bio-polyol was further oxypropylated and tested in the same RPUF formulation resulting in a negligible density increase, a significant improvement in compressive strength (327 kPa to 515 kPa), and a 12% improvement in thermal conductivity (0.033 to 0.020 W/(m.K)).

Mahmood et al [205] have undertaken liquefaction of HL in a water-ethanol mixture (5/50 v/v) at 250°C under a N_2 atmosphere to afford a solid bio-polyol at a 70% yield (plus solid char at 8% w/w) which was then oxypropylated as a suspension in glycerol to form a viscous liquid bio-polyol. They subsequently tested the liquid bio-polyol in a model RPUF based on a sucrose DEG polyether polyol and glycerol mixture (90/10% w/w) using acetone and water as blowing agents with a pMDI index of 1.0 by replacing 50% of the polyether polyol. The RPUF with the liquid bio-polyol was found to have a similar density (45 vs 43 kg/m^3) and over 100% improvement in compressive strength (182 to 385 kPa). It was noted that the RPUF also has residual pMDI in the foam which suggests that the viscosity of the polyol blend (part B) may have been too high for efficient mixing with the pMDI.

Gosz et al [204] have studied liquefaction of SKL in a mixture of crude glycerol (from biodiesel production) and 1,4-butanediol (1:1) without catalyst at 150°C. The bio-polyol was tested in a polyether polyol based RPUF at a pMDI index of 200 using both water and n-pentane as blowing agent by replacement of the polyether polyol at 25% and 50% w/w and it was reported that it increased the apparent density (from 83 to 99 and 150 kg/m^3 respectively), decreased the cell size (from 236 to 203 to 168 μm respectively) and decreased the calculated specific compressive strength by around 24% (from 7.5 to 5.7 kPa/g). It was also reported that the extractable content from the bio-polyol reduced as the bio-lignin content increased which implies that the KL bio-polyol was significantly cross-linked into the polymer matrix.

The liquefaction of biomass is not strictly liquefaction of lignin as it is a mixture of lignin, hemicellulose, and cellulose. Thus, the resultant ‘polyol’ has an even greater chemical complexity than lignin alone as it contains an abundance of C5 sugars (from hemicellulose) and C6 sugars (from cellulose). Finally, the liquefaction process often produces a residual solid (char) and to date, the performance of these ‘polyols’ has not been satisfactory in RPUF [76, 206].

So, in conclusion, to date, the incorporation of depolymerised lignin into RPUF has not yet proved its value in terms of improved thermal conductivity or compressive strength properties. Further, the extra cost of chemicals and the cost of the process itself makes it an uneconomic alternative to traditional polyether polyols currently without a significant performance improvement.

4.2.3. Functionalisation of Lignin

Typically, new functional groups are introduced to particular positions of the lignin molecule that promote reactivity (ortho-position) [93]. Potential methods that could be applicable for functionalisation of lignin for RPUF include thiolation, thiol-ene functionalisation, aldehyde stabilisation, formylation, phenolation, demethylation, and etherification which are detailed elsewhere [98, 220-223]. Yang et al [203] have investigated hydroxymethylation, epoxidation, and phenolation of KL and tested them in RPUF. However, such chemical modification approaches of technical lignin are not cost-effective for large scale production [190, 203] of polyols and RPUF to date.

5. Outlook and Future Perspectives

There is an ongoing interest in the improvement of the key properties (**Table 1**) of RPUF for thermal insulation without compromising the sustainability in terms of raw materials and cost-effectiveness. The incorporation of technical lignin into RPUF will continue to be of industrial and academic interest because of its abundance, low cost, and high aromatic content. The analysis of the reported studies indicates that the exploitation of the full potential of technical lignin in RPUF is still hindered by the following challenges.

- First, the current production of technical lignin has issues with purity and inconsistency within batches.
- Second, technical lignin has not been optimised for use as a polyol or polyol precursor. For example, ideally, the Mw of RPUF polyols fall in the range of 400-1200 [44] but current commercial KL products are reported from 2,400 to 10,000 (**Table 7**).

- Third, there are issues in the characterisation of the relevant properties of technical lignin, such as OHv and Mw, needed in the formulation of RPUF.
- Fourth, there should be increased research on OSL given the quantity that will be generated by the bio-fuels industry [110] in the near future.
- Lastly, the degree of dispersion of technical lignin in polyols and its tendency to self-aggregate hinders reactive groups participating in the polyurethane reaction.

Hence, future research could be undertaken on kraft pulping to look at if the extended treatment might produce a KL with better molecular weight distribution, through controlled acidification (neutralisation) [224], fractionation [103, 225-236], aldehyde-stabilisation [221, 237], or other methods. Further, more valid and reliable quality control standards must be employed for large scale production of lignin with consistency.

The use of chemically modified technical lignin addresses the issue of lignin agglomeration and increases the accessibility of the functional groups. However, this approach is only favourable as long as the cost of treatment is not excessive. Future research will continue to explore desirable and realistic chemical treatments that are sustainable not only through raw materials and cost of production but also, through performance. In contrast, direct incorporation of unmodified technical lignin in RPUF is potentially a more economical and environmentally sustainable process but has issues due to poor dispersion in the polyol system. So, further work is required to investigate the dispersion, long-term colloidal stability, and rheological behaviour of lignin in polyols and their interaction in polyurethane networks.

The potential of lignin in RPUF will only be demonstrated by the achievement of consistently improved physical properties, (dimensional stability, compressive strength, and thermal insulation) and their retention against aging. In such an effort, we recommend the judicious selection of steps/pathways and lab-to-medium scale test methods proposed in **Figure 11**.

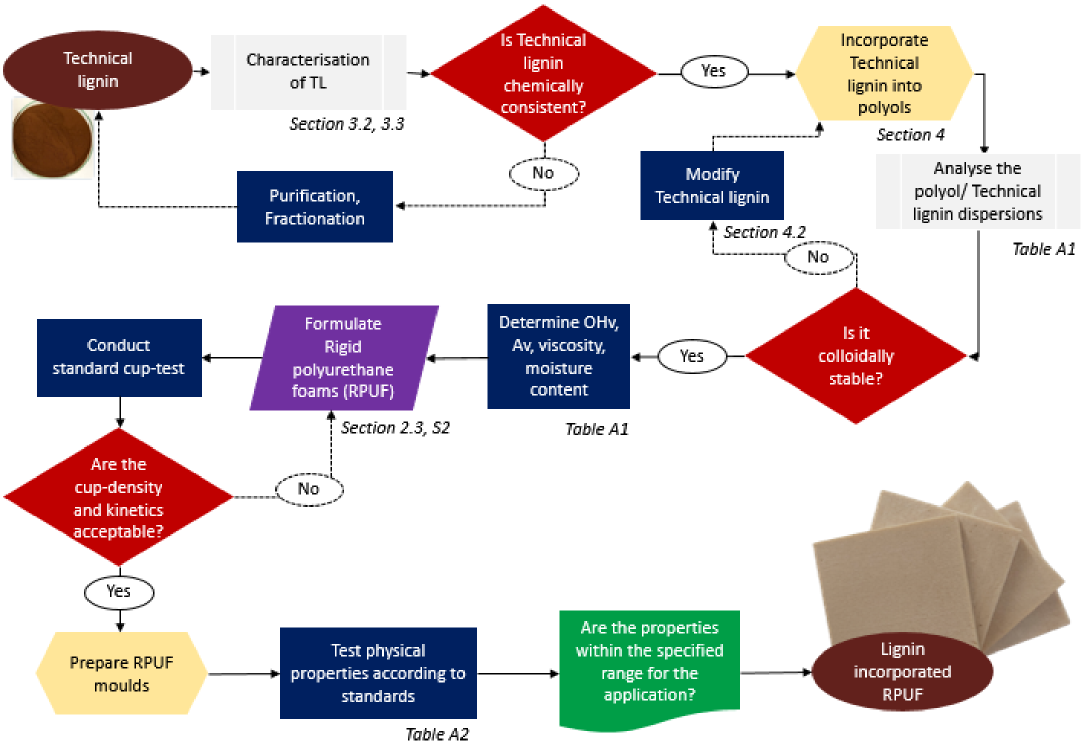


Figure 11 Key recommended steps for developing protocols for lignin incorporated RPUF and relevant sections in the review.

In addition, several studies have been reported on the improvement of the performance of lignin incorporated RPUF by the addition of other fillers such as nanocellulose [238], microcrystalline cellulose (MCC) powder [239], cellulose nano-whiskers [240], ammonium polyphosphate [4], graphene oxide [241], pulp fibres [212], organically modified layered double hydroxides [242]. Such approaches could open future studies to the development of high-performing multifunctional lignin incorporated RPUF.

Finally, Yang et al [243] recently reviewed the progress in lignin-derived flame retardants in polymers for improving sustainability and performance. While this review has focussed on the improvement of the thermal insulation and compressive strength properties of RPUF, possible improvements in fire performance have potential commercial applications. The work of Rogers et al [191] who incorporated KL into an aromatic polyester polyol which was subsequently tested in a low-density PIR formulation and found to have a reduced (~16%) peak heat release rate in cone calorimeter tests suggest that this could also be a fruitful area for future research.

6. Conclusions

In this review, we have systematically evaluated the literature on incorporating technical lignin into RPUF. To date, there are no commercially available products due to a variety of reasons. First, the variability of the molecular structure of technical lignin by source, by the process, and inconsistency in batch production by the supplier. Second, some key properties of technical lignin, such as OHv and Mw, still cannot be consistently quantified to elucidate the nature of the interaction and its influence on the morphological, thermal, and mechanical properties of RPUF. Third, the lignin industry has not invested enough research into designing a product that is better suited to the polyurethane industry.

To date reported studies on direct incorporation of KL lignin in RPUF suggest it is possible to improve thermal insulation performance but at the expense of compressive strength unless the loading levels are kept below about 1% w/w in the polyol. (~ <5% w/w in the polyol). No conclusion is possible on NaLS, OSL, or other technical lignins based on the studies reported to date. Progress in the direct incorporation of technical lignin in RPUF will require improvements in the degree of dispersion and reactivity of lignin in polyols to increase optimal loading levels which can only be engineered through careful selection of RPUF components and processing conditions.

