LIGNIN VALORIZATION VIA RIGID POLYURETHANE/POLYISOCYANURATE FOAM PRODUCTION FOR INSULATION APPLICATIONS

By

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ABSTRACT

Due to increased demand for more sustainable products, producers of rigid polyurethane (PUR) and polyurethane/polyisocyanurate (PUR/PIR) foams are searching for ways to use more renewable materials. One way to increase sustainability of foams is to incorporate lignin, an abundant natural polymer, to replace fossil-fuel based polyol. The incorporation of lignin as a polyol substitute in rigid PUR foam has been reported to improve mechanical performance, oil sorption capacity, and biodegradability, but this is the first study to investigate the impacts lignin incorporation on the performance of rigid polyurethane/polyisocyanurate. The focus of this study was to expand the application of lignin in low-density rigid PUR and PUR/PIR foams, while ensuring that the developed foams met standard requirements for insulation applications. Another aspect was to find the most suitable lignins for this application by evaluating the performance of foams made with a wide range of unmodified commercial lignins. Lastly, the maximum loading percentage of lignin as polyol replacement in rigid PUR and PUR/PIR foams was elucidated using a commercial kraft lignin. The results showed that the corn stover lignin isolated through enzymatic hydrolysis process was the best for rigid PUR/PIR foam applications. Additionally, replacing 30 wt.% of polyols with lignins showed that lignins with higher hydroxyl and metal contents, and more neutral pH resulted in foams with higher compression strengths and closed cell contents. Moreover, the incorporation of lignin with decreased molecular weight (via ALPHA processes developed at Clemson University) enhanced PUR/PIR foam compression strength and closed cell content compared to control formulations with no lignin. We were also able to formulate rigid PUR and PUR/PIR foams where 50 and 100% of commercial polyol (respectively) was replaced with unmodified lignin, while meeting standard requirements for insulative foam applications.

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LIST OF ABBREVIATIONS

GPC	Gel Permeation Chromatography	
PIR	Polyisocyanurate	
³¹ P NMR	Phosphorus Nuclear Magnetic Resonance	
PUR	Polyurethane	
PUR/PIR	Polyurethane/Polyisocyanurate	

CHAPTER 1 INTRODUCTION

1.1 Background

The polyaddition polymerization reaction of polyols with isocyanates to form polyurethane was discovered by Otto Bayer and his coworkers in 1937.¹ Since then, the market value, production, and end-use applications of polyurethanes have consistently increased.² Polyurethanes are the most versatile category of polymers that allow for a wide array of property ranges due to their easily customizable chemistries. The customizable chemistries of polyurethanes allow users to tweak properties and performance based on choosing different types and amounts of isocyanates and polyols; along with additives like catalysts, surfactants, and fire retardants.³

1.2 Isocyanate

In general, Isocyanates have five main reactions in polyurethanes, including reactions with hydroxyl functional groups, water, amines, urea, and itself (isocyanate).² The most important isocyanate reaction is with hydroxyl groups or polyol(s).² This reversible exothermic reaction (120-180°C) creates carbamate, or the more popular term, urethane linkages (Figure 1.1).⁴



Figure 1.1 Polyol and isocyanate reaction to form polyurethane⁵

The second reaction in the polyurethanes process is between isocyanate and water (Figure 1.2). This highly exothermic reaction initially creates carbamic acid, which then breaks down to primary amine and carbon dioxide.² The water/isocyanate reaction is often used as a chemical blowing agent in polyurethane foams since the generated carbon dioxide gas gets trapped inside closed foam cells. If a physical blowing agent is used, it will be heated and turned to gas by the exothermic water and isocyanate reaction. Trapped carbon dioxide gas along with a physical blowing agent, can lower polyurethane foam density and decrease foam thermal conductivity.²

R — NCO +	H₂0 →	R — NHCOOH →	R NH ₂ +	CO ₂
lsocyanate	Water	Carbamic Acid	Amine	Carbon Dioxide

Figure 1.2 Reaction of isocyanate with water

The third main reaction in polyurethanes is the reaction between isocyanate and amines (Figure 1.3). This heat reversible reaction creates urea.¹ Depending on whether a primary or secondary amine is used, di- or tri-substituted urea will be produced, respectively.² Tertiary

amines do not usually react with isocyanate but can be used as catalysts in polyurethanes. Since primary amines react with isocyanate 100-1000 times faster than primary alcohols, catalysis within the foam formulation must be meticulously managed via raw material selection.¹

R — NCO +	$R' \longrightarrow NH_2 \longrightarrow$	R — NHCONH — R'
lsocyanate	Amine	Urea

Figure 1.3 Reaction of isocyanate and amine

The fourth reaction in rigid foam is the reaction between the isocyanate and urea (Figure 1.4), creating biuret. This is another heat reversible reaction that occurs at around 100°C.⁴ Shortly after biuret, isocyanate reacts with urethane to form allophanate around 120-140°C. Both biuret and allophanate reactions are reversible at elevated temperatures (~150°C) and create branching in the final polyurethane, which can increase mechanical properties.

$$R \longrightarrow NCO + R \longrightarrow NHCONH \longrightarrow R' \implies R' \longrightarrow NCONH \longrightarrow R''$$
Isocyanate Urea
$$Isocyanate = Urea$$
Biuret

Figure 1.4 Reaction of isocyanate with urea

The final main reactions of polyurethanes are the various isocyanate self-addition reactions.¹ These reactions: uretonimine, carbodiimide, and di/trimerization of isocyanate will vary based on the isocyanate used and various reaction conditions, including solvents, catalysts, and temperature. The uretidinedione dimer is created by the mildly exothermic

reaction/cyclo-addition of two usually aromatic isocyanates.² For toluene diisocyanate (TDI), this reaction usually needs to be catalyzed, but for methylene diisocyanate (MDI), it can happen slowly at room temperature.² At temperatures above 180°C, isocyanates can react to form carbodiimides.¹ Since CO₂ is lost, the carbodiimide reaction is irreversible and goes on to react with more isocyanate to create uretonimine.⁴ Most popularly, the six-membered ring created by the cyclisation reaction of three isocyanates is called a trimer or isocyanurate (Figure 1.5). This exothermic reaction can be formed by aliphatic or aromatic isocyanates and imparts enhanced flammability properties to the polyurethane due to bond stability and branching. Each of these reactions are utilized or corrected for through additive choice based on their final polyurethane application.



Figure 1.5 Reaction of isocyanate with itself

1.3 Polyols

Polyols are the second main component in rigid foam, representing about 30% of the rigid foam system.⁶ The term polyol refers to a compound containing two or more hydroxyl groups making up a polymer backbone.⁶ The polyols usually are designed to provide flexibility and softness in the urethane backbone, whereas isocyanates and other additives like crosslinkers provide stiffness and hardness.⁶ The choice of polyol will vary based on the application requirements, but the range of functionalities of polyols are endless.⁶ Most

commercial polyols for polyurethanes contain ether or ester-based backbones, but others include acrylics and carbonates for use in high-performance applications.^{6,7} In general, the choice of polyol will depend on structure, availability, function, and cost.⁶

Polyether polyols make up about 70% of commercial polyols and are produced mainly through the exothermic reaction of ethylene oxide.⁶ Whereas polyesters, making up about 20% of commercial polyols, are formed from polyhydroxy and polyacid monomers in a condensation polymerization reaction.⁶ Polyether polyols are generally hydrolytically stable, low cost, have low viscosity, and impart flexibility into the polyurethane, but they are flammable and have low oxidative stability and strength.⁶ On the other hand, polyester polyols have oxidative stability and high strength, but are not hydrolytically stable and have high viscosities.²

1.4 Rigid Polyurethane Foam

Polyurethane foams are derived from the polyaddition reaction of polyisocyanates and polyols to form thermosets. Rigid polyurethane foams can be broken into two types of chemical architectures, polyurethane (PUR) and polyisocyanurate (PIR).⁸ In addition to PUR reactions (Figures 1.1-1.4), PIR foams are formed from the trimerization of diisocyanates to form isocyanurate rings in the final foam (Figure 1.5). If the developed foam exclusively PIR linkages and no PUR, the resultant foams become incredibly brittle.⁴ Because of this, most PIR foams use a mixture of PUR and PIR, called PUR/PIR. The advantages of PUR/PIR over solely PUR foam formulations come from increased mechanical strength and fire resistance from the trimerized isocyanate.¹

Rigid foams are created using three main processes: one-step, quasi-prepolymer, and full prepolymer systems.³ The one-step foaming process mixes A-side isocyanate with a premixed B-side blend of polyol and additives to create foam. Whereas the quasi-prepolymer system has the A-side isocyanate component in excess mixed with polyol and then adds the B-side component with the remaining polyol/additives.³ Lastly, the full prepolymer system has the isocyanate and polyol mixed together, and then both are mixed with the remaining additives to complete foaming. The one-step process is the most commonly used system for producing rigid foams.²

1.5 Biobased Rigid Polyurethane Foam

About 90% of all polyols for rigid foam synthesis are petroleum-derived.⁹ Aside from petrochemical dependence, which can lead to price fluctuation in the final polyurethane product, the toxicity of these raw materials (ethylene oxide) used to make polyols are pushing industry and other researchers to find more sustainable options. Common biobased polyols include vegetable oils,^{10–14} sorbitol,¹⁵ crude glycerol,¹⁶ tannins,¹⁷ walnut shell, milled cellulose,¹⁸ and diatomite.¹⁸

Of the bio-based polyols used for rigid foam synthesis, vegetable oils are the most popular due to their liquid state, renewability, and low cost. Soy oil, soy polyol, or soyol is the most widely explored bio-based polyol and has been reported to increase some of the physical and chemical properties of polyurethanes.¹² Furtwengler et al.⁸ reported using 25% sorbitol-based polyol as petrochemical polyol replacement increased longitudinal young's modulus of rigid foam by 96%. Foams with up to 15% of walnut shell, cellulose, and diatomite¹⁸ have also been reported to show similar enhancements to mechanical properties

compared to control foams made entirely with petroleum-based polyols. Additionally, foams made with complete substitution of petrochemical polyol with sorbitol and soyoil polyols had enhanced thermal resistance compared to control foams.⁸