Research on the incorporation of chemically modified technical lignin in RPUF shows mixed results in terms of the thermal insulation or compressive strength at this time. Further, depolymerisation of lignin has issues with “char” formation, removal of by-products, and the need to use oxypropylation as a further step to produce a liquid bio-polyol. Oxypropylation can improve the compatibility of technical lignin with RPUF raw materials but the additional production costs and utilisation of petroleum-derived propylene oxide are of questionable sustainability versus a standard polyether polyol produced from sucrose and propylene oxide for example.

To conclude, to date most of the reviewed works have shown compromised or limited improvement in the thermal conductivity and compressive strength properties of RPUF by the incorporation of technical lignin. The absence of data on formulation, density, and thermal conductivity, together with some fundamental issues like neglecting water content or thiol content of raw materials make it difficult to understand the impact of technical lignin on the properties of RPUF to date. This is not unexpected in early work to open a new area of investigation and despite the limitations, they do provide a valuable contribution. While the current results are not yet competitive with commercial petrochemical based RPUF, the interest in incorporating technical lignin into RPUF will continue because of the potential to develop innovative products with improved thermal conductivity, mechanical, and fire performance.

Acknowledgments

Hima Haridevan expresses her gratitude for the financial support of the University of Queensland Research Training scholarships. Pratheep Kumar Annamalai thanks the Queensland Government for the Advance Queensland Research Fellowship and the University of Queensland for the Vice-Chancellor Strategic Fund.

Supporting Information

S1. Rigid Polyurethane Foams (RPUF)

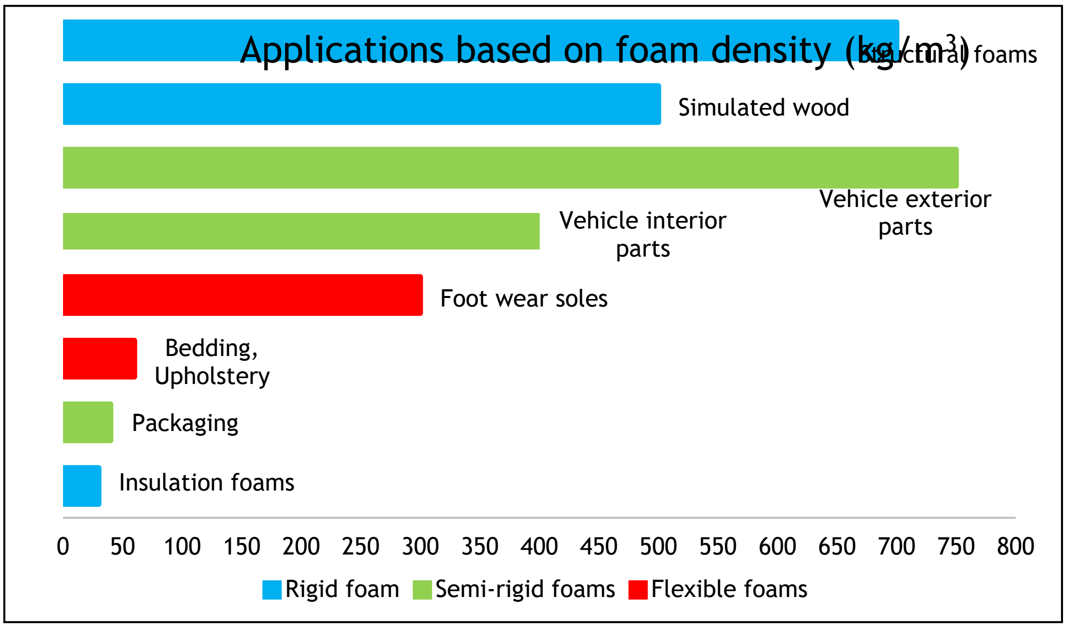


Figure A1 Polyurethane foam applications with respect to its density [1, 4, 13, 18]

S2. Rudiments in Formulation of RPUF

The polyols used in RPUF are chosen to have a hydroxyl value of 250-1000 mg KOH/g, a functionality of 3.0-8.0 and a Mw of 150-1,200 Da [54]. For example, Voranol $^{\mathrm{TM}}$ 446 from **Table 1** is a sucrose-glycerine initiated polyether polyol with a functionality of 4.5 and a hydroxyl value of 446 mg KOH/g which means it has an average Mw of 566 Da [49]. Polyether polyols for RPUF are manufactured by reacting propylene oxide (PO) with an initiator, illustrated with glycerine [41]. Propylene oxide polyols largely terminate (95%) with secondary hydroxyl groups and are less reactive than primary hydroxyl groups [1]. The final product, however, is not a discrete Mw but has a multimodal distribution around the desired Mw plus a mixture of diols (PPG) and monols produced as side reactions during the oxypropoxylation [41].

In a typical RPUF formulation, polyols which are polymers with two or more hydroxyl groups per molecule and they are selected by their characteristic chemical and physical properties such as *molecular weight (Mw), average functionality (f), hydroxyl value (OHv), acid value (Av) and the viscosity*. They are interrelated by the following formula

$$Mw = \frac{\mathrm{f\,x\,56100}}{(\mathrm{OHv} + \mathrm{Av})} \qquad \text{(I)}$$

where *f***,** the average functionality is the total moles of hydroxyl groups divided by the total moles of polyol; *OHv*, the hydroxyl value is the weight of KOH in mg that will neutralise the acetic anhydride capable of reacting with 1g of polyol [54]; and *Av*, the acid value is defined as the weight of KOH in mg, that neutralises the acid on 1 g of polyol [54], it is usually ignored if below a value of around 1 mg KOH/g.

Polyols are highly viscous in nature and exhibit properties depending on their OHv, f, and Mw [244]. Polyols are produced from a wider range of precursor biomolecules and chemical pathways mainly yielding three kinds of polyols; namely; short, aliphatic and aromatic polyols. The precursors or initiators are selected depending upon the chain architecture, functionality, molecular weight and are chemically modified to afford particular requirements of the application [41].

Isocyanates are compounds with -NCO functional groups, particularly reactive towards nucleophiles such as amines, alcohols, carboxylic acids, thiols, water, urea, and urethane [50]. Polymeric isocyanates or Polyisocyanates (denoted by ‘p’ in pMDI) are a mixture of dimers and trimers generating cyclic structures that provides rigidity and stability to the RPUF [245]. Hence, aromatic diisocyanates are frequently used in RPUF production as they enable crosslinking during foaming and gelling reactions, thereby controlling the rigidity and heat resistance of the foams. pMDI in **Table 1** is a mixture of aromatic compounds containing on average around 2.7 isocyanate groups per molecule (functionality of 2.7) which are particularly reactive towards nucleophiles such as amines, alcohols, carboxylic acids, thiols, water, urea, and urethane [50].

The isocyanate index for a formulation is a measure of the excess isocyanate used relative to the theoretical amount required to react with all the hydroxyl groups. For example, in **Table 1**, pMDI has an index of 103 (or 1.03) indicates a 3% excess of isocyanate [246]. An efficient method to calculate the Isocyanate index is using the concept of the equivalent number of reacting groups taking account of the available number of hydroxyl groups in the polyol as well as the water added in the formulation [174]. Typically, polyurethane foams have an index from 90 - 130 [51], whereas Polyisocyanurate (PIR) foams have a higher index above 180 [52, 53].

S3. ASTM and ISO Standards used for Raw Materials and Physical Properties of RPUF

Table A1 ASTM and ISO standards used for determination of characteristic parameters of polyols used in RPUF

ASTM Standard	**ISO standard**	**Key parameters / characteristics**
ASTM D4273	ISO 14900	Hydroxyl number
ASTM D7253		Acid value
ASTM D 6437		Alkaline value
ASTM D4878		Viscosity
ASTM D4890		Colour
ASTM D4672	ISO 14897	Water content
ASTM D4670		Suspended matter
ASTM D4662		Acid and Alkalinity Numbers of Polyols
ASTM D4671	ISO 17710	Unsaturation of Polyols
ASTM D4669		Specific Gravity
ASTM D4273		Primary Hydroxyl Content of Polyether Polyols
ASTM D6979	ISO 25761	Basicity in Polyols, Expressed as Percent Nitrogen

ASTM D4875		Polymerized Ethylene Oxide Content of Polyether Polyols
ASTM D6342	ISO 15063	Hydroxyl number by NIR spectroscopy

Table A2 ASTM and ISO standards used for determination / measurements of physical properties of RPUF

ASTM Standard	ISO standard	Description
ASTM D1622	ISO 845	Density
ASTM C518	ISO 8301	Thermal conductivity measurements
ASTM D2856	ISO 4590	Closed Cell Content
ASTM E96	ISO 1663	Water vapour permeance
ASTM D2126	ISO 2796	Dimensional stability
ASTM D1621	ISO 844	Compression properties
ASTM D1623	ISO 1926	Tensile Strength
ASTM D2842	ISO 2896	Water absorption
ASTM C1303	ISO 2440	Ageing
	ISO 6187	Friability
ASTM D7487		Foam cup test
ASTM C1338	ISO 846	Fungi resistance
ASTM D3576		Cell size
ASTM D3014		Fire resistance
ASTM D5113		Adhesive attack

ASTM C1029	ISO 8873	Spray foam
	ISO 4898	Thermal insulation products for buildings
ASTM C1289		PIR Thermal Insulation Board
ASTM E1730		Structural Sandwich Panel Cores
Other tests		
ASTM E-84	AS1530.3, DIN 4102-1, BS 476-7	Small scale fire tests
	ISO 13785-2	
	FM 4880,	
	LPS 1181, AS5113:2016, BS8414,	Large scale fire tests
	DIN 4201-20	

S4. Summary of Lignin Incorporated RPUF Included in the Review

Table A3 Reported data on physical properties of lignin incorporated RPUF

Approach	Lignin type	Polyol	Lignin% w/w in polyol	NCO index	Density (kg/m^3)	Thermal conductivity (mW/m.K)	Compressive strength (MPa) Parallel to foam rise	Compressive strength (MPa) Perpendicular to rise	Compressive modulus (MPa) Parallel to foam rise	Compressive modulus (MPa) Perpendicular to foam rise	Tg (°C)	References
Direct Incorporation	KL	Voranol™ 360, glycerol	0	110	36.2	25.6	0.18	0.16	4.8	3.6	131	Hayati et al [124]a
			2.5		38.6	24.7	0.14	0.12	4.5	3.5	133	
			5		40.1	24.7	0.15	0.13	4.5	3.52	135	
			10		38.8	25.2	0.15	0.15	4.3	4.1	145	

Direct incorporation	KL	Voranol ™ 270	0	1.1	116	NR	0.5	NR	NR	NR	NR	Pan and Saddler [130]
			23		100		0.24					
			46		70		0.23					
			55		80		0.2					
			64		83		0.1					
Direct incorporation	HL	PEG-400	0	105	120	NR	0.47	NR	NR	NR	NR	Xue et al [208]
			9		85		0.28					
			18		70		0.18					
			27		60		0.07					
			36		52		0.06					

			45		50		0.05					
Direct incorporation	Softwood lignin	JEFFOL® A-360, Soybean phosphate ester polyol	0	105	62	NR	0.39	NR	NR	NR	173	Luo et al [186]
			5		65		0.4				177	
			10		76		0.46				181	
			15		86		0.32				182	
Direct incorporation	BIOLIGNIN ™	Lupranol ® 3330,	0	120	53	NR	0.26	NR	NR	NR	NR	Arshanitsa et al [145]
		Lupranol ® 3422	5		48		0.22					
			10		47		0.21					

			20		45		0.21					
			30		42		0.19					
			40		42		0.17					
			50		40		0.15		NR			
Direct incorporation	Softwood lignin	Soy based polyol	0	110	303	NR	NR	NR	NR	NR	NR	Luo et al [77]
			5		264							
			10		257							
			15		223							
			20		220							
			25		196							

Direct incorporation	LS	DEG	0	120	NR	NR	NR	NR	NR	NR	~130	Asano et al [183]
		TEG	0								~95	
		PEG-200	0								~75	
		DEG	19.8								~120	
		TEG	19.8								~100	
		PEG-200	19.8								~90	
Direct incorporation	BIOLIGNIN ™	Tall oil polyol, Lupranol ® 3422, glycerol	0	155	50	35.2	0.31	0.28	NR	NR	NR	Paberza et al [175]
			1.88		51	NR	0.33	0.3				
			3.75		52	NR	0.35	0.31				
			7.5		51	32.4	0.33	0.26				

			15		59	NR	0.34	0.17				
			22.5		63	29.8	0.28	0.21				
Direct incorporation	KL	DEG/PEG	0	110	62	NR	0.33	NR	8.15	NR	NR	Luo et al [189]
			5		100		0.73		10			
			10		108		0.69		10.4			
			15		111		0.66		10.5			
			20		115		0.64		14.7			
Direct incorporation	LS	PPG/ glycerol (100:0)	0	107	17	NR	1.62	NR	NR	NR	100	Wysocka et al [187]
		0/0	100		20		4.42				29	
		70/0	30		18		3.81				23	

		60/10	30		36		1.11				48	
		60/20	20		22		0.95				21	
		70/10	20		20		3.11				62	
Direct incorporation	KL	Castor oil/glycerol	17.5	110	54.9	NR	0.04	NR	0.01	NR	NR	Carrico et al [176]
Water					54.9		0.04		0.01			
n-pentane					71.1		0.03		0.03			
Cyclopentane					81.3		0.02		0.04			
Water/ cyclopentane					71.4		0.02		0.03			
Direct incorporation		PEG-2000	0	110	207	NR	NR	NR	0.02	NR	NR	Wang et al [247]

	Alkali lignin		20	108	344				0.02			
Direct incorporation	SL	polyether polyol 330	0	1.73	75	NR	0	NR	0.01	NR	NR	Zhu et al [73]
			2.5	1.25	60		0.001		0.02			
			5	0.98	66		0.002		0.04			
			7.5	0.81	75		0.003		0.04			
			10	0.69	85		0.003		0.05			
			15	0.53	115		0.06		0.09			
Lignin-polyol grafting	Alkali lignin/PEG 2000	PEG-2000	20	104	120				0.09			Wang et al [198]

			33.3	98	130				0.27			
			50	95	201				0.09			
Modification of existing functional groups	KL	Voranol™ 360 glycerol	0	110	38.2	25.2	0.14	0.15	3.9	3.99	135	Hayati et al [124]b
			2.5		38.7	25	0.16	0.16	4.5	3.95	133	
			5		39.3	24.6	0.2	0.17	5.4	4.05	149	
			10		36.9	26.7	0.09	0.07	2.7	1.8	171	
Modification of existing functional groups		PEG/ glycerol (9:1)	0	105	NR	NR	NR	NR	NR	NR	NR	Muller et al [188]

	KL	Glycerol/KL (9:1)	10	105	79	39	0.35					
	LS	Glycerol/LS (9:1)	10		154	48	0.25					
	OL	Glycerol/OL (9:1)	10		70	42	0.05					
Oxypropylation	Alcell	Lupranol® 3323, (lignin/propylene oxide/ KOH catalyst; 30/70/2)	100	110	22.3	25.7	NR	NR	3.1	NR	NR	Cateto et al [177]
	Alcell		50		25.1	26.9			3			
	Indulin At		100		23.1	27.4			4			
	Indulin At		50		23.7	29.1			3.6			
Oxypropylation	Alcell	Lupranol® 3323) (lignin/propylene	100	110	20.9	26.7	NR	NR	2.5	NR	NR	Cateto et al [177]

	Alcell	oxide/ KOH catalyst; 20/80/5)	50		23.9	30.5			3.3			
	Indulin AT		100		19.2	26.8			2.6			
	Indulin AT		50		22.4	32.9			2.4			
	Curan 27		100		18.4	28.5			2.3			
	Curan 27		50		19.4	31.3			2.7			
	Reference polyol		0		31.1	30.3			4.6			
Oxypropylation	KL	JEFFOL SD-361, JEFFOL ® FX31-240 (15 w/w % held constant)	0	120	NR	NR	0.1	NR	1.45	NR	NR	Li and Ragauskas [132]

			10				0.1		1.56			
			30				0.11		1.58			
			60				0.1		1.13			
			100				0.09		1.11			
		Oxypropylated KL	100				0.14		3.41			
Oxypropylation	Alcell	Rokopol ® RF551	0	110	45.4	22.9	0.38	0.19	NR	NR	NR	Kuranska et al [201]
			10		43.8	22.8	0.38	0.18				
			20		43	22.8	0.35	0.18				
			30		41.4	22.9	0.34	0.16				

Oxypropylation	KL	Rokopol ® RF551	0	200	83	NR	0.63	NR	NR	NR	NR	Gosz et al [204]
			25		99		0.7					
			50		150		0.86					
Oxypropylation	BIOLIGNIN™	Lupranol ® 3330, Lupranol ® 3422	0	120	53		0.26	NR	NR	NR	NR	Arshanitsa et al [145]
			1.9		NR	NR	0.23					
			3.8				0.26					
			5.7				0.27					
			7.5				0.31					

Glycolysis	KL	Recycled aromatic PET polyol	0	260	29.3	23.9	0.19	NR	NR	NR	NR	Rogers et al [191]
			2.5		29.8	24.3	0.21					
			5		29.3	24.1	0.24					
			10		30.3	24.3	0.23					
			15		30.3	24.5	0.24					
Fractionation and oxypropylation	OSL	Polyether polyol (polyether 4110)	0	105	130	46.5	0.7	NR	NR	NR	NR	Li et al [200]
	8.87% (yield%)		50		73	37	0.75					
			100		85	37.1	0.83					

	20.12%		50		85	38.4	0.75					
			100		95	38.6	0.78					
	8.37%		50		102	36	0.25					
			100		105	45.1	0.5					
	1.63%		50		91	33.5	0.21					
			100		70	49.1	0.16					
Depolymerisation, oxypropylation	KL	Sucrose polyol	0	110	54	33	0.327	NR	NR	NR	NR	Mahmood et al [178]
		Depolymerised KL	50		104	32	0.374					

		Oxypropylated-Depolymerised KL	100		55	29	0.515					
Liquefaction, oxyproprylation	HL	JEFFOL SD-361,	50/50	110	44.7	29	0.39	NR	9.2	NR	NR	Mahmood et al [205]
		Liquefied/ Oxypropylated lignin	60/40		61	30	1.09		19.8			
			70/30		64.5	30	1.06		21.2			
Liquefaction	Phenolated lignin	PEG	0	NR	NR	NR	NR	NR	NR	NR	NR	Yang et al [203]
			0.5				0.07					

			1				0.11					
			1.5				0.13					
			2				0.12					
			2.5				0.09					
			3				0.09					
Introduction of New Functional Groups	Epoxidated lignin	PEG	0	NR	NR	NR	NR	NR	NR	NR	NR	Yang et al [203]
			0.5				0.05					
			1				0.06					
			1.5				0.08					
			2				0.08					

			2.5				0.09					
			3				0.09					
Hydrolyis	LS	PPG /glycerol	100	107	NR	NR	NR	NR	NR	NR	NR	Wysocka et al [187]
		70/0	30		13		0.46				100	
		60/10	30		11		0.9				41	
		60/20	20		19		0.86				36	
		70/10	20		18		0.84				56	
Liquefaction	HL	PPG400 and glycerol	0	120	58	45	0.52	NR	9.2	NR	NR	Mahmood et al [107]a
			30		55.6	38	0.16		0.18		138	
			50		99	39	0.09		0.11		146	

		JEFFOL SD-361	0	120	30.1	44	0.09	NR	1.03	NR	N	Mahmood et al [107]b
			30		35.4	35	0.19		3.34		178	
			50		65.1	37	0.25		3.29		189	
Modification of existing functional groups		PEG-400	0	NR	149	14	0.94	NR	NR	NR	311	Liu et al [190]
	Refined KL		15		79.5	12	0.41				281	
	Modified KL		15		110	10	0.5				320	
Oxyalkylation with ethylene	KL	PEG-400/EC	0	120	NR	NR	NR	NR	NR	NR	NR	Zhang et al [197]

carbonate and polyethylene glycol			
	20	120	0.18
	25	110	0.18
	30	123	0.17
	35	125	0.16
	40	122	0.14
	45	120	0.14
	50	128	0.14

References

[1] Engels HW, Pirkl HG, Albers R, Albach RW, Krause J, Hoffmann A, et al. Polyurethanes: versatile materials and sustainable problem solvers for today's challenges. Angew Chem Int Ed Engl. 2013;52:9422-41.

[2] Mahmood N, Yuan ZS, Schmidt J, Xu C. Depolymerization of lignins and their applications for the preparation of polyols and rigid polyurethane foams: A review. Renew Sust Energ Rev. 2016;60:317-29.