Though the use of soy and other vegetable oils as petrochemical polyol replacements can improve foam properties, the use of these biobased polyols has caused some controversy.¹⁹ Since these polyols are sourced from food, some researchers believe that valorization in the polyol sector could increase the price of foodstuffs, which would add to food insecurity issues around the world.^{20,21} One biobased polyol that comes without this hindrance is lignin. 1.6 Lignin

Lignin is a naturally occurring complex polymer found in trees and other woody biomass.²² Within biomass, lignin provides hydrophobicity, microbial resistance, and rigidity within the cell walls of plants.²³ It is comprised of three phenylpropane units (guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H)), also known as monolignols (coniferyl, sinapyl, and p-coumaryl alcohols).²³ These units combine via interunit linkages to form a complex 3D lignin structure.²⁴ The most common interunit linkage within lignin is β -O-4.²³ Interunit linkages of lignin include phenyl coumaran (β -5), resinols (β - β '), spirodienone (β -1), dibenzodioxocins (5-5'-O- β ' and 4-O- β ') and the most common β -O-4. All lignin units and linkages will vary based on the source of lignin.²³

The three main sources of lignin biomass are hardwoods, softwoods, and annual crops. Of these sources, softwoods have the highest percent dry mass of lignin (27-33%) followed by hardwoods (18-25%) and annual crops (17-24%).²⁵ Each of these biomass sources of lignin contain varying amounts of monolignols/phenyl propane units. Hardwood lignins are

mainly composed of coniferyl and sinapyl alcohols, while softwood lignins have mainly coniferyl. Annual crops have a mixture of all three monolignols with the highest amount of p-coumaryl of all lignin sources.

The proportion of these monolignols within the lignin determine lignin reactivity, branching, and the type of inter-unit linkages.²⁶ In general, due to their higher proportion of p-hydroxyphenyl units/p-coumaryl alcohols and vacant ortho/para sites in these groups, lignins derived from annual crops are more reactive than hardwood and softwood lignins.²⁷ Additionally, non-wood lignins, in general, have lower molecular weight, higher ash, and higher polydispersity than wood lignins, but these properties can also be affected by the extraction process of lignin from biomass.^{28,29}

1.6.1 Extraction Processes of Lignin

Lignin extraction methods can be broken down into three main categories; thermal, chemical, or biological, with the chemical being the most widely commercialized.²⁴ Thermal pretreatments of biomass include steam explosion and autohydrolysis, which take advantage of high-temperature water to recover mildly modified lignin.²⁴ Biological isolation techniques include using bacteria, enzymes, or fungi to degrade biomass and extract lignin.²⁴ Lastly, the chemical pretreatment of lignin can be broken into two categories: sulfur and sulfur free.²⁵

Of the commercial chemical lignin extraction processes, sulfur-free processes include mainly soda and organosolv, while sulfur-based processes include kraft and sulfite processes. These chemical pretreatments utilize acidic, alkaline, or oxidative conditions along with elevated temperature and pressure to isolate lignin from biomass.²⁴

Of the various extraction methods, the most abundant commercial methods are kraft, followed by sulfite, organosolv, soda, and enzymatic hydrolysis.²⁴ About 145 million tons of technical lignin byproducts are created each year, with the majority coming from the kraft isolation process.^{25,30}

1.6.2 Kraft

Currently, the kraft process is the most dominat chemical pulping technique,³¹ making up about 85% of world pulp production.³² During the kraft process, sodium hydroxide, and sodium sulfide are used to dissolve lignin at 140-170°C.³³ It has been reported that the kraft cooking process can be broken into three phases: initial, bulk, and residual.³⁴ The initial process begins at a temperature around 150°C, the bulk is where 90% of the isolation occurs around 170°C, and the residual where the remaining 5% of lignin is removed using bleaching.³⁵ Most of the α and β -aryl ether bonds (phenolic) are cleaved during the initial phase, whereas β -aryl ether bonds (non-phenolic) are cleaved in the bulk phase.³⁶ Residual lignin is linked to lower reactivity due to the presence of more carbohydrates.³⁶

Chemical reactions occurring during kraft pulping can be broken into two categories: degradation and condensation.³⁴ Degradation is a favorable reaction since it enhances lignin solubility and liberates lignin fragments from pulp. The two most important degradation reactions are the cleavage of α and β -aryl ether bonds.³⁷ If no free or etherified phenolic group is present, the reaction is less likely to happen and a condensation reaction can take place instead.³⁴ The β -aryl ether linkage is the most copious unit in lignin.³⁴ When this linkage is broken, phenolic hydroxyl groups are

created increasing the solubility (water/alkali) ³⁴ and reactivity of the lignin.²⁹ The cleavage of this linkage is the principal pathway in kraft isolation/pulping.³⁴ Of the ether bonds present in lignins, only the four aryl ether bonds can be cleaved by the kraft process; all others are virtually stable and remain essentially unaffected.³⁸ It has been estimated that there are 27 phenolic hydroxyl groups per 100 C-9 units, falling in between wood lignins (around 13/100) and other dissolved lignins (60-70/100).³⁹ Phenolic hydroxyl content is an important factor since it enhances the solubility of lignin in aqueous solutions, in kraft pulping specifically.⁴⁰ The sulfur present in the pulping liquor cleaves most methyl aryl ether bonds which creates methyl mercaptan and dimethyl sulfide which are responsible for the foul odor produced by kraft lignins.⁴¹

The second category of reactions during the kraft process are condensation³⁴ also known as conjugate additions. These reactions are usually unfavorable due to their interference with delignification⁴² because of the increase in molecular weight and possible precipitation.³⁶ Condensed lignin structures refer to groups of lignin that contain substituents at the C-5 or C-6 position of the aromatic ring, usually alkyl or aryl.³⁴ Catechol structures are also formed during the kraft cooking process.⁴³ They are created by the demethylation reaction of aromatic methoxy moieties.³⁷ Oxidation can cause the creation of *0*-quinones which one of multiple chromophoric groups responsible for the color of kraft pulps.⁴⁴ Though the presence of other structures in lignin are small, the kraft process also has an effect on *p*-hydroxyphenyl and carboxylic acid content of lignins. The kraft process has been shown to decrease the amount of *p*-hydroxyphenyl compared to normal wood, compression wood, and milled wood lignin.⁴⁵ Other reactions

include the creation of biphenyl and condensed structures caused by high temperatures (423-453°K) and pH (10+) which can increase with the duration of cooking (1-2+ hours).^{29,31} Though this process dissolves lignin fragments and breaks down native protolignin, it cannot break all lignin-carbohydrate complexes.⁴⁶ This can result in a high amount of residual sugars and other minerals. The high ash content of lignin after cooking is removed by washing with water and sometimes a treatment of sulfuric acid, creating higher purity lignins.³⁴ Other factors during cooking that can affect kraft lignins are oxidation. Oxidative conditions in the process system can cause quinine, catechol, and carboxyl structures/functional groups to form.³⁴

The commercial kraft process is mostly utilized for softwood and hardwood sources respectively, but some bagasse and other grass sources have been used. Since the structural makeup of hardwoods, softwoods, and grasses vary it is important to note their differences. The variation between softwood species has been reported to vary very little.⁴¹ As opposed to hardwoods that vary greatly between species.⁴⁷

1.6.3 Sulfite

Lignosulfonates are a byproduct of sulfite cooking and are extracted via sulfite and hydrogen sulfite ions.⁴⁸ More specifically, the sulfite pulping process is accomplished using a mixture of sulfurous acids and alkali at a pH of 1-2 and temperatures between 130-170°C to extract lignin from wood. ⁴⁹ This results in water soluble lignin with numerous charged groups like sulphonic, phenylic hydroxyl, and alcoholic hydroxyl.⁵⁰ These groups enhance hydrophilic properties of lignin and increase their solubility in water.

The pH of the sulfite pulping process varies from 1-5 but some neutral, semichemical pulping occurs at 5-7 pH. Along with reaction conditions, solvents will determine the final properties of lignosulfonate lignins. The most commonly used solvents are sodium, calcium, and sometimes, magnesium or ammonium based hydroxides.⁵¹ The two main reactions when creating lignosulfonates via sulfite pulping are sulfonation and hydrolysis. Sulfonation occurs at the α position which creates benzyl sulfonic acid units. Using acidic over neutral conditions allow for hydrolysis to occur not only with phenolic-type intermediates, but the beta position as well; allowing for the depolymerization reaction of the beta aryl ether bond.⁵¹

Lignosulfonates contain more sulfur groups and have been reported to have higher average molecular weights than kraft lignins.⁵² Properties of lignosulfonates include high polydispersity index, molecular weight, ash, and colloidal properties.⁵³ Since lignosulfonates are water soluble, unlike kraft and soda lignins, they cannot be precipitated by acidification.⁵⁰ After the cooking process, lignosulfonates must be separated from spent liquor. The spent liquor contains mostly lignin, hemicellulose, and inorganics. Industry utilizes membrane filtration to recover lignosulfonates due to their high molecular weight, which allows for effective separation.⁵⁰ Another separation method is ultrafiltration. This method outperforms traditional membrane separation but is not as economical.⁵⁰

1.6.4 Soda

The soda process was the first chemical pulping method whose creation led to the creation of kraft pulping.²⁷ Patented in 1845, the soda process now focuses on the

isolation of annual crops and is the preferred method due to its economic viability.²⁷ The soda process is a sulfur-free system which makes its lignin closer to native lignins than other isolation processes like sulfite and kraft.⁵⁴ In brief, the soda process is an alkaline pulping process (13-16% sodium hydroxide, sodium carbonate, and/or calcium oxide) where fibrous material is mixed in a pressurized reactor (140-170°C) at a ratio of 5:1.²⁷ In this liquid phase, the liquid is called black liquor. The black liquor is then separated from the solid phased, called liberated cellulose or pulp.²⁷ The pulp goes on for further processing while the black liquor goes through evaporation, combustion, and causticisation in order to recover alkaline solvents and return them to the processing system.²⁷ The combusted black liquor creates a sodium oxide (fly ash) which is dissolved in water and reacted with calcium carbonate in order to recover more soda.²⁷ This creates calcium oxide as a byproduct.²⁷ The presence of silicate ions in non-wood plant materials cause issues with this process, specifically salt recovery (sodium carbonate), scaling, and high viscosities.²⁷

1.6.5 Organosolv

The organosolv process uses a mixture of solvent(s), acetic acid, formic acid, peroxiorganic acids, and ethanol during its alkaline cooking process⁵⁵ in order to solubilize lignin and hemicellulose. Invented as an environmentally benign alternative to kraft pulping in 1968, organosolv lignin has high quality and is less chemically modified than other processes like kraft and soda.²⁶ Organosolv lignins generally have low molecular weights and have very high purity.