[3] Bernardini J, Cinelli P, Anguillesi I, Coltelli MB, Lazzeri A. Flexible polyurethane foams green production employing lignin or oxypropylated lignin. European Polymer Journal. 2015;64:147-56.

[4] Gama NV, Ferreira A, Barros-Timmons A. Polyurethane Foams: Past, Present, and Future. Materials (Basel). 2018;11.

[5] Furtwengler P, Averous L. Renewable polyols for advanced polyurethane foams from diverse biomass resources. Polymer Chemistry. 2018;9:4258-87.

[6] Cornille A, Auvergne R, Figovsky O, Boutevin B, Caillol S. A perspective approach to sustainable routes for non-isocyanate polyurethanes. European Polymer Journal. 2017;87:535-52.

[7] Agrawal A, Kaur R, Walia RS. PU foam derived from renewable sources: Perspective on properties enhancement: An overview. European Polymer Journal. 2017;95:255-74.

[8] Clark JH, Farmer TJ, Ingram IDV, Lie Y, North M. Renewable Self-Blowing Non-Isocyanate Polyurethane Foams from Lysine and Sorbitol. Eur J Org Chem. 2018:4265-71.

[9] Grignard B, Thomassin JM, Gennen S, Poussard L, Bonnaud L, Raquez JM, et al. CO2-blown microcellular non-isocyanate polyurethane (NIPU) foams: from bio- and CO2-sourced monomers to potentially thermal insulating materials. Green Chemistry. 2016;18:2206-15.

[10] Bruijnincx PCA, Rinaldi R, Weckhuysen BM. Unlocking the potential of a sleeping giant: lignins as sustainable raw materials for renewable fuels, chemicals and materials. Green Chemistry. 2015;17:4860-1.

[11] Ragauskas AJ, Beckham GT, Biddy MJ, Chandra R, Chen F, Davis MF, et al. Lignin valorization: improving lignin processing in the biorefinery. Science. 2014;344:1246843.

[12] Wang YY, Cai CM, Ragauskas AJ. Recent advances in lignin-based polyurethanes. Tappi J. 2017;16:203-7.

[13] Akindoyo JO, Beg MDH, Ghazali S, Islam MR, Jeyaratnam N, Yuvaraj AR. Polyurethane types, synthesis and applications – a review. RSC Advances. 2016;6:114453-82.

[14] Alinejad M, Henry C, Nikafshar S, Gondaliya A, Bagheri S, Chen N, et al. Lignin-Based Polyurethanes: Opportunities for Bio-Based Foams, Elastomers, Coatings and Adhesives. Polymers (Basel). 2019;11.

[15] Gouveia JR, da Costa CL, Tavares LB, dos Santos DJ. Synthesis of Lignin-Based Polyurethanes: A Mini-Review. Mini-Rev Org Chem. 2019;16:345-52.

[16] Mimini V, Kabrelian V, Fackler K, Hettegger H, Potthast A, Rosenau T. Lignin-based foams as insulation materials: a review. Holzforschung. 2019;73:117-30.

[17] Szycher M. Rigid Polyurethane Foams. In: Szycher M, editor. Szycher's Handbook of Polyurethanes. Second ed. Taylor & Francis Group: CRC Press; 2012. p. 257-308.

[18] Szycher M. Szycher's Handbook of Polyurethanes. Boca Raton: CRC Press; 2013.

[19] Verdolotti L, Di Caprio MR, Lavorgna M, Buonocore GG. Chapter 9 - Polyurethane Nanocomposite Foams: Correlation Between Nanofillers, Porous Morphology, and Structural and Functional Properties. In: Thomas S, Datta J, Haponiuk JT, Reghunadhan A, editors. Polyurethane Polymers. Amsterdam: Elsevier; 2017. p. 277-310.

[20] Lee LJ, Zeng C, Cao X, Han X, Shen J, Xu G. Polymer nanocomposite foams. Composites Science and Technology. 2005;65:2344-63.

[21] Dolomanova V, Rauhe JCM, Jensen LR, Pyrz R, Timmons AB. Mechanical properties and morphology of nano-reinforced rigid PU foam. Journal of Cellular Plastics. 2011;47:81-93.

[22] Kim H, Miura Y, Macosko CW. Graphene/Polyurethane Nanocomposites for Improved Gas Barrier and Electrical Conductivity. Chemistry of Materials. 2010;22:3441-50.

[23] PU Europe. PU- Premium solution. Belgium.

[24] Aditya L, Mahlia TMI, Rismanchi B, Ng HM, Hasan MH, Metselaar HSC, et al. A review on insulation materials for energy conservation in buildings. Renewable and Sustainable Energy Reviews. 2017;73:1352-65.

[25] Recticel Insulation. Eurowall®+: High performance PIR insulation for full fill masonry cavity wall applications. In: sheet Td, editor. Professional Products. UK: Recticel Insulation; 2018.

[26] Kumar D, Alam M, Zou PXW, Sanjayan JG, Memon RA. Comparative analysis of building insulation material properties and performance. Renewable and Sustainable Energy Reviews. 2020;131:110038.

[27] Septevani AA, Evans DAC, Annamalai PK, Martin DJ. The use of cellulose nanocrystals to enhance the thermal insulation properties and sustainability of rigid polyurethane foam. Industrial Crops and Products. 2017;107:114-21.

[28] Bing: Federation of European rigid polyurethane foam Associations. Thermal insulation materials made of rigid polyurethane foam. Report No 1. Brussels2006.

[29] Septevani AA, Evans DAC, Chaleat C, Martin DJ, Annamalai PK. A systematic study substituting polyether polyol with palm kernel oil based polyester polyol in rigid polyurethane foam. Industrial Crops and Products. 2015;66:16-26.

[30] Gibson LJ, Ashby MF. The mechanics of foams: basic results. In: Gibson LJ, Ashby MF, editors. Cellular Solids: Structure and Properties. 2 ed. Cambridge: Cambridge University Press; 1997. p. 175-234.

[31] Thirumal M, Khastgir D, Singha NK, Manjunath BS, Naik YP. Effect of foam density on the properties of water blown rigid polyurethane foam. Journal of Applied Polymer Science. 2008;108:1810-7.

[32] Cao X, Lee LJ, Widya T, Macosko C. Polyurethane/clay nanocomposites foams: processing, structure and properties. Polymer. 2005;46:775-83.

[33] Ridha M, Shim VPW. Microstructure and Tensile Mechanical Properties of Anisotropic Rigid Polyurethane Foam. Exp Mech. 2008;48:763-76.

[34] Randall D, Lee S. The Polyurethanes Book. New York: John Wiley & sons; 2002.

[35] Glicksman LR. Heat transfer in foams. In: Hilyard NC, Cunningham A, editors. Low density cellular plastics: Physical basis of behaviour. Dordrecht: Springer Netherlands; 1994. p. 104-52.

[36] Thoen JA. Rigid Cellular Plastics. In: Gum WF, Reise W, Ulrich H, editors. Reaction Polymers. Munich: Hanser; 1992.

[37] Dinçer İ, Zamfirescu C. Appendix B Thermophysical Properties of Water. In: Zamfirescu eİDaC, editor. Drying Phenomena. Chichester, West Sussex, United Kingdom: John Wiley & Sons, Incorporated; 2016. p. 457-9.

[38] Loebel O. Thermal insulation materials made of rigid polyurethane foam. Federation of European Rigid Polyurethane Foam Associations. 2012;1:1-33.

[39] Dutta S, Sarkanen S. Noncovalent interactions between kraft lignin components: consequences and origins. TAPPI Proceedings 5th International Symposium on Wood and Pulping Chemistry. Raleight189. p. 329–32.

[40] Boström L, Hofmann-Böllinghaus A, Colwell S, Chiva R, Tóth P, Moder I, et al. Development of a European approach to assess the fire performance of facades. Brussels: Clean Technologies and Products, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs, Directorate Industrial Transformation and Advanced Value Chains; 2018.

[41] Ionescu M. Chemistry and Technology of Polyols for Polyurethanes. UK: Rapra Technology Limited; 2005.

[42] Furtwengler P, Bournbimba RM, Sarbu A, Averous L. Novel Rigid Polyisocyanurate Foams from Synthesized Biobased Polyester Polyol with Enhanced Properties. Acs Sustainable Chemistry & Engineering. 2018;6:6577-89.

[43] Zammarano M, Kramer RH, Harris R, Ohlemiller TJ, Shields JR, Rahatekar SS, et al. Flammability reduction of flexible polyurethane foams via carbon nanofiber network formation. Polymers for Advanced Technologies. 2008;19:588-95.

[44] Hansen R. Handbook of polymeric foams and foam technology. Germany: Hanser Publishers; 1992.

[45] Gibson LJ, Ashby MF. Cellular Solids. 2 ed. Cambridge: Cambridge University Press; 1997.

[46] Dawson JR, Shortall JB. The microstructure of rigid polyurethane foams. Journal of Materials Science. 1982;17:220-4.

[47] Lay DG, Cranley P. Polyurethane adhesives. In: Pizzi A, Mittal KL, editors. Handbook of adhesive technology. 2 ed. New York: Marcel Dekker Inc.; 2003. p. 679-702.

[48] Furtwengler P, Avérous L. Renewable polyols for advanced polyurethane foams from diverse biomass resources. Polymer Chemistry. 2018;9:4258-87.

[49] Plastics D. Technical information of Voranol ™ 446. Voranol ™ 446 Technical data sheet. U.S.A: The Dow Chemical Company; 2001.

[50] Aneja A, Wilkes GL, Yurtsever E, Yilgor I. Influence of lithium chloride on the morphology of flexible slabstock polyurethane foams and their plaque counterparts. Polymer. 2003;44:757-68.

[51] Kim SH, Kim BK, Lim H. Effect of Isocyanate Index on the Properties of Rigid Polyurethane Foams Blown by HFC 365mfc. Journal of macromolecular research. 2008;16:467-72.

[52] Inohara H, Nanno H, Kimura T, Yoshida K, Yamamoto K. Newly Developed Superior Flame Retardant All Water-Blown Polyisocyanurate Foams.

[53] Furtwengler P, Matadi Boumbimba R, Sarbu A, Avérous L. Novel Rigid Polyisocyanurate Foams from Synthesized Biobased Polyester Polyol with Enhanced Properties. ACS Sustainable Chemistry & Engineering. 2018;6:6577-89.

[54] Woods G. The ICI Polyurethane Book. New York, NY, USA: John Wiley & Sons; 1990.

[55] Hinrichsen G. Polyurethane Handbook (2nd ed.). Edited by G. Oertel, Hanser Publishers, Munich 1993, 770 pp., DM 358, ISBN 3-446-17198-3. Acta Polymerica. 1994;45:398-.

[56] Choe KH, Lee DS, Seo WJ, Kim WN. Properties of Rigid Polyurethane Foams with Blowing Agents and Catalysts. Polymer Journal. 2004;36:368-73.

[57] Nistor A, Toulec M, Zubov A, Kosek J. Tomographic Reconstruction and Morphological Analysis of Rigid Polyurethane Foams. Macromolecular Symposia. 2016;360:87-95.

[58] Seo WJ, Jung HC, Hyun JC, Kim WN, Lee YB, Choe KH, et al. Mechanical, morphological, and thermal properties of rigid polyurethane foams blown by distilled water. Journal of Applied Polymer Science. 2003;90:12-21.

[59] Šebenik A, Osredkar U, Vizovišek I. Identification of Oligomers in the Reaction of Polyols with Isocyanates by13C-NMR and GPC. Journal of Macromolecular Science: Part A - Chemistry. 2006;23:369-79.

[60] Kogon IC. Chemistry of Aryl Isocyanates: Rate and Equilibrium Constants for the Formation of Ethyl α,γ-Diarylallophanate. The Journal of Organic Chemistry. 1959;24:83-6.

[61] Guo A, Javni I, Petrovic Z. Rigid polyurethane foams based on soybean oil. Journal of Applied Polymer Science. 2000;77:467-73.

[62] Fan HY, Tekeei A, Suppes GJ, Hsieh FH. Physical Properties of Soy-Phosphate Polyol-Based Rigid Polyurethane Foams. International Journal of Polymer Science. 2012;2012:1-8.

[63] Centre for Polyurethanes Industry. Polyurethane Amine Catalysts: Safe Handling Guidelines. In: Council AC, editor. Washington, DC 20002 2011.

[64] Sonnenschein MF. Polyurethanes: Science, Technology, Markets, and Trends: Wiley Blackwell; 2014.

[65] Tavares LB, Boas CV, Schleder GR, Nacas AM, Rosa DS, Santos DJ. Bio-based polyurethane prepared from Kraft lignin and modified castor oil. Express Polymer Letters. 2016;10:927-40.

[66] Yusuf AK, Mamza PAP, Ahmed AS, Agunwa U. Physico-Mechanical Properties of Rigid Polyurethane Foams Synthesized From Modified Castor Oil Polyols. International Journal of Scientific and Research Publications. 2016;6:548-56.

[67] Gama NV, Soares B, Freire CSR, Silva R, Neto CP, Barros-Timmons A, et al. Bio-based polyurethane foams toward applications beyond thermal insulation. Materials & Design. 2015;76:77-85.

[68] Soares B, Gama N, Freire CSR, Barros-Timmons A, Brandao I, Silva R, et al. Spent coffee grounds as a renewable source for ecopolyols production. J Chem Technol Biot. 2015;90:1480-8.

[69] Kakroodi AR, Khazabi M, Maynard K, Sain M, Kwon OS. Soy-based polyurethane spray foam insulations for light weight wall panels and their performances under monotonic and static cyclic shear forces. Industrial Crops and Products. 2015;74:1-8.

[70] Hu S, Wan C, Li Y. Production and characterization of biopolyols and polyurethane foams from crude glycerol based liquefaction of soybean straw. Bioresour Technol. 2012;103:227-33.

[71] Kuranska M, Prociak A, Michalowski S, Cabulis U, Kirpluks M. Microcellulose as a natural filler in polyurethane foams based on the biopolyol from rapeseed oil. Polimery. 2016;61:625-32.

[72] Shao Q, Li HQ, Huang CP, Xu J. Biopolyol preparation from liquefaction of grape seeds. Journal of Applied Polymer Science. 2016;133.

[73] Zhu SY, Chen KF, Xu J, Li J, Mo LH. Bio-based polyurethane foam preparation employing lignin from corn stalk enzymatic hydrolysis residues. RSC Advances. 2018;8:15754-61.

[74] Naseem A, Tabasum S, Zia KM, Zuber M, Ali M, Noreen A. Lignin-derivatives based polymers, blends and composites: A review. Int J Biol Macromol. 2016;93:296-313.

[75] Zheng ZF, Pan H, Huang YB, Chung YH. Bio-Based Rigid Polyurethane Foam from Liquefied Products of Wood in the Presence of Polyhydric Alcohols. Advances in Building Materials,. 2011:1281-4.

[76] Huang XY, Qi JQ, de Hoop CF, Xie JL, Chen YZ. Biobased Polyurethane Foam Insulation from Microwave Liquefaction of Woody Underbrush. Bioresources. 2017;12:8160-79.

[77] Luo X, Xiao Y, Wu Q, Zeng J. Development of high-performance biodegradable rigid polyurethane foams using all bioresource-based polyols: Lignin and soy oil-derived polyols. Int J Biol Macromol. 2018;115:786-91.

[78] Demilec (USA) Inc. Heatlok Soy® 200 Plus Technical Data Sheet. Demilec Products. U.S.A: Demilec USA, Inc.; 2018.

[79] Inc DU. Heatlok XT Technical data sheet. Demilec Products. U.S.A: Demilec USA, Inc.; 2019.

[80] Inc DU. Heatlok HFO Pro Technical Data Sheet. Demilec Products. U.S.A.: Demilec USA, Inc; 2019.

[81] Zhang C, Garrison TF, Madbouly SA, Kessler MR. Recent advances in vegetable oil-based polymers and their composites. Progress in Polymer Science. 2017;71:91-143.

[82] BRE global Ltd. Life cycle environmental and economic analysis of polyurethane insulation in low energy buildings. Client report number 254-6652010.

[83] Llantoy N, Chàfer M, Cabeza LF. A comparative Life Cycle Assessment (LCA) of different insulation materials for buildings in the continental Mediterranean climate. Energy and Buildings. 2020:110323.

[84] Croda International Plc. Turning the World's Products Green: 100% Renewable, 100% Bio-Based ECO Range of Surfactants. Croda Sustainable manufacturing: ECO plant. USA: Croda International Plc 2018.

[85] Climalife. Technical data sheet Solstice® zd (R-1233zd). HFO. France: Climalife Groupe Dehon; 2014.

[86] Gary Loh JAC, Mark L. Robin. DuPont™ Formacel Development program update for low GWP: DuPont Fluorochemicals; 2009.

[87] Singh SN. Blowing Agents for Polyurethane Foams. In: Polyurethanes) H, editor.

[88] Feldman D. Lignin nanocomposites. Journal of Macromolecular Science, Part A. 2016;53:382-7.

[89] Hatakeyama Tatsuko HH. Lignin Structure, Properties, and Application. In: Akihiro Abe KD, Shiro Kobayashi, editor. Biopolymers : Lignin, Proteins, Bioactive Nanocomposites: Springer; 2010. p. 1-63.

[90] Zakzeski J, Bruijnincx PC, Jongerius AL, Weckhuysen BM. The catalytic valorization of lignin for the production of renewable chemicals. Chem Rev. 2010;110:3552-99.

[91] Fortunati E, Yang W, Luzi F, Kenny J, Torre L, Puglia D. Lignocellulosic nanostructures as reinforcement in extruded and solvent casted polymeric nanocomposites: an overview. European Polymer Journal. 2016;80:295-316.

[92] Kai D, Tan MJ, Chee PL, Chua YK, Yap YL, Loh XJ. Towards lignin-based functional materials in a sustainable world. Green Chemistry. 2016;18:1175-200.

[93] Laurichesse S, Averous L. Chemical modification of lignins: Towards biobased polymers. Progress in Polymer Science. 2014;39:1266-90.

[94] Upton BM, Kasko AM. Strategies for the conversion of lignin to high-value polymeric materials: Review and perspective. Chemical Reviews2016. p. 2275-306.

[95] Kun D, Pukánszky B. Polymer/lignin blends: Interactions, properties, applications. European Polymer Journal. 2017;93:618-41.

[96] Bajwa DS, Pourhashem G, Ullah AH, Bajwa SG. A concise review of current lignin production, applications, products and their environmental impact. Industrial Crops and Products. 2019;139:111526.

[97] Collins MN, Nechifor M, Tanasă F, Zănoagă M, McLoughlin A, Stróżyk MA, et al. Valorization of lignin in polymer and composite systems for advanced engineering applications – A review. International Journal of Biological Macromolecules. 2019;131:828-49.

[98] Eraghi Kazzaz A, Fatehi P. Technical lignin and its potential modification routes: A mini-review. Industrial Crops and Products. 2020;154:112732.

[99] Graglia M, Kanna N, Esposito D. Lignin Refinery: Towards the Preparation of Renewable Aromatic Building Blocks. ChemBioEng Reviews. 2015;2:377-92.

[100] Barakat A, Mayer-Laigle C, Solhy A, Arancon RAD, de Vries H, Luque R. Mechanical pretreatments of lignocellulosic biomass: towards facile and environmentally sound technologies for biofuels production. RSC Adv. 2014;4:48109-27.

[101] Barakat A, de Vries H, Rouau X. Dry fractionation process as an important step in current and future lignocellulose biorefineries: a review. Bioresour Technol. 2013;134:362-73.

[102] Klett AS, Chappell PV, Thies MC. Recovering ultraclean lignins of controlled molecular weight from Kraft black-liquor lignins. Chemical Communications. 2015;51:12855-8.

[103] Sadeghifar H, Ragauskas A. Perspective on Technical Lignin Fractionation. ACS Sustainable Chemistry & Engineering. 2020;8:8086-101.

[104] Schuerch C. The Solvent Properties of Liquids and Their Relation to the Solubility, Swelling, Isolation and Fractionation of Lignin. Journal of the American Chemical Society. 1952;74:5061-7.

[105] Lora J. Industrial Commercial Lignins: Sources, Properties and Applications. In: Belgacem MN, Gandini A, editors. Monomers, Polymers and Composites from Renewable Resources. Amsterdam: Elsevier; 2008. p. 225-41.