1.6.6 Hydrolysis

The hydrolysis process is used by cellulosic ethanol plants on wood and nonwood biomass sources. In general, hydrolysis lignins can be broken into two categories: acid and alkaline.⁵⁶ Acid hydrolysis lignin is created using organic or inorganic acids, including formic and acetic or sulfuric and hydrochloric, respectively.⁵⁷ This process breaks down lignocellulose via hydronium ion breakdown along with inter/intramolecular bond attack between cellulose, hemicellulose, and lignin. Various acids and acid concentrations are utilized in acid hydrolysis biomass fractionation, specifically HCL, H₂SO₄, and HNO₃.⁵⁶ Alkaline hydrolysis is done under milder conditions than acid using NaOH, KOH, and Ca(OH)₂, to name a few.⁵⁸ This form of hydrolysis saponifies intermolecular ester bonds, causing crosslinks between hemicellulose and lignin while swelling cellulose. This leads to destruction in lignin/carbohydrate linkages and in the lignin itself, i.e., glycosidic ether bonds.⁵⁶

1.6.7 Lignin Modification Methods

Native and even commercially extracted lignins are difficult to fully characterize due to their complex, phenol-rich, 3D structure. Additionally, lignin tends to agglomerate due to van der Waals chain attractions, strong hydrogen bonding, and π - π aromatic ring stacking in lignin, causing issues with compatibility in various polymeric applications.⁵⁹ Because of this, lignins are often modified to increase solubility, reactivity, and their hydroxyl content.⁶⁰ Lignin modifications produce either solid or liquid lignin products. Lignin modification methods that create solid lignin products include: phosphorylation,⁶¹ oxidation²¹, acetylation,⁵⁹ and oxyalkylation.⁶²

The phosphorylation of lignin is performed to improve fire behavior, increase reactivity and analysis ability of lignin using ³¹P NMR/¹H NMR.⁶³ Phosphorylation imparts phosphorus onto lignin chains to combine the charring properties of lignin with the flame-retardant properties of phosphorus. The phosphorylation of lignin is usually completed using a mixture of 60-85% phosphoric acid in deionized water.⁶¹ After stabilization at 80°C, urea is added to the acid and stirred. After the urea is fully dissolved, the lignin is then added under vigorous agitation. Upon completion of the reaction, the solution is dried, washed with ethanol, and redried to obtain solid lignin powder.⁶¹

Oxidation significantly decreases the molecular weight of lignin which can be beneficial in numerous applications.²¹ Oxidated lignin is obtained by mixing NaOCl solution with lignin in a 30°C-water bath. After ~10 minutes, HCL is added to precipitate lignin at around pH 2.²¹ The precipitate is then washed with distilled water, dried, and ground.

Lignin acetylation is usually performed to increase the solubility of lignin in various analytical solvents, decrease hydroxyl groups of lignin, and decrease the agglomeration of lignin particles.⁵⁹ Acetylation can be performed by treating lignin with acetic anhydride to replace hydroxyl groups of lignin with acetyl groups^{59,64} with pyridine⁵⁹ as solvent and 1-methylimidazole can as a catalyst.⁶¹ The reaction is stopped by incorporating cold deionized water into the reaction vessel to precipitate lignin, and the final solid lignin is obtained by centrifugation⁶¹ or oven drying.⁵⁹

Oxyalkylation uses propylene carbonate to liquefy lignin at a ~10:1 ratio, along with potassium carbonate as a catalyst (~0.1).⁶² This reaction takes place under a nitrogen atmosphere at around 170°C for 3 h. After completion, the solution is then precipitated with deionized acidified water, membrane filtered, washed, and oven-dried. This final solid lignin product has solely aliphatic hydroxyl groups, decreased total hydroxyl content, and increased bulk molecular properties.⁶² Along with oxyalkylation, hydroxymethylation increases bulk molecular properties and thermal stability of lignin while creating a solid lignin product.⁶⁵ Hydroxymethylation of lignin is done by reacting technical lignin with formaldehyde using 1:2-6 molar ratios of lignin to formaldehyde along with 0.1-3 parts of sodium hydroxide as catalyst.⁶⁵

In addition to the lignin modifications that create solid products, there are various lignin modification techniques that create liquid lignin products. These methods have been reported to significantly increase hydroxyl content, specifically aliphatic, of lignin samples.⁶⁶ One of the most popular lignin modification methods with liquid products is oxypropylation. Other liquefaction methods utilize various co-polyols, catalysts, and elevated temperatures to liquefy lignin.^{68,71–77}

Oxypropylation of lignin is done to not only liquefy lignin but also convert various phenolic hydroxyl groups to majority aliphatic while significantly decreasing molecular properties (weight, number, and polydispersity).⁶⁷ In general, oxypropylation is carried out in a parr reactor using lignin, propylene oxide as a solvent, and potassium hydroxide as catalyst.^{68–74} The solution of lignin, propylene oxide, and catalyst (~1:5:0.5 ratio) is

heated to ~150°C with a pressure of ~2 MPa, and after cooling, a liquid lignin polyol is obtained.

General liquefication of lignin is usually performed using various polyols, elevated temperatures, and a plethora of catalysts.^{16,66,81,71,72,75–80} Some common co-polyols used in liquefaction are polyethylene glycol, glycerol, and castor oil, while common catalysts included in lignin liquefaction are sulfuric acid and sodium hydroxide.^{71–77} Reaction conditions for lignin liquefaction use 80/20 wt./wt. of polyol/lignin and 10-20/1 wt./wt. sulfuric acid/lignin under reflux at 130-170°C for 1-3 hours.⁸² After liquefaction, a dark, thick mixture is usually obtained that has excessive amounts of catalyst. This excess catalyst is usually neutralized with aqueous sodium hydroxide, and rotary evaporated to remove water.⁸³ The final liquid lignin product contains ~30% of lignin and enhances reactivity due to its liquid state.

1.7 Lignin-Based Rigid Polyurethane Foam

No studies outside of this dissertation work have focused on lignin for use in lowdensity rigid PUR/PIR foam formulations. Lignin has been incorporated as polyol replacement in rigid PUR foam creating high and low-density (LD) foams; with most works reporting high-density foams (HD).⁸⁴ Lignins were incorporated into these PUR foams as unmodified solids (HD),^{14,85–87} unmodified solid fillers (LD and HD),^{9,88–91} modified solids (HD and LD),^{92,93} and most popularly, modified liquids (HD and LD).^{14,16,96,72–74,79–81,94,95} Additional lignin incorporation methods include prepolymer synthesis^{60,97} and surface/post functionalization^{49,98} of foam. In general, the incorporation of lignin into rigid PUR foam increases the mechanical strength,^{71,72,80} fire

resistance,^{80,93} and biodegradability of the foam^{14,84} But, too much lignin significantly increases polyol blend viscosity,^{79,86} decreases mechanical properties, ^{70–72,80} and creates inhomogeneous foam.^{70,79,80,99}

1.7.1 Incorporation of Unmodified Lignin in Rigid Polyurethane Foam

Using unmodified lignin (wheat straw organosolv^{88,89} and hardwood kraft^{9,90,91}) as filler in rigid polyurethane foam adds up to 20% (parts per hundred polyols) of lignin into the foam,^{9,88–91} which has been reported to reduce water uptake of foam,⁹ increase oil sorption capacity,⁹¹ decrease cell size,⁹ decreased thermal conductivity,⁸⁸ and increase color stability.⁹⁰ Negative effects of lignin as filler in rigid PUR foam begin at 2% (parts per hundred polyol) lignin loading and include decreases in compression strength,⁹ foam reactivity,^{88,89} increased viscosity⁸⁹ and water uptake.⁸⁸ This reduction in foam properties with unmodified lignin as filler is due to increases in viscosity with increased lignin content which increases cell size, decreases foam reactivity, and creates weak urethanic linkages within filled foams.⁹

Higher lignin incorporation percentages (~40%) can be achieved with using unmodified lignin as polyol replacement in high-density (HD) rigid foam since lignin can react with isocyanate to form polyurehane.^{85–87,90} The one study that reported low-density (LD) unmodified lignin-based foam did not meet minimum compression strength requirements for rigid foam.⁸⁷ The addition of unmodified lignin into HD rigid PUR foams significantly reduces foam density^{85– ⁸⁷ and compression strength^{85–87} while increasing bending strength⁸⁵ at all lignin}

loading percentages. Up to 15% loading, the incorporation of unmodified lignin into HD rigid PUR foam significantly increased bending strength of foam.⁸⁵

Though most unmodified lignin-based PUR foam studies report the use of one lignin (hardwood kraft⁸⁵ or corncob⁸⁷), Pan and Saddler⁸⁶ used two different lignins to replace ~40% of polyol in HD rigid PUR foam. All lignin-based foams had significantly lower mechanical properties than the control, but the use of hardwood organosolv lignin over hardwood kraft lignin created foams with lower polyol blend viscosities and higher compression strengths.⁸⁶ These improved properties are reportedly due to the enhanced lignin solubility in petroleum-based polyol provided by the organosolv isolation process, even though the hardwood kraft lignin had lower molecular weight and higher hydroxyl content.⁸⁶

Properties of unmodified lignin-based foams can be enhanced via lignin dispersion in petrochemical polyol with up to 25% replacement.^{14,79,81} Dispersion utilizes a small amount of lignin 2-25%, elevated temperature, and rigorous stirring or sonication for up to 6 hours to liquefy/disperse lignin.^{14,79,81} Luo et al.¹⁴ reported that the incorporation of up to 25% unmodified lignin (source and isolation process not reported) as polyol replacement in HD rigid PUR foam increased specific modulus compared to the control. Additionally, the enhancement of biodegradability¹⁴ and thermal conductivity⁸¹ properties were reported up to 25% loading.

1.7.2 Incorporating Modified Lignins in Rigid Polyurethane Foam

Common lignin modifications include oxypropylation,^{68–74,95,100} liquefaction,^{16,72,76,80,101} and functionalization/fractionation.^{65,93,94,96} These methods produce lignin that is either a liquid polyol (oxypropylation and liquefaction) or precipitated solid (functionalization/fractionation) that is then incorporated into foam. The most popular lignin modification techniques are oxypropylation and liquefaction using co-polyol.⁸⁴ Both techniques liquefy lignin, making it easier to incorporate into liquid polyurethane precursors. Oxypropylation not only liquefies lignin but also converts phenolic hydroxyl groups to more reactive aliphatic hydroxyl groups while significantly reducing lignin molecular weight and polydispersity properties.⁶⁷

Researchers have used varying ratios of lignin, propylene oxide, and catalyst to replace 10-100% of petrochemical polyols with the resulting lignin polyol in high and low-density rigid PUR foam.^{68–74,95} When softwood kraft, nonwood soda, and hardwood organosolv lignins were oxypropylated and used to formulate foam at 50 and 100% polyol replacements, hardwood organosolv and softwood kraft lignin polyols performed best.⁶⁹ Foams made with the oxypropylated non-wood soda lignin created brittle, untestable foams, while the softwood kraft oxypropylated lignin polyol performed better but still decreased compressive modulus and thermal conductivity ompared to the control foam.⁶⁹ Similarly, oxypropylated softwood and hardwood kraft lignins outperformed nonwood soda lignin in thermal conductivity and dimensional stability.⁶⁸ The

decrease in performance with the non-wood lignins is reportedly due to large and heterogenous cell size/distribution of formulated foam.⁶⁹

Liquefied lignins are obtained using 5-30% lignin. Common liquefying agents include various co-polyols like polyester polyol,⁷⁹ diethylene glycol,^{77,80,81} soyoil,¹⁴ glycerol,^{16,72,76} and ethanol/water/acetone solutions.^{75,102} In general, solid lignin is dispersed in solvent and catalyst at elevated temperature and pressure to liquefy lignin. Then the liquefied lignin polyol is used to replace 10-100% of petrochemical polyol in rigid PUR foam. In general, liquefied lignin increases density and compression strength with up to 50% petrochemical polyol replacement.⁸⁰ Above 50% polyol replacement with liquefied lignins, the compression strength decreases compared to control formulations.^{72,77}

Up to 30% polyol substitution has been reported for solid modified lignin incorporation into rigid polyurethane foams. ^{65,93,94} The incorporation of hydroxymethylated lignin decreased apparent density while decreasing foam compression strength in low-density polyurethane foams.⁶⁵ The low-density foams⁶⁵ did not meet minimum compression strength requirements for rigid foam application (>104 kPa) but the high-density formulations exceeded minimum requirements and even outperformed the control.⁹⁴ Jeong et al.⁹³ used sodium hypochlorite (NaOCl) along with elevated temperature (100°C) to modify kraft lignin. This modification created solid lignin with significantly higher dissolution levels in the water. Polyurethane foams made with these lignins, up to 6% wt.

polyol replacement, showed a 27.3% reduction in heat release rate (HRR) compared to the control with no lignin.⁹³

1.7.3 Lignin Prepolymer Synthesis and Surface/Post functionalization in RigidPolyurethane Foam

Lignin has also been incorporated into polyurethanes as a prepolymer^{60,97} and through surface/post functionalization.^{49,98} Cao et al.⁶⁰ used gradient acid precipitated corn straw bagasse lignins to create a lignin prepolymer that was then used to replace 25% and 50% of petrochemical polyol in rigid polyurethane foam. The lignins were mixed with silicone oil and excess isocyanate, then heated to 80 °C, and mixed at 800 rpm for 30 minutes. The lignin prepolymers were then reacted with additional polyols and additives to create low-density rigid polyurethane foams. The 25% lignin-based foams with higher adjusted pH (>5) were found to outperform the control in compression strength and thermal conductivity testing. While, the 50% lignin-based foams had a combination of higher foam apparent densities, compression strength, and thermal conductivities compared to the control.⁶⁰

1.8 Objectives

The main objectives of this work were to fill the knowledge gaps around lignin-based rigid PUR and PUR/PIR foams by:

• Expanding testing of lignin-based rigid foams based on polyurethane industry suggestions and ASTM International standard requirements for rigid foams

- Utilizing a wide range of lignin to determine the effect of lignin properties on rigid PUR/PIR foam performance
- Determine the maximum amount of lignin in rigid PUR and PUR/PIR foam while evaluating the effect of increasing lignin content on foam properties
- Evaluating the effect of molecular weight on lignin-based rigid PUR/PIR foam performance

To achieve this, we first substituted 30 wt.% of petrochemical polyols with nineteen different lignins using a one-pot method. After this, we used one lignin, optimized based on the percent lignin substitution, to determine the maximum loading percentage of lignin in PUR/PIR and PUR foams while evaluating the effect of lignin loading on foam properties from 0-100% lignin loading. Lastly, we evaluated the effect of molecular properties of lignin on foam performance by using a feed hybrid poplar lignin and fractionated hybrid poplar lignin to replace 80% of petrochemical polyol in PUR/PIR foam. All formulated foams were compared to control foams made with no lignin along with ASTM International requirements for foam reactivity, compression strength, closed cell content, cell size, and thermal conductivity.

1.9 Hypotheses

- 1. Lignins with the following properties will make better rigid foams:
 - >274 mgKOH/g hydroxyl values
 - Moderate molecular weight ($\leq \sim 5000 \text{ Da}$)
 - More neutral pH (> 4.0)
 - Low polydispersity index (<2.5)

2. Higher substitution percentages of petrochemical polyol with lignin will be achieved with PUR/PIR formulations compared to PUR due to lignin impurities acting as trimerization catalyst.

CHAPTER 2

STUDYING THE SUITABILITY OF NINETEEN LIGNINS AS PARTIAL POLYOL REPLACEMENT IN RIGID POLYURETHANE/POLYISOCYANURATE FOAM

2.1 Abstract

In this study, nineteen unmodified lignins from various sources (hardwood, softwood, wheat straw, and corn stover) and isolation processes (kraft, soda, organosoly, sulfite, and enzymatic hydrolysis) were used to replace 30 wt.% of petroleum-based polyol in rigid polyurethane/polyisocyanurate (PUR/PIR) foam formulations. Lignin samples were characterized by measuring their ash content, hydroxyl content (Phosphorus Nuclear Magnetic Resonance Spectroscopy), impurities (Inductively Coupled Plasma), and pH. After foam formulation, properties of lignin-based foams were evaluated and compared with a control foam (with no lignin) via cell morphology, closed-cell content, compression strength, apparent density, thermal conductivity, and color analysis. Lignin-based foams passed all measured standard specifications required by ASTM International C1029-15 for type 1 rigid insulation foams, except for three foams. These three foams had poor compressive strengths, significantly larger cell sizes, darker color, lower closed-cell contents, and slower foaming times. The foam made with corn stover enzymatic hydrolysis lignin showed no significant difference from the control foam in terms of compressive strength and outperformed all other lignin-based foams due to its higher aliphatic and p-hydroxyphenyl hydroxyl contents. Lignin-based foams that passed all required performance testing were made with lignins having higher pH, potassium, sodium, calcium, magnesium, and aliphatic/p-hydroxyphenyl hydroxyl group contents than those that failed.

2.2 Introduction

Rigid polyurethane foams are widely used in structural and insulative applications because of their combination of good adhesion to various substrates, low-density to high-compression strength ratio, and high thermal insulation properties.² Polyurethane (PUR) and polyisocyanurate (PIR) foams are the two main types of isocyanate-based rigid foams using urethane chemistry.³ Rigid polyurethane foams are created by the step-growth polymerization reaction of polyisocyanates and polyols in the presence of additives, including catalysts, surfactants, and blowing agents. Polyisocyanurate foams are prepared by reacting an excess of isocyanate (200– 350 isocyanate index²), polyol, and additives, including trimerization catalysts such as amines, bases, and metal oxides.¹ Due to stricter worldwide fire regulations, polyisocyanurate foams have become more popular since their commercialization in 1996.^{2,3} Trimerization of isocyanate in polyisocyanurate foams results in improved fire performance and decreased smoke generation compared to polyurethane foam.^{15,17,103} Because pure polyisocyanurate foam creates brittle products, a mixture of polyurethane and polyisocyanurate (PUR/PIR) is used for most applications.⁴

The increase in polyurethane foam consumption, fluctuations in the price of polyurethane raw materials, and the toxicity of the raw materials used for manufacturing polyols (e.g., propylene oxide) all have pushed researchers to find greener alternatives.^{21,104} Lignin, the most abundant natural aromatic polymer on earth, has excellent potential to replace petrochemical polyols due to its hydroxyl functional groups that can react with isocyanate to form polyurethane linkages.^{97,105–107} Lignin is a byproduct of chemical pulping and bioethanol production, and only 2–5% is used in value-added products.^{108–110} The renewable fuel standard program announced that 60 billion gallons

of biofuel will be produced by 2030,¹¹¹ which will further increase the supply of lignin, encouraging lignin valorization.¹¹² The addition of lignin into polyurethanes has been reported to improve antioxidant,¹¹³ antimicrobial,¹¹⁴ fire resistance,⁹⁶ and biodegradability properties.¹⁴