[106] Mathew AK, Abraham A, Mallapureddy KK, Sukumaran RK. Chapter 9 - Lignocellulosic Biorefinery Wastes, or Resources? In: Bhaskar T, Pandey A, Mohan SV, Lee D-J, Khanal SK, editors. Waste Biorefinery: Elsevier; 2018. p. 267-97.

[107] Mahmood N, Yuan ZS, Schmidt J, Xu CC. Valorization of Hydrolysis Lignin for Polyols and Rigid Polyurethane Foam. Journal of Science & Technology for Forest Products and Processes. 2013;3:26-31.

[108] Figueiredo P, Lintinen K, Hirvonen JT, Kostiainen MA, Santos HA. Properties and chemical modifications of lignin: Towards lignin-based nanomaterials for biomedical applications. Progress in Materials Science. 2018;93:233-69.

[109] Kun D, Pukanszky B. Polymer/lignin blends: Interactions, properties, applications. European Polymer Journal. 2017;93:618-41.

[110] Langholtz M, Downing M, Graham R, Baker F, Compere A, Griffith W, et al. Lignin-Derived Carbon Fiber as a Co-Product of Refining Cellulosic Biomass. SAE Int J Mater Manf. 2014;7:115-21.

[111] Lupoi JS, Singh S, Parthasarathi R, Simmons BA, Henry RJ. Recent innovations in analytical methods for the qualitative and quantitative assessment of lignin. Renewable and Sustainable Energy Reviews. 2015;49:871-906.

[112] Ahvazi B, Ngo T-D. Application of Lignins in Formulation and Manufacturing Bio-Based Polyurethanes by 31P NMR Spectroscopy: IntechOpen; 2018.

[113] Sameni J, Krigstin S, Rosa DD, Leao A, Sain M. Thermal Characteristics of Lignin Residue from Industrial Processes. BioResources. 2014;9:725-37.

[114] Schorr D, Diouf PN, Stevanovic T. Evaluation of industrial lignins for biocomposites production. Industrial Crops and Products. 2014;52:65-73.

[115] Cateto CA, Barreiro MF, Rodrigues AE, Brochier-Solan MC, Thielemans W, Belgacem MN. Lignins as macromonomers for polyurethane synthesis: A comparative study on hydroxyl group determination. Journal of Applied Polymer Science. 2008;109:3008-17.

[116] Gosselink RJA, Abächerli A, Semke H, Malherbe R, Käuper P, Nadif A, et al. Analytical protocols for characterisation of sulphur-free lignin. Industrial Crops and Products. 2004;19:271-81.

[117] Zhao WW, Xiao LP, Song GY, Sun RC, He LL, Singh S, et al. From lignin subunits to aggregates: insights into lignin solubilization. Green Chemistry. 2017;19:3272-81.

[118] Tomani P. The lignoboost process. Cellulose Chemistry & Technology. 2010;44:53.

[119] Nowak AP, Hagberg J, Leijonmarck S, Schweinebarth H, Baker D, Uhlin A, et al. Lignin-based carbon fibers for renewable and multifunctional lithium-ion battery electrodes. Holzforschung. 2018;72:81-90.

[120] Kouisni L, Gagné A, Maki K, Holt-Hindle P, Paleologou M. LignoForce System for the Recovery of Lignin from Black Liquor: Feedstock Options, Odor Profile, and Product Characterization. ACS Sustainable Chemistry & Engineering. 2016;4:5152-9.

[121] El Mansouri N-E, Salvadó J. Structural characterization of technical lignins for the production of adhesives: Application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins. Industrial Crops and Products. 2006;24:8-16.

[122] Sameni J, Krigstin S, Sain M. Characterization of Lignins Isolated from Industrial Residues and their Beneficial Uses. BioResources. 2016;11:8435-56.

[123] Goldlust D, Chalut J, Rault JJ. [Case of aneurysm of the dorsal pancreatic artery]. J Radiol Electrol Med Nucl. 1970;51:519-21.

[124] Hayati AN, Evans DAC, Laycock B, Martin DJ, Annamalai PK. A simple methodology for improving the performance and sustainability of rigid polyurethane foam by incorporating industrial lignin. Industrial Crops and Products. 2018;117:149-58.

[125] Mahmood N, Yuan Z, Schmidt J, Charles Xu C. Production of polyols via direct hydrolysis of kraft lignin: effect of process parameters. Bioresour Technol. 2013;139:13-20.

[126] Zhang CQ, Wu HC, Kessler MR. High bio-content polyurethane composites with urethane modified lignin as filler. Polymer. 2015;69:52-7.

[127] Muller LC, Marx S, Vosloo HCM. Polyol Preparation by Liquefaction of Technical Lignins in Crude Glycerol. J Renew Mater. 2017;5:67-80.

[128] Vazquez G, Freire S, Rodriguez-Bona C, Gonzalez J, Antorrena G. Structures, and reactivities with formaldehyde, of some acetosolv pine lignins. Journal of Wood Chemistry and Technology. 1999;19:357-78.

[129] Vazquez G, Antorrena G, Gonzalez J, Freire S. The influence of pulping conditions on the structure of acetosolv eucalyptus lignins. Journal of Wood Chemistry and Technology. 1997;17:147-62.

[130] Pan X, Saddler JN. Effect of replacing polyol by organosolv and kraft lignin on the property and structure of rigid polyurethane foam. Biotechnol Biofuels. 2013;6:12.

[131] Vainio U, Maximova N, Hortling B, Laine J, Stenius P, Simola LK, et al. Morphology of dry lignins and size and shape of dissolved kraft lignin particles by X-ray scattering. Langmuir. 2004;20:9736-44.

[132] Li Y, Ragauskas AJ. Kraft Lignin-Based Rigid Polyurethane Foam. Journal of Wood Chemistry and Technology. 2012;32:210-24.

[133] Constant S, Wienk HLJ, Frissen AE, de Peinder P, Boelens R, van Es DS, et al. New insights into the structure and composition of technical lignins: a comparative characterisation study. Green Chemistry. 2016;18:2651-65.

[134] Griffini G, Passoni V, Suriano R, Levi M, Turni S. Polyurethane Coatings Based on Chemically Unmodified Fractionated Lignin. ACS Sustainable Chemistry & Engineering. 2015;3:1145-54.

[135] Yang M, Zhao W, Singh S, Simmons B, Cheng G. On the solution structure of kraft lignin in ethylene glycol and its implication for nanoparticle preparation. Nanoscale Advances. 2019;1:299-304.

[136] Aldrich S. Product specification PRD.2.ZQ5.10000068720. Lignosulfonic acid sodium salt: Merck; 2018.

[137] Jablonskis A, Arshanitsa A, Telysheva G. Solvent Pretreatment of Lignin for Obtaining of Low Viscosity Lignopolyols by Oxypropylation for Synthesis of Polyurethanes. IOP Conference Series: Materials Science and Engineering. 2016;111.

[138] Thring RW, Vanderlaan MN, Griffin SL. Polyurethanes from Alcell® lignin. Biomass and Bioenergy. 1997;13:125-32.

[139] Pye EK, Lora JH. The Alcell Process - a Proven Alternative to Kraft Pulping. Tappi J. 1991;74:113-8.

[140] Glasser W, Davé V, Frazier CE. Molecular Weight Distribution of (Semi-) Commercial Lignin Derivatives. Journal of Wood Chemistry and Technology. 1993;13:545-59.

[141] Kathahira R, Elder TJ, Beckham GT. A Brief Introduction to Lignin Structure. 2018. p. 1-20.

[142] Zieglowski M, Trosien S, Rohrer J, Mehlhase S, Weber S, Bartels K, et al. Reactivity of Isocyanate-Functionalized Lignins: A Key Factor for the Preparation of Lignin-Based Polyurethanes. Frontiers in Chemistry. 2019;7.

[143] Lievonen M, Valle-Delgado JJ, Mattinen ML, Hult EL, Lintinen K, Kostiainen MA, et al. A simple process for lignin nanoparticle preparation. Green Chemistry. 2016;18:1416-22.

[144] Pan X, Saddler JN. Effect of replacing polyol by organosolv and kraft lignin on the property and structure of rigid polyurethane foam. Biotechnology for Biofuels. 2013;6:1.

[145] Arshanitsa A, Paberza A, Vevere L, Cabulis U, Telysheva G. Two approaches for introduction of wheat straw lignin into rigid polyurethane foams. AIP Conference Proceedings2014. p. 388-91.

[146] El Mansouri N-E, Salvadó J. Analytical methods for determining functional groups in various technical lignins. Industrial Crops and Products. 2007;26:116-24.