Unmodified, lignin-based rigid polyurethane (PUR) foams have been successfully formulated by replacing up to 30 wt.% of the petrochemical polyol, with the majority of the work focusing on high-density foams (>60 kg/m³).^{14,80,85–87} Luo et al.¹⁴ incorporated 0–25% lignin, dispersed in soy polyol for 3 h, into high-density rigid PUR foam. They reported that incorporating lignin decreased foam density while improving biodegradability, as well as the mechanical and thermal properties of the foams.¹⁴ Pan and Saddler⁸⁶ compared the performance of high-density rigid PUR foams made by substituting 19–30% of a commercial polyol with organosolv and kraft hardwood lignins. They found that foams made with hardwood organosolv had higher compressive strength than the foams made with hardwood kraft lignin due to better miscibility of the organosolv lignin in the petroleum-based polyol. Compared to the control foam without lignin, they reported that incorporation of both lignins decreased foam density and compression strength.⁸⁶ Liu et al.⁸⁵ replaced 15 wt.% of a petroleum-based polyol with refined alkali lignin in the formulation of highdensity rigid PUR foam and reported that lignin-based foams had lower apparent density and thermal conductivity than the control foam. The incorporation of unmodified lignin in low-density rigid PUR foam significantly increased polyol viscosity over 6.3 wt.% lignin loading (high-density foams were produced above 4.3 wt.%).⁸⁸ At 1.2 wt.% lignin loading, the maximum compression strength of lignin-based foam was greater than the control. However, compression strengths of lignin-based foams decreased over 2 wt.% lignin loading while foam densities increased.⁸⁸ Xue et al.⁸⁷ reported that compression strength and density of lignin-based low-density polyurethane foams decreased with lignin addition (high-density foams were made up to 16% lignin loading and lignin loading above 24% created low-density foam). Low-density lignin-based rigid PUR foams did not meet compression strength requirements for insulative applications.⁸⁷

A knowledge gap exists in using lignins in low-density polyurethane/polyisocyanurate (PUR/PIR) rigid foam applications. Previously, sorbitol,¹⁵ tannin,¹⁷ crude glycerol, algae, and castor oil ¹¹⁵ have been used to formulate low-density PUR/PIR foams at various polyol replacement percentages (10–100%). This is the first study to focus on partially replacing petrochemical polyol in low-density PUR/PIR rigid foam with unmodified lignin while comparing the suitability of a wide range of unmodified, mostly industrially isolated lignins. As the molecular structure of lignin varies considerably based on both source and isolation method,^{86,116,117} it is crucial to characterize lignin samples to determine their differences and choose the most suitable lignin for a specific application. Utilizing a wide variety of unmodified lignin to prepare low-density rigid PUR/PIR foams will help elucidate the best lignin for PUR/PIR foam applications.

In this study, nineteen unmodified lignin samples were analyzed and used to replace 30 wt.% of petrochemical polyol in rigid PUR/PIR foam formulations. Thirty percent polyol substitution was chosen based on previous works in the literature that reported a decline in foam properties with higher than 30 wt.% loading of unmodified lignin.^{84,87} The objective of this research was to determine the most suitable lignin for rigid PUR/PIR foam applications and study the correlations between lignin properties and foam performance.

2.3 Materials and Methods

Commercial lignin samples from hardwood (HW), softwood (SW), corn stover (CS), and wheat straw (WS) sources and from enzymatic hydrolysis (E), sulfite or lignosulfonate (L), soda (S),

organosolv (O), and kraft (K) processes were purchased from or provided by lignin producers and used without further modification. Huntsman LLC. (The Woodlands, TX, USA) graciously provided foam raw materials. As shown in Table 2.1, formulations included polymeric methylene diphenyl diisocyanate (pMDI), polyol (polyester-based), surfactant (polyalkylene), catalysts (amine), blowing agents (water and n-pentane), viscosity reducer, and phosphate-based flame retardant. Other reagents for lignin characterization, including tetrahydrofuran (THF), pyridine, and acetic anhydride, were purchased from Fisher Scientific (Waltham, MA, USA) and were used as received without any further purification.

Raw Materials (g)	Control Foam without Lignin	30 wt.% Polyol Substitution with Lignin
Polyol	15	10.5
Lignin	0	4.5
Viscosity Reducer	1.5	1.5
Water	0.04	0.04
Surfactant	0.15	0.15
Catalysts	0.76	0.76
Flame Retardant	1.5	1.5
Blowing Agent	3.3	3.3
Isocyanate	28.79	28.79

Table 2.1. Foam formulations.

Lignin Characterization Methods

Each lignin sample was sieved using an 80 μ m mesh sieve to reduce the effect of lignin particle size on foam properties. The samples were then oven-dried (80 °C) until a constant weight was achieved to ensure no moisture remained in the lignin to react with isocyanate.

Ash Content

The percent ash content of lignin samples was determined gravimetrically following TAPPI T 211 om-02.¹¹⁸ Firstly, ceramic crucibles were oven-dried at 105 °C to a constant weight, cooled in a

desiccator, and weighed (nearest 0.1 mg). Two grams of lignin were then loaded into each crucible, oven-dried at 105 °C to a constant weight, cooled, and weighed. The crucibles were then placed in a Thermolyne Furnatrol muffle furnace (Fisher Scientific, Waltham, MA, USA) and heated with a 5 °C/minute ramp to 525 °C with a 4 h dwell time. Samples were then cooled to 100 °C, transferred to a desiccator, and weighed. Percent ash was then determined from the weight of ash and of oven-dried lignin.

Impurity Analysis

To determine the effect of impurities, the amount of calcium, sodium, magnesium, and potassium in lignin samples were measured (A&I Great Lakes Laboratories, Fort Wayne, IN, USA). Lignin samples were prepared following the 922.02 ¹¹⁹ and 980.03 ¹¹⁹ methods developed by the Association of Analytical Chemists (AOAC). In brief, samples were ground using a Wiley Mill (#10 sieve) and oven-dried at 105 °C overnight. After preparation, lignin samples (0.2 g each) were open vessel microwave digested (MARS 5, CEM Corp, Matthews, NC, USA) following SW 846-3051A ¹²⁰ in a two-step process. First, samples were diluted with 2 mL of nitric acid, heated up to 90 °C, and held at that temperature for 90 s. Second, the solution was cooled to 50 °C; then, 1 mL of peroxide was added, and the solution was heated to 105 °C and held at that temperature for 10 min. The samples were cooled and brought to a final dilution volume of 25 mL with peroxide and analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES), Thermo Scientific iCAP 6000 series 6500 Duo, according to AOAC 985.01.¹²¹ Multi-element standards from Inorganic Ventures (Christiansburg, VA, USA) along with a blank sample were used for calibration.
pH Measurements

The pH of lignin samples was determined in at least triplicate by adding 0.1 g lignin in 10 mL distilled water and stirring for 5 min at 350 rpm. Stirring was stopped 20–30 s before measuring the pH on a Fisher brand Mettler Toledo SevenCompact pH/Ion meter (Columbus, OH, USA).

Hydroxyl Content

The hydroxyl content of each lignin was determined using phosphorus nuclear magnetic resonance (³¹P NMR) spectroscopy following previously published methods.^{26,122,123} First, 40 mg lignin was dissolved in a solvent solution (325 μ L, 1.6:1 ν/ν) of pyridine and deuterated chloroform along with 300 μ L of dimethylformamide (DMF). Then 100 μ L of cyclohexanol solution (22 mg/mL in anhydrous pyridine and deuterated chloroform, 1.6:1, ν/ν) was added as an internal standard. In the next step, 50 μ L of chromium (III) acetylacetonate solution (5.8 mg/mL in anhydrous pyridine and deuterated chloroform (1.6:1, ν/ν). Lastly, 100 μ L of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was added as phosphitylation reagent. The spectra were acquired using an Agilent DDR2 500 MHz NMR spectrometer (Billerica, MA, USA) equipped with 7600AS, running VnmrJ 3.2 A. Data were obtained using a 5 mm tube (600 μ L solution), a 90° pulse angle flip with a relaxation delay of 5 s, and 128 scans. Hydroxyl values were then calculated for each lignin by multiplying the total hydroxyl content in mmol/g by 56.1 (mass of KOH) ^{2.26}.

Foam Preparation Methods

All foam samples were formulated in accordance with the standard practice for polyurethane raw materials: polyurethane foam cup test ASTM D7487-13¹²⁴ using a 237 mL cup. B-side polyol blends were prepared by mixing specified amounts of polyol, lignin, catalysts, surfactant, and

blowing agent in a predetermined ratio (Table 2.1) for thirty seconds using an overhead digital high-speed mixer (3000 rpm). Isocyanate was added to the polyol blend and mixed until the heat was felt on the outside of the cup. Foam reaction time was determined by measuring various characteristics, including mix, cream, top of the cup, tack-free, and end of rise times ^{75,106}. These measurements allow for the prediction of mixture reaction time and foam performance in industrial applications ⁴, specifically spray polyurethane foams. In brief, the timer was started after isocyanate was poured into B-side components for 3 s. The first measurement, "mix time", was taken once the heat was felt on the outside of the cup, showing the onset of the isocyanate and water reaction. Cream time was measured when the mixture turned to a creamy color and began to rise. The top of the cup (time) was recorded once the foam reached the top of the cup, and tack-free time was noted when the skin/surface of the foam could be touched without sticking. End of rise time was taken when the foam stopped rising, signaling the end of major reactions. Foams with tack-free times higher than three minutes were assigned a value of 300 s.

Foam Characterization Methods

Foam properties were measured at least 72 h after formulation. After 24 h, samples were cut to size using a razor blade and a tabletop band saw (Grizzly G0803Z). After cutting, samples were stored at room temperature for at least 48 h before each analysis.

Foam Lightness

Foam lightness was determined using the CIEL*a*b* color system as measured with a Konica Minolta CM-2300d spectrophotometer (Ramsey, NJ, USA) using the L* measurement (L* or lightness ranges from 0–100 with 0 being the darkest and 100 being the lightest). Three

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measurements were taken on each foam sample 25 mm below the top of the cut foam (perpendicular to the foam rise direction) and averaged.

Apparent Density

The apparent density of formulated foams was determined according to ASTM D1622 ¹²⁵. Twentyfive-millimeter cube samples were measured volumetrically to 0.01 mm using a digital caliper. Each side was measured three times and averaged. The weight of each cube was measured using a digital scale (0.0001 g). Averages of at least five foam samples were used to calculate the density reported in kg/m³. Foams were not reformulated to have the same density in order to allow us to measure the effect of lignin properties. The effect of density has been reported as insignificant when rigid foams are within the range of 30–60 kg/m.³⁴

Compression Strength

The compression strength of each foam sample was determined via ASTM D1621-16¹²⁶ using an Instron 5565 universal testing machine (Norwood, MA, USA). Twenty-five-millimeter cube samples were tested perpendicular to the foam rise in at least triplicate using a 2.5 mm/min strain rate until specimens were 13% of their initial thickness. Compression strength was recorded for each sample as the maximum compressive stress divided by the initial cross-sectional area of each specimen.

Cell Size

The average cell size (diameter) of each foam sample was measured using a Dino-Lite Edge digital microscope (Torrance, CA, USA) following a modified version of ASTM D3576-15¹²⁷. Three-millimeter slices were cut from 25 mm below the top of each foam. Cell size was calculated by

averaging the size of at least twenty cells ($160 \times$ magnification) from formulated foams perpendicular to the foam rise.

Closed-Cell Content

Closed-cell content was determined according to ASTM D6226-15.¹²⁸ A micromeritics gas pycnometer (AccuPyc II 1340, Norcross, GA, USA) under nitrogen atmosphere was used to perform the analysis following micromeritics method B.¹²⁹ Analysis conditions included 10 purges and 10 cycles along with 27.58 kPa purge and cycle fill pressures at 0.03 kPa/min. First, the foam resin density was found by grinding 12 g of foam and running the sample using the above conditions. The resin density was then entered into the pycnometer to begin closed-cell content analysis. Two 25 mm cube samples were weighed, run, cut three times, and run again. Cutting the sample three times doubled the number of cuts, allowing the pycnometer to correct for the cells that were open due to cutting and actual open-cell content.

Thermal Conductivity

Thermal conductivity is the most important property of rigid foams used for insulation application and is usually measured via steady-state heat transfer [1,59,60]. This method is not always feasible for lab-scale foaming due to large sample requirements $(0.3 \text{ m} \times 0.3 \text{ m} \times 0.05 \text{ m})^{13}$. The following needle probe technique has been reported to have accuracy within 5% and has been widely used in liquid and solid material for thermal conductivity measurements.^{13,130} In our study, the thermal conductivity of the foams was determined using a Meter TEMPOS TPA machine (Pullman, WA, USA). Measurements were taken in the center of the foams, perpendicular to foam rise (in at least triplicate) using a 60 mm KS-3 probe. In order to convert thermal conductivity to R Value, the reciprocal of the probe length in meters (0.06 m) divided by the thermal conductivity was taken.

Statistical Analysis

SAS software (Cary, NC, USA) running the GLM procedure was used to compare lignin and foam data. Lignin-based foams were grouped based on pass/fail in compression strength tests and compared to the control foam with no lignin. Tukey HSD was used for mean separation (p < 0.05) between lignin (source and process), lignin-based foam (pass/fail), and control foam data. Outliers were determined using the 1.5 IQR rule. Pearson's correlation was used to assess correlations between lignin and lignin-based foam properties. To obtain more specific correlation data between lignin and foam properties, data were grouped/separated by process and then rerun. Heat maps were created using R Studio: openxlsx, graphics, plyr, corrplot, pairwise.complete.obs, and correlmatcom.

2.4 Results and Discussion

The ash and impurity analysis results of lignin samples are important parameters to consider because high cation levels are known to catalyze both polyurethane (PUR) and polyisocyanurate (PIR) reactions in PUR/PIR foams ², increasing compression and fire properties. However, asynchronous gelling/blowing reactions¹³¹ and too much PIR formation as a result of isocyanate trimerization are known to create brittle foams ⁴. Transition metals, strong bases, alkali metal alkoxides, carboxylic acid salts, acetates, carbonates, carboxylates (K, Na, Ca, Mg, etc.), and various organometallic compounds can also catalyze the isocyanate trimerization (PIR) reaction.^{1,2,4} The maximum acceptable level of potassium and sodium in rigid PUR foams using petrochemical polyols is around 100 ppm or 0.01%.² Ideally, higher cation content (impurities) of lignins would not be as detrimental for PIR/PUR foams and could increase the reactivity of solid

lignins with isocyanate. Impurity analysis results in Table 2.2 show that the majority of lignins had potassium and sodium contents, over the acceptable limit for PUR foams (>0.01%²).

The pH of lignin samples (Table 2.2) ranged from 3.7-7.9 and showed no significant difference based on the lignin source or isolation process. Overall, kraft lignins had the highest average pH (5.4 ± 1.3), followed by enzymatic hydrolysis (5.0 ± 0.2), organosolv (4.6 ± 1.1), soda (4.4 ± 0.3), and lignosulfonate (4.3 ± 0.1) lignins. Maillard et al.¹³² reported that lignin's pH has a significant effect on the reaction time of lignin with isocyanate when used in flexible polyurethane foam. They used kraft lignin with pHs ranging from 2.4–6.6 and observed that foam reaction time decreased with increasing pH.¹³² The decrease in reactivity with acidic lignins and isocyanate is likely due to the neutralization of polyurethane catalysts.¹³²

Label	Ash Content (%)	pН	K (%)	Mg (%)	Na (%)	Ca (%)
1-CS-E	0.63 ± 0.01	4.99 ± 0.16	0.01	0.00	0.03	0.01
2-SW-K	3.92 ± 0.35	6.65 ± 0.11	0.12	0.01	0.68	0.04
3-SW-O	0.37 ± 0.11	5.04 ± 0.58	0.01	0.00	0.01	0.01
4-HW-O	0.13 ± 0.03	6.42 ± 0.44	0.01	0.00	0.01	0.01
5-SW-L	11.5 ± 0.18 *	4.35 ± 0.07	0.22	0.17	0.11	3.81
6-SW-K	1.99 ± 0.20	3.97 ± 0.09	0.16	0.00	0.95	0.01
7-HW-K	1.11 ± 0.07	4.49 ± 0.26	0.06	0.01	0.18	0.06
8-SW-K	0.01 ± 0.01	6.64 ± 0.09	0.04	0.02	0.28	0.05
9-WS-O	0.50 ± 0.17	3.69 ± 0.10	0.01	0.00	0.01	0.01
10-SW-K	0.54 ± 0.02	4.83 ± 0.19	0.02	0.01	0.06	0.03
11-SW-K	0.65 ± 0.01	4.80 ± 0.17	0.02	0.00	0.17	0.01
12-SW-K	0.76 ± 0.02	4.90 ± 0.10	0.02	0.01	0.20	0.01
13-HW-O	0.04 ± 0.02	4.02 ± 0.07	0.02	0.00	0.01	0.03
14-WS-O	0.09 ± 0.03	3.88 ± 0.03	0.01	0.00	0.01	0.02
15-HW-S	0.11 ± 0.05	4.23 ± 0.15	0.15	0.01	0.76	0.17
16-WS-S	0.86 ± 0.15	4.71 ± 0.17	0.00	0.00	0.37	0.02
17-SW-K	0.94 ± 0.01	4.28 ± 0.09	0.03	0.02	0.40	0.04
18-HW-S	4.84 ± 0.09	4.17 ± 0.17	0.86	0.01	0.89	0.02
19-HW-K	5.19 ± 0.01	7.94 ± 0.04	0.28	0.02	1.12	0.17

Table 2.2. Ash, pH, K, Mg, Na, and Ca content of lignin samples.

* Significantly different p < 0.05. CS = corn stover, SW = softwood, HW = hardwood, WS = wheat

straw, E = enzymatic hydrolysis, K = kraft, O = organosolv, S = soda, and L = lignosulfonate.

Hydroxyl content is mostly determined using titration for industrial polyurethane applications,¹³³ but since the dark color of lignin makes it difficult to determine the titration point of the polyol, phosphorus nuclear magnetic resonance spectroscopy (³¹P NMR) was utilized in this study. The percent weight replacement of lignin (30 wt.% of polyol) was used in this study instead of the molar ratio/hydroxyl value replacement of polyol (to calculate isocyanate) to better compare the effect of various lignins on foam performance. Using weight percent substitution instead of equivalent weight/molar ratio allowed us to study the impact of lignin properties (i.e., ash, impurities, and hydroxyl contents) on foam performance. All lignins were within the acceptable hydroxyl value range (>200 mg KOH/g or equal to 3.56 Total OH content in mmol/g)^{2,4} for rigid polyurethane foam production (Table 2.3). It is important to note that the 3.56 minimum does not take individual hydroxyl group types and ratios into account, just the total hydroxyl content. Therefore, more work needs to be conducted to determine the exact amount or ratio of each type of hydroxyl group to create optimal foams. Lignin 5-SW-L was insoluble in ³¹P NMR solvents, so we were unable to measure its hydroxyl value. Lignin 1-CS-E, enzymatic corn stover lignin, had the highest (p < 0.05) aliphatic (3.41 mmol/g), p-hydroxyphenyl (1.16 mmol/g), and total hydroxyl (7.84 mmol/g) contents of all lignins. Hydroxyl contents of lignins were significantly different based on the lignin source and isolation process (p < 0.05).