[147] Melro E, Alves L, Antunes FE, Medronho B. A brief overview on lignin dissolution. Journal of Molecular Liquids. 2018;265:578-84.
[148] Zhao WW, Simmons B, Singh S, Ragauskas A, Cheng G. From lignin association to nano-/micro-particle preparation: extracting higher value of lignin. Green Chemistry. 2016;18:5693-700.
[149] Cheng G, Zhang X, Simmons B, Singh S. Theory, practice and prospects of X-ray and neutron scattering for lignocellulosic biomass characterization: towards understanding biomass pretreatment. Energy and Environmental Science. 2015;8:436-55.
[150] Giummarella N, Lindgren C, Lindström ME, Henriksson G. Lignin Prepared by Ultrafiltration of Black Liquor: Investigation of Solubility, Viscosity, and Ash Content. BioResources; Vol 11, No 2 (2016). 2016.
[151] Ni H, Ren S, Fang G, Ma Y. Determination of Alkali Lignin Solubility Parameters by Inverse Gas Chromatography and Hansen Solubility Parameters. BioResources; Vol 11, No 2 (2016). 2016.
[152] Deng Y, Feng X, Zhou M, Qian Y, Yu H, Qiu X. Investigation of aggregation and assembly of alkali lignin using iodine as a probe. Biomacromolecules. 2011;12:1116-25.
[153] Vainio U, Lauten RA, Serimaa R. Small-Angle X-ray Scattering and Rheological Characterization of Aqueous Lignosulfonate Solutions. Langmuir. 2008;24:7735-43.
[154] Nyman V, Rose G, Ralston J. The Colloidal Behavior of Kraft Lignin and Lignosulfonates. Colloids and Surfaces. 1986;21:125-47.
[155] Sarkanen S, Teller DC, Stevens CR, McCarthy JL. Lignin. 20. Associative Interactions Between Kraft Lignin Components. Macromolecules. 1984;17:2588-97.
[156] Lindstrom T. The colloidal behavior of lignin. Colloid Polymer Science. 1979;257:271-85.
[157] Connors WJ, Sarkanen S, McCarthy JL. Gel Chromatography and Association Complexes of Lignin. Holzforschung. 1980;34:80-5.
[158] Kirk TK, Brown W, Cowling EB. Preparative fractionation of lignin by gel-permeation chromatography. Biopolymers. 1969;7:135-53.
[159] Sarkanen S, Teller DC, Abramowski E, Mccarthy JL. Lignin .19. Kraft Lignin Component Conformation and Associated Complex Configuration in Aqueous Alkaline-Solution. Macromolecules. 1982;15:1098-104.
[160] Woerner DL, Mccarthy JL. Lignin-24 Ultrafiltration and Light-Scattering Evidence for Association of Kraft Lignins in Aqueous-Solutions. Macromolecules. 1988;21:2160-6.
[161] Sarkanen S, Teller DC, Hall J, McCarthy JL. Lignin. 18. Associative effects among organosolv lignin components. Macromolecules. 1981;14:426-34.
[162] Cheng G, Kent MS, He L, Varanasi P, Dibble D, Arora R, et al. Effect of ionic liquid treatment on the structures of lignins in solutions: molecular subunits released from lignin. Langmuir. 2012;28:11850-7.
[163] Contreras S, Gaspar AR, Guerra A, Lucia LA, Argyropoulos DS. Propensity of lignin to associate: light scattering photometry study with native lignins. Biomacromolecules. 2008;9:3362-9.
[164] Guerra A, Lucia LA, Argyropoulos DS. Isolation and characterization of lignins from Eucalyptus grandis Hill ex Maiden and Eucalyptus globulus Labill. by enzymatic mild acidolysis (EMAL). Holzforschung. 2008;62:24-30.
[165] Guerra A, Gaspar AR, Contreras S, Lucia LA, Crestini C, Argyropoulos DS. On the propensity of lignin to associate: a size exclusion chromatography study with lignin derivatives isolated from different plant species. Phytochemistry. 2007;68:2570-83.
[166] Arnold RG, Nelson JA, Verbanc JJ. Recent Advances In Isocyanate Chemistry. Chemical Reviews. 1957;57:47-76.
[167] Calvo-Flores FG, Dobado JA, Isac-García J, Martín-MartíNez FJ. Applications of Modified and Unmodified Lignins. Lignin and Lignans as Renewable Raw Materials. 2015.

[168] Obaid N, Kortschot MT, Sain M. Lignin-Based Foaming Materials. Lignin in Polymer Composites2016. p. 217-32.

[169] Cateto CA, Barreiro MF, Rodrigues AE, Belgacem MN. Kinetic study of the formation of lignin-based polyurethanes in bulk. Reactive and Functional Polymers. 2011;71:863-9.

[170] Girouard NM, Xu S, Schueneman GT, Shofner ML, Meredith JC. Site-Selective Modification of Cellulose Nanocrystals with Isophorone Diisocyanate and Formation of Polyurethane-CNC Composites. ACS Appl Mater Interfaces. 2016;8:1458-67.

[171] Rueda L, d'Arlas BF, Zhou Q, Berglund LA, Corcuera MA, Mondragon I, et al. Isocyanate-rich cellulose nanocrystals and their selective insertion in elastomeric polyurethane. Composites Science and Technology. 2011;71:1953-60.

[172] Gwon JG, Cho HJ, Chun SJ, Lee S, Wu Q, Li MC, et al. Mechanical and thermal properties of toluene diisocyanate-modified cellulose nanocrystal nanocomposites using semi-crystalline poly(lactic acid) as a base matrix. Rsc Advances. 2016;6:73879-86.

[173] Siqueira G, Bras J, Dufresne A. New process of chemical grafting of cellulose nanoparticles with a long chain isocyanate. Langmuir. 2010;26:402-11.

[174] Pinto ML. Formulation, Preparation, and Characterization of Polyurethane Foams. Journal of Chemical Education. 2010;87:212-5.

[175] Paberza A, Cabulis U, Arshanitsa A. Wheat straw lignin as filler for rigid polyurethane foams on the basis of tall oil amide. Polimery. 2014;59:477-81.

[176] Carrico CS, Fraga T, Pasa VMD. Production and characterization of polyurethane foams from a simple mixture of castor oil, crude glycerol and untreated lignin as bio-based polyols. European Polymer Journal. 2016;85:53-61.

[177] Cateto CA, Barreiro MF, Ottati C, Lopretti M, Rodrigues AE, Belgacem MN. Lignin-based rigid polyurethane foams with improved biodegradation. Journal of Cellular Plastics. 2014;50:81-95.

[178] Mahmood N, Yuan ZS, Schmidt J, Xu CB. Preparation of bio-based rigid polyurethane foam using hydrolytically depolymerized Kraft lignin via direct replacement or oxypropylation. European Polymer Journal. 2015;68:1-9.

[179] Chauhan M, Gupta M, Singh B, Singh AK, Gupta VK. Effect of functionalized lignin on the properties of lignin-isocyanate prepolymer blends and composites. European Polymer Journal. 2014;52:32-43.

[180] Zhang X, Kim Y, Eberhardt TL, Shmulsky R. Lab-scale structural insulated panels with lignin-incorporated rigid polyurethane foams as core. Industrial Crops and Products. 2019;132:292-300.

[181] Zieglowski M, Trosien S, Rohrer J, Mehlhase S, Weber S, Bartels K, et al. Reactivity of Isocyanate-Functionalized Lignins: A Key Factor for the Preparation of Lignin-Based Polyurethanes. Frontiers in Chemistry. 2019;7.

[182] Zhang X, Jeremic D, Kim Y, Street J, Shmulsky R. Effects of Surface Functionalization of Lignin on Synthesis and Properties of Rigid Bio-Based Polyurethanes Foams. Polymers. 2018;10.

[183] Asano Y, Hatakeyama H, Hatakeyama T. Thermal and mechanical properties of sodium lignosulfonate-based rigid polyurethane foams prepared with three kinds of polyols. Sen-I Gakkaishi. 2003;59:465-70.

[184] Hatakeyama H, Hirogaki A, Matsumura H, Hatakeyama T. Glass transition temperature of polyurethane foams derived from lignin by controlled reaction rate. Journal of Thermal Analysis and Calorimetry. 2013;114:1075-82.

[185] Hatakeyama H, Kosugi R, Hatakeyama T. Thermal properties of lignin- and molasses-based polyurethane foams. Journal of Thermal Analysis and Calorimetry. 2008;92:419-24.

[186] Luo XG, Mohanty A, Misra M. Lignin as a reactive reinforcing filler for water-blown rigid biofoam composites from soy oil-based polyurethane. Industrial Crops and Products. 2013;47:13-9.

[187] Wysocka K, Szymona K, McDonald AG, Maminski M. Characterization of Thermal and Mechanical Properties of Lignosulfonate-and Hydrolyzed Lignosulfonate-based Polyurethane Foams. Bioresources. 2016;11:7355-64.
[188] Muller LC, Marx S, Vosloo HCM, Fosso-Kankeu E, Chiyanzu I. Rigid polyurethane foams from unrefined crude glycerol and technical lignins. Polymers from Renewable Resources. 2018;9:111-32.
[189] Luo S, Gao L, Guo W. Effect of incorporation of lignin as bio-polyol on the performance of rigid lightweight wood–polyurethane composite foams. Journal of Wood Science. 2020;66:23.
[190] Liu Z-m, Yu F, Fang G-z, Yang H-j. Performance characterization of rigid polyurethane foam with refined alkali lignin and modified alkali lignin. Journal of Forestry Research. 2009;20:161-4.
[191] Rogers KA, Mukerjee SL, Cupp JN, Tabor RL. Flame retardant characteristics of recycled- and lignin-based PET polyols for rigid foam applications. PU magazine International. Germany: Dr. Gupta Verlags GmbH; 2018. p. 482-9.
[192] Cateto CA, Barreiro MF, Rodrigues AE, Belgacem MN. Rigid polyurethane foams from lignin based polyols. In: Aciemo D, D'Amore A, Grassia L, editors. IVth International Conference on Times of Polymers (TOP) and Composites: American Institute of Physics; 2008. p. 243-5.
[193] Cateto CA, Barreiro MF, Rodrigues AE, Belgacem MN. Oxypropylation of lignins and characterization of the ensuing polyols. 8th ILI Forum. Rome: ILI - The International Lignin Institute; 2007. p. 115-8.
[194] Cateto CA, Barreiro MF, Rodrigues AE, Belgacem MN. Optimization Study of Lignin Oxypropylation in view of the Preparation of Polyurethane Rigid Foams. Ind Eng Chem Res. 2009;48:2583-9.
[195] Nadji H, Bruzzese C, Belgacem MN, Benaboura A, Gandini A. Oxypropylation of lignins and preparation of rigid polyurethane foams from the ensuing polyols. Macromolecular Materials and Engineering. 2005;290:1009-16.
[196] Muller LC, Marx S, Vosloo HCM, Chiyanzu I. Functionalising lignin in crude glycerol to prepare polyols and polyurethane. Polymers from Renewable Resources. 2019;10:3-18.
[197] Zhang X, Kim Y, Elsayed I, Taylor M, Eberhardt TL, Hassan EIB, et al. Rigid polyurethane foams containing lignin oxyalkylated with ethylene carbonate and polyethylene glycol. Industrial Crops and Products. 2019;141:111797.
[198] Wang S, Liu W, Yang D, Qiu X. Highly Resilient Lignin-Containing Polyurethane Foam. Ind Eng Chem Res. 2019;58:496-504.
[199] Ahvazi B, Wojciechowicz O, Ton-That T-M, Hawari J. Preparation of Lignopolyols from Wheat Straw Soda Lignin. J Agr Food Chem. 2011;59:10505-16.
[200] Li B, Zhou M, Huo W, Cai D, Qin P, Cao H, et al. Fractionation and oxypropylation of corn-stover lignin for the production of biobased rigid polyurethane foam. Industrial Crops and Products. 2020;143:111887.
[201] Kurańska M, Pinto JA, Salach K, Barreiro MF, Prociak A. Synthesis of thermal insulating polyurethane foams from lignin and rapeseed based polyols: A comparative study. Industrial Crops and Products. 2020;143:111882.
[202] Saffar T, Bouafif H, Braghiroli FL, Magdouli S, Langlois A, Koubaa A. Production of Bio-based Polyol from Oxypropylated Pyrolytic Lignin for Rigid Polyurethane Foam Application. Waste and Biomass Valorization. 2019.
[203] Yang L, Wang XF, Cui Y, Tian YM, Chen HZ, Wang ZC. Modification of renewable resources-lignin-by three chemical methods and its applications to polyurethane foams. Polymers for Advanced Technologies. 2014;25:1089-98.
[204] Gosz K, Kosmela P, Hejna A, Gajowiec G, Piszczyk L. Biopolyols obtained via microwave-assisted liquefaction of lignin: structure, rheological, physical and thermal properties. Wood Science and Technology. 2018;52:599-617.