Tabal	Hydroxyl Content ³¹ P NMR Data (mmol/g)									
Label	Aliphatic	Syringyl	Condensed Phenolic	Guaiacyl	<i>p-</i> Hydroxy Phenyl	Carboxylic	Total OH	(mg KOH/g)		
1-CS-E	3.41 *	0.74	0.39	1.08	1.16 *	1.06	7.84 *	439		
2-SW-K	1.98	-	1.09	1.9	0.24	0.45	5.66	318		
3-SW-O	1.04	-	0.47	1.57	0.18	0.47	3.73	209		
4-HW-O	1.38	1.44	0.43	0.77	0.17	0.32	4.51	253		
6-SW-K	2.10	-	1.31	2.82	0.25	0.68	7.16	402		
7-HW-K	1.09	2.47	0.63	1.03	0.17	0.34	5.73	321		
8-SW-K	2.08	-	1.29	2.13	0.18	0.59	6.27	352		
9-WS-O	0.72	0.79	0.38	0.99	0.35	0.42	3.65	205		
10-SW-K	2.07	-	1.29	2.16	0.19	0.54	6.25	351		
11-SW-K	1.78	-	0.91	2.09	0.27	0.45	5.50	309		
12-SW-K	2.49	-	1.43	2.26	0.24	0.37	6.79	381		
13-HW-O	0.92	1.79	0.89	0.68	0.12	0.28	4.68	263		
14-WS-O	1.12	0.69	0.24	0.87	0.34	0.41	3.67	206		
15-HW-S	1.92	0.42	1.01	2.22	0.29	0.77	6.63	372		
16-WS-S	1.36	1.24	0.42	1.04	0.25	1.18	5.49	308		
17-SW-K	1.51	-	0.62	1.68	0.21	0.39	4.41	247		
18-HW-S	1.80	0.68	0.31	0.64	0.42	1.03	4.88	274		
19-HW-K	1.52	1.93	0.65	0.97	0.13	0.21	5.41	304		

Table 2.3. Hydroxyl content determination results of lignin samples.

*Significantly different p < 0.05. Lignin 5-SW-L was not soluble; thus, we were unable to analyze it.

Figure 2.1 shows foam reaction times, including mix, cream, top of the cup, tack-free, and end of rise times. These reactivity measurements indicate various reactions, including the onset of the isocyanate and water reaction (mix time), the isocyanate and polyol reaction (cream time), blowing activity (top of cup time), foam curing (tack-free time), and lastly, the foam reaction rate (end of rise and total reaction times).^{2,124} It is crucial to control the timing of these reactions to create optimal foam properties such as density, compression strength, and cell size. ⁴



Figure 2.1. Foam reaction time in seconds.

The mix, cream, top of the cup, and end of rise times of lignin-based foams were comparable to the control foam (with no lignin), and statistically, there was no significant difference between them. However, the tack-free time of lignin-based foams, indicating the curing times of foams, were significantly higher (>129%) than the control foam. The higher tack-free times increased the total reaction time of lignin-based foams, making total reaction times of lignin-based foams about 60–400% higher than the control foam without lignin. This result was expected due to the incorporation of solid lignin and has also been observed by previous researchers when incorporating lignin into rigid PUR foam.^{80,88}

On average, the total reaction times for all lignin-based foams were 157% higher than the control, indicating that the reactivity of the foams decreased with the addition of lignin. Since lignin was in a solid-state, unlike the commercial polyol (liquid-state), decreased reactivity was anticipated. The increase in lignin-based foam reaction times is also due to the steric hindrance effect of lignin hydroxyl groups, which decreases their reactivity with isocyanate.^{80,134,135} It has

also been reported that the addition of lignin increases the viscosity of the polyol blend mixture, which also affects foam reactivity by reducing the mobility of raw materials in the solution.^{10,80}

The total reaction time of kraft, soda, and organosolv lignin-based foams negatively correlated with lignin pH, r = -0.4, -0.6, and -0.3, respectively (Figure 2.2). Overall, lignin-based foams made with more alkaline lignins (higher pH) had faster reaction times than lignins with lower pH (r = -0.3). This is because acidic/low pH can neutralize polyurethane catalysts, increasing reaction time. For example, since the kraft isolation process utilizes aqueous sodium hydroxide and various sulfides, the higher pH can lead to phenolic hydroxyl group ionization, increasing lignin solubility (in co-polyol).¹³⁶ This increased solubility of lignin in co-polyol could also improve the reactivity of lignin (reduced reaction time).⁸⁶

Lignin-based foams were 2–50% darker than the control foam with no lignin (measured by spectrophotometer) shown in Table 2.4. This can also be observed in Figure 2.3, which shows all the prepared control and lignin-based foam samples. Foam brittleness and lignin agglomeration can be observed in samples 7-HW-K and 11-SW-K, which affected various foam properties (discussed later). The average foam lightness (the higher the L value, the whiter or lighter the foam) of lignosulfonate foam (78) was significantly higher than enzymatic hydrolysis (69), kraft (57), soda (57), and organosolv (49) lignin-based foams. Though lignin-based foams are darker than the control, the color of foam is not an issue, as the foams would be hidden behind wall or ceiling panels when used for insulation applications.



B: Organosolv Lignin-Based Foams



OH OH OH OOH OH Total_React_Time 0.8 Lightness 0.6 Therm_Cond 0.4 R_Value 0.2 App_Density 0 -0.2 Comp Strength C/D_Ratio -0.4 -0.6 Closed_Cell_Cont -0.8 Cell_Size

C: Soda Lignin-Based Foams

Figure 2.2. Heat map of correlations (r ranges from 1 to -1) between lignin properties vs. ligninbased foam performance based on (**A**) kraft lignin-based foams, (**B**) organosolv lignin-based foams, (**C**) soda lignin-based foams. Values above ± 0.7 show a high correlation

Tahal	Lightness	Cell Size	Closed-Cell	Thermal Conductivity	R-Value
Label	(Color Analysis)	(mm)	Content (%)	(mW/mK)	(Km ² /W at 0.06 m)
Control	81 ± 0.5	0.22 ± 0.02	98.6 ± 0.03	9.2 ± 0.7	6.5 ± 0.6
1-CS-E	69 ± 0.7	0.23 ± 0.01	99.0 ± 0.05	9.1 ± 0.3	6.6 ± 0.2
2-SW-K	61 ± 0.6	0.22 ± 0.01	99.6 ± 0.05	10.1 ± 0.2	6.0 ± 0.1
3-SW-O	47 ± 0.5	0.22 ± 0.01	97.2 ± 0.01	9.9 ± 0.2	6.1 ± 0.1
4-HW-O	49 ± 0.3	0.15 ± 0.01	99.1 ± 0.02	9.4 ± 0.1	6.4 ± 0.1
5-SW-L	78 ± 0.2	0.26 ± 0.02	97.3 ± 0.02	9.2 ± 1.0	6.6 ± 0.8
6-SW-K	58 ± 1.5	0.16 ± 0.02	99.1 ± 0.13	9.8 ± 0.4	6.1 ± 0.2
7-HW-K	41 ± 0.7	0.32 ± 0.02	83.1 ± 0.14	12.9 ± 0.7	4.7 ± 0.3
8-SW-K	61 ± 0.8	0.20 ± 0.03	98.4 ± 0.05	9.0 ± 0.5	6.7 ± 0.4
9-WS-O	45 ± 0.4	0.19 ± 0.02	96.9 ± 0.06	9.4 ± 0.6	6.4 ± 0.5
10-SW-K	64 ± 0.9	0.11 ± 0.02	99.6 ± 0.04	9.3 ± 0.2	6.4 ± 0.1
11-SW-K	54 ± 1.4	0.39 ± 0.04	77.0 ± 0.04	10.9 ± 1.8	5.7 ± 1.0
12-SW-K	67 ± 1.7	0.20 ± 0.00	98.2 ± 0.05	10.2 ± 0.3	5.9 ± 0.2
13-HW-O	55 ± 1.1	0.19 ± 0.03	99.0 ± 0.14	10.0 ± 0.4	6.0 ± 0.3
14-WS-O	48 ± 1.0	0.25 ± 0.03	97.8 ± 0.04	10.1 ± 1.0	6.0 ± 0.5
15-HW-S	58 ± 1.7	0.19 ± 0.02	98.5 ± 0.02	10.5 ± 0.5	5.7 ± 0.3
16-WS-S	63 ± 1.2	0.17 ± 0.00	99.4 ± 0.02	9.7 ± 0.4	6.2 ± 0.2
17-SW-K	60 ± 0.9	0.22 ± 0.04	99.0 ± 0.05	10.5 ± 0.5	5.7 ± 0.2
18-HW-S	55 ± 0.6	0.26 ± 0.01	99.2 ± 0.02	10.4 ± 1.0	5.8 ± 0.4
19-HW-K	50 ± 0.8	0.19 ± 0.01	98.5 ± 0.02	10.1 ± 0.8	6.0 ± 0.4
ASTM	N/A	0.33-0.39 127	90 Min ¹³⁷	<257 138	-

 Table 2.4. Measured properties of formulated foams.

Note: CS = corn stover, SW = softwood, HW = hardwood, WS = wheat straw, E = enzymatic hydrolysis, K = kraft, O = organosolv, S = soda, and L = lignosulfonate. ASTM = ASTM International, American Society for Testing and Materials. R-Value = measure of material's ability to reduce heat flow.



Figure 2.3. Images of lignin-based (30 wt.%) and control foams. Samples 3-SW-O, 7-HW-K, and 11-SW-K failed the compression strength and/or closed-cell content tests.

With respect to density (Figure 2.4), the lignin-based foams (except 5-SW-L) showed no significant difference from the control and were within the acceptable 30–60 kg/m³ range for low-density rigid polyurethane foams. Foams made with enzymatic hydrolysis lignin had an average density (43 kg/m³) that was significantly higher than foams made with kraft (38 kg/m³), soda (37 kg/m³), organosolv (35 kg/m³), and lignosulfonate (28 kg/m³) lignins. Compared to control foams (Figure 2.4), on average, lignin-based foams had 13% lower densities. The decrease in density with lignin addition has been reported in other lignin-based rigid PUR foam studies at 1–15% lignin loading,^{85,88} but to the best of our knowledge, this is the first time this has been reported in low-density lignin-based rigid PUR/PIR foam.