[205] Mahmood N, Yuan ZS, Schmidt J, Tymchyshyn M, Xu CB. Hydrolytic liquefaction of hydrolysis lignin for the preparation of bio-based rigid polyurethane foam. Green Chemistry. 2016;18:2385-98.

[206] Xie JL, Qi JQ, Hse CY, Shupe TF. Effect of Lignin Derivatives in the Bio-Polyols from Microwave Liquefied Bamboo on the Properties of Polyurethane Foams. Bioresources. 2014;9:578-88.

[207] Xie JL, Hse CY, Shupe TF, Qi JQ, Pan H. Liquefaction Behaviors of Bamboo Residues in a Glycerol-Based Solvent Using Microwave Energy. Journal of Applied Polymer Science. 2014;131.

[208] Xue BL, Sun RC. Producing lignin-based polyols through microwave-assisted liquefaction for rigid polyurethane foam production. Abstr Pap Am Chem S. 2015;249.

[209] Lorenzetti A, Roso M, Bruschetta A, Boaretti C, Modesti M. Polyurethane-graphene nanocomposite foams with enhanced thermal insulating properties. Polymers for Advanced Technologies. 2016;27:303-7.

[210] Modesti M, Lorenzetti A, Besco S. Influence of nanofillers on thermal insulating properties of polyurethane nanocomposites foams. Polymer Engineering & Science. 2007;47:1351-8.

[211] Duval A, Lawoko M. A review on lignin-based polymeric, micro- and nano-structured materials. Reactive and Functional Polymers. 2014;85:78-96.

[212] Xue B-L, Wen J-L, Sun R-C. Lignin-Based Rigid Polyurethane Foam Reinforced with Pulp Fiber: Synthesis and Characterization. ACS Sustainable Chemistry & Engineering. 2014;2:1474-80.

[213] Mu LW, Shi YJ, Wang HY, Zhu JH. Lignin in Ethylene Glycol and Poly(ethylene glycol): Fortified Lubricants with Internal Hydrogen Bonding. Acs Sustainable Chemistry & Engineering. 2016;4:1840-9.

[214] Xu C, Arancon RA, Labidi J, Luque R. Lignin depolymerisation strategies: towards valuable chemicals and fuels. Chem Soc Rev. 2014;43:7485-500.

[215] Sun Z, Fridrich B, de Santi A, Elangovan S, Barta K. Bright Side of Lignin Depolymerization: Toward New Platform Chemicals. Chemical reviews. 2018;118:614-78.

[216] Chio C, Sain M, Qin W. Lignin utilization: A review of lignin depolymerization from various aspects. Renewable and Sustainable Energy Reviews. 2019;107:232-49.

[217] Fink JK. 2 - Poly(urethane)s. In: Fink JK, editor. Reactive Polymers: Fundamentals and Applications (Third Edition): William Andrew Publishing; 2018. p. 71-138.

[218] Nagy T, Antal B, Dékány-Adamoczky A, Karger-Kocsis J, Zsuga M, Kéki S. Uncatalyzed reactions of 4,4′-diphenylmethane-diisocyanate with polymer polyols as revealed by matrix-assisted laser desorption/ionization mass spectrometry. RSC Advances. 2016;6:47023-32.

[219] Kühnel I, Saake B, Lehnen R. Oxyalkylation of lignin with propylene carbonate: Influence of reaction parameters on the ensuing bio-based polyols. Industrial Crops and Products. 2017;101:75-83.

[220] Duval A, Avérous L. Cyclic Carbonates as Safe and Versatile Etherifying Reagents for the Functionalization of Lignins and Tannins. ACS Sustainable Chemistry & Engineering. 2017;5:7334-43.

[221] Bertella S, Luterbacher JS. Lignin Functionalization for the Production of Novel Materials. Trends in Chemistry. 2020;2:440-53.

[222] Podschun J, Saake B, Lehnen R. Catalytic demethylation of organosolv lignin in aqueous medium using indium triflate under microwave irradiation. React Funct Polym. 2017;119:82-6.

[223] Sawamura K, Tobimatsu Y, Kamitakahara H, Takano T. Lignin Functionalization through Chemical Demethylation: Preparation and Tannin-Like Properties of Demethylated Guaiacyl-Type Synthetic Lignins. Acs Sustainable Chemistry & Engineering. 2017;5:5424-31.

[224] Velez J, Thies MC. Temperature Effects on the Molecular Properties of Liquid Lignin Recovered from Kraft Black Liquor. Acs Sustainable Chemistry & Engineering. 2015;3:1032-8.

[225] Morck R, Yoshida H, Kringstad KP, Hatakeyama H. Fractionation of Kraft Lignin by Successive Extraction with Organic-Solvents .1. Functional-Groups, C-13-Nmr-Spectra and Molecular-Weight Distributions. Holzforschung. 1986;40:51-60.
[226] Wallberg O, Jonsson AS, Wimmerstedt R. Fractionation and concentration of kraft black liquor lignin with ultrafiltration. Desalination. 2003;154:187-99.
[227] Stoklosa RJ, Velez J, Kelkar S, Saffron CM, Thies MC, Hodge DB. Correlating lignin structural features to phase partitioning behavior in a novel aqueous fractionation of softwood Kraft black liquor. Green Chemistry. 2013;15:2904-12.
[228] Teng NY, Dallmeyer I, Kadla JF. Effect of Softwood Kraft Lignin Fractionation on the Dispersion of Multiwalled Carbon Nanotubes. Ind Eng Chem Res. 2013;52:6311-7.
[229] Saito T, Perkins JH, Vautard F, Meyer HM, Messman JM, Tolnai B, et al. Methanol Fractionation of Softwood Kraft Lignin: Impact on the Lignin Properties. Chemsuschem. 2014;7:221-8.
[230] Duval A, Vilaplana F, Crestini C, Lawoko M. Solvent screening for the fractionation of industrial kraft lignin. Holzforschung. 2016;70:11-20.
[231] Passoni V, Scarica C, Levi M, Turri S, Griffini G. Fractionation of Industrial Softwood Kraft Lignin: Solvent Selection as a Tool for Tailored Material Properties. Acs Sustainable Chemistry & Engineering. 2016;4:2232-42.
[232] Jiang X, Savithri D, Du XY, Pawar S, Jameel H, Chang HM, et al. Fractionation and Characterization of Kraft Lignin by Sequential Precipitation with Various Organic Solvents. Acs Sustainable Chemistry & Engineering. 2017;5:835-42.
[233] Dominguez-Robles J, Tamminen T, Liitia T, Peresin MS, Rodriguez A, Jaaskelainen AS. Aqueous acetone fractionation of kraft, organosolv and soda lignins. Int J Biol Macromol. 2018;106:979-87.
[234] Goldmann WM, Ahola J, Mikola M, Tanskanen J. Solubility and fractionation of Indulin AT kraft lignin in ethanol-water media. Sep Purif Technol. 2019;209:826-32.
[235] Tagami A, Gioia C, Lauberts M, Budnyak T, Moriana R, Lindstrom ME, et al. Solvent fractionation of softwood and hardwood kraft lignins for more efficient uses: Compositional, structural, thermal, antioxidant and adsorption properties. Industrial Crops and Products. 2019;129:123-34.
[236] Nunes RS, Tudino TC, Vieira LM, Mandelli D, Carvalho WA. Rational production of highly acidic sulfonated carbons from kraft lignins employing a fractionation process combined with acid-assisted hydrothermal carbonization. Bioresource Technol. 2020;303.
[237] Amiri MT, Dick GR, Questell-Santiago YM, Luterbacher JS. Fractionation of lignocellulosic biomass to produce uncondensed aldehyde-stabilized lignin. Nat Protoc. 2019;14:921-54.
[238] Faruk O, Sain M, Farnood R, Pan Y, Xiao H. Development of Lignin and Nanocellulose Enhanced Bio PU Foams for Automotive Parts. Journal of Polymers and the Environment. 2013;22:279-88.
[239] Hatakeyama H, Kato N, Nanbo T, Hatakeyama T. Water absorbent polyurethane composites derived from molasses and lignin filled with microcrystalline cellulose. Journal of Materials Science. 2012;47:7254-61.
[240] Li Y, Ragauskas AJ. Ethanol organosolv lignin-based rigid polyurethane foam reinforced with cellulose nanowhiskers. Rsc Advances. 2012;2:3347-51.
[241] Oribayo O, Feng X, Rempel GL, Pan Q. Synthesis of lignin-based polyurethane/graphene oxide foam and its application as an absorbent for oil spill clean-ups and recovery. Chemical Engineering Journal. 2017;323:191-202.
[242] Gao LP, Zheng GY, Zhou YH, Hu LH, Feng GD. Improved mechanical property, thermal performance, flame retardancy and fire behavior of lignin-based rigid polyurethane foam nanocomposite. Journal of Thermal Analysis and Calorimetry. 2015;120:1311-25.

[243] Yang H, Yu B, Xu X, Bourbigot S, Wang H, Song P. Lignin-derived bio-based flame retardants toward high-performance sustainable polymeric materials. Green Chemistry. 2020.

[244] Dutta AS. 2 - Polyurethane Foam Chemistry. In: Thomas S, Rane AV, Kanny K, V.K A, Thomas MG, editors. Recycling of Polyurethane Foams: William Andrew Publishing; 2018. p. 17-27.

[245] Sharmin E, Zafar F. Polyurethane: An Introduction. Polyurethane2012.

[246] Dow Answer Center. Dow Polyurethanes: The Dow Chemical Company.

[247] Wang G, Pang T, Xia Y. Subdivision of bamboo kraft lignin by one-step ethanol fractionation to enhance its water-solubility and antibacterial performance. Int J Biol Macromol. 2019;133:156.