Interestingly, foams made with lignins 7HW-K and 11-SW-K had higher densities than the control foam. Their significantly higher reaction times (447 and 488 s, respectively) compared to other lignin-based foams (< 285 s) can explain their increased density compared to the control foam (as is evident from their photos in Figure 2.3). These two lignins are likely acting as fillers. Moreover, their significantly slower gelation reaction rates lead to more blowing agent loss, which can create foam with higher densities.^{80,139} On the other hand, the small increased density of foams made with lignins 1-CS-E and 17-SW-K is likely due to the increased reactivities in these lignins, creating thicker cell walls and more crosslinking within the foams,¹⁴⁰ which was also confirmed by our compression strength results shown in (Figure 2.4).



Figure 2.4. Compression strength and apparent density of foams. Blue bars failed the compression test (<104 kPa). Note that the axis does not start at 0 for apparent density.

Compression strength is one of the most important properties of rigid foams because it can be a predictor of other foam properties such as volumetric change during the service life of foams.¹⁴¹ All but three lignin-based foams (3-SW-O, 7-HW-K, and 11-SW-K) met or exceeded the 104 kPa minimum compressive strength requirement for type 1 rigid foams.¹³⁷ Eight lignin-based foams also met more stringent compression strength requirements for type 2 rigid foams of 173 kPa (1, 2, 4, 10, 13, 16, 17, and 19). Lignin-based foams that passed the minimum compression strength requirement (orange bars in Figure 2.4) had significantly lower reaction times, apparent density, cell size, and thermal conductivity than those that failed (blue bars in Figure 2.4/2.5).



Figure 2.5. Compression–density ratio (CDR) of formulated foams. Foams in blue failed in compression testing.

The compression strength of lignin-based foams was negatively correlated (r = -0.7) with foam reaction times, meaning lignins with faster reaction times made better foams. In general, the addition of lignin into PUR/PIR foams decreased compression strength compared to the control foam with no lignin. This decrease in compression strength of lignin-based foams is likely due to solid lignin particles in the foam matrix causing decreased reactivity and increasing polyol mixture viscosity, creating more irregular cell sizes in the final foam.^{10,80} The average compression strength of foam made with 1-CS-E (267 kPa) showed no significant difference from the control foam (267 kPa) made with petroleum-based polyol and was significantly higher than foams made with soda (169 kPa), kraft (150 kPa), organosolv (144 kPa), and lignosulfonate (126 kPa) lignins. Compared to other lignin-based foams, the increased compression strength of foam made with 1-CS-E lignin is likely due to the higher aliphatic and *p*-hydroxyphenyl hydroxyl contents (Table 2.3) of corn stover lignin, creating more crosslinking within the foam and increasing foam reactivity, density, and compression strength (Figures 2.1 and 2.4).

Since each foam was not formulated with the same density, we calculated the foam compression to density ratio (CDR) shown in Figure 2.5. Given that all foams (excluding lignin 5-SW-L) fell within the low-density range of 30–60 kg/m³ for polyurethane foams, the effect of density is not significant.⁴ This was also proven by our correlation data, finding no correlation between apparent density and compression strength of formulated foams (r = 0.04). Foams with CDR values < 2.9 did not meet the minimum required compression strength of 104 kPa for the spray insulation applications. CDR was found to have high correlation with closed-cell content (r = 0.8), total reaction time (r = -0.8), and cell size (r = -0.6) of lignin-based foams.

Cell morphology, i.e., cell size/shape and closed-cell content, is essential in producing rigid polyurethane foams with consistent performance. Smaller and more uniform cells make the foam act as a homogenous material with similar properties throughout,² whereas larger cells hold more blowing agents, decreasing the thermal conductivity of foam. As seen in Table 2.4, lignin-based foams that passed the compression test had cell sizes comparable to the control (~6% smaller). Figure 2.6 shows digital microscope images of formulated foams used to measure foam cell size. Foams that failed compression testing (3-SW-O, 7-HW-K, and 11-SW-K) showed more visual irregularity and had significantly larger (31%) cell sizes than those that passed (p < 0.05). The increase in cell size for these lignin-based foams can be explained by their higher reaction times than the control formulation (Figure 2.1). The cell size of lignin-based foams was found to correlate with foam total reaction time (r = 0.8) and closed-cell content (r = -0.8). Closed cells (>90% content) are crucial in maintaining the thermal conductivity properties of formulated rigid foams. High closed-cell content ensures less blowing agent loss and creates foams with lower thermal conductivities. All foams except 7-HW-K and 11-SW-K passed the minimum 90% closed-cell requirement for rigid foams (Table 2.4). Lignin-based foams that failed in compression strength testing (3-SW-O, 7-HW-K, and 11-SW-K) had significantly lower closed-cell contents than lignin-based foams that passed (86 and 99%, respectively). Closed-cell content of lignin-based foams was found to correlate with the total reaction time of foam (r = -0.9), CDR (r = 0.8), and foam compression strength (r = 0.7). Lignin-based foams that passed the minimum requirement for closed-cell content showed comparable results (within 2%) to the control formulation.

Thermal conductivity consists of λ gas, λ radiation, λ solid, and λ convection, with λ gas being the main component.² Higher-density foams have higher λ solid and therefore higher thermal conductivity. Because the majority of thermal conductivity comes from λ gas, our foams were within the low-density range of 30–60 kg/m³, and all foams were made with the same blowing agent, there was no significant difference between the thermal conductivities of control and ligninbased foams. All foams were significantly below the maximum (257 mW/mK) acceptable thermal conductivity (Table 2.4) in rigid insulation foams (type 1–4) ¹³⁷ and had high R values, making them suitable for insulation applications.



Figure 2.6. Digital microscope images of formulated foams using 160× magnification. Ligninbased foams 3-SW-O, 7-HW-K, 11-SW-K failed in compression testing.

The high impurity content of lignin (Table 2.2) and the solid state of lignin are likely why other researchers have reported issues with polyol viscosity, foam cell structure, and other foam properties with lignin loadings over 30% in rigid polyurethane foam.^{84,87} Strong correlations between lignin-based foam properties and impurity content were most prominent in soda and organosolv lignin-based foams (Figure 2.2). Specifically, calcium (organosolv and soda) and sodium (soda) affected foam properties such as apparent density, compression strength, closed-cell content, and cell size. To the best of our knowledge, this is the first study to measure the effect

of lignin impurities on lignin-based polyurethane/polyisocyanurate foam properties (effects on rigid polyurethane foams have not been studied either). Since these impurities would likely have a greater impact at higher lignin loading percentages, more in-depth work needs to be conducted to study the effect of lignin impurity content on rigid polyurethane and polyurethane/ polyisocyanurate foam properties.

2.5 Conclusion

This is the first study to partially replace petroleum-based polyol with nineteen lignins from various sources and isolation processes in low-density rigid polyurethane/polyisocyanurate (PUR/PIR) foam formulations. Lignins with higher aliphatic and p-hydroxyphenyl contents, higher pH, and higher sodium, calcium, magnesium, and potassium contents performed well in foam preparation and testing, demonstrating that the properties of lignin have a profound impact on foam performance regardless of lignin source and isolation process. Except for three, all the other lignin-based foams met or exceeded required performance based on ASTM standards for insulation spray foams. The lignin-based foams that failed the compression test had significantly lower reactivity, higher density, cell size, and thermal conductivity than those lignin-based foams that passed. However, the three lignings that did not pass testing could still be used in flexible foams or other applications where compression strength and closed-cell content are not as critical. Among tested lignins, the biorefinery corn stover lignin was found to be the most suitable lignin for partially replacing petroleum-based polyols in formulating PUR/PIR rigid foam due to its significantly higher aliphatic and *p*-hydroxyphenyl hydroxyl content. The results of this study will allow lignin producers to optimize their ligning for rigid foam production, foam producers to select the best lignins for foam application and scale-up, and, last but not least, expand the body of knowledge for lignin and lignin-based rigid PUR/PIR foams.

CHAPTER 3 LIGNIN-BASED LOW-DENSITY RIGID POLYURETHANE/POLYISOCYANURATE FOAMS

3.1 Abstract

In this study, unmodified kraft lignin was used to replace 100% of petroleum-based polyol in low-density rigid polyurethane/polyisocyanurate (PUR/PIR) foam for the first time. The effect of lignin incorporation content (0, 25, 50, 75, and 100%) on foam properties were measured. The developed lignin-based foams were evaluated by measuring their reactivity, polyol viscosity (rheometer), apparent density, compression strength (Instron), closed cell content (gas pycnometer), thermal conductivity, fire resistance, and foam morphology (SEM). All the lignin-based foams passed the ASTM International standards minimum requirements for rigid foams. The foam made by replacing 100% of petrochemical polyol with this commercially available kraft softwood lignin significantly enhanced the fire performance of foam, decreasing burn length by 127%.

3.2 Introduction

Polyurethanes, one of the most versatile polymeric materials, are used in multiple products including foams, coatings, adhesives, sealants, and elastomers.^{60,142,143} Rigid polyurethane foams (rigid foams) are a collection of multi-purpose polymers consisting of polyurethane (PUR) and polyurethane/polyisocyanurate (PUR/PIR) foams. These foams can have a wide range of properties and are used in various applications like insulation, construction, and appliances.⁶⁰ Due to the combination of strength and low density, the global market of rigid foams have rapidly increased over the last few decades, with their total market value predicted to reach \$80.76 billion USD in 2023.^{60,71}

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Commercial polyols used in rigid foam synthesis are currently sourced from toxic and energy intensive starting materials like propylene oxide.¹⁴⁴ Efforts to replace these petrodependent polyols with lignocellulosic biomass has increased over the years due to their reactive hydroxyl groups, being abundantly available, and their relative lower cost.^{60,145} The incorporation of lignin into rigid PUR foams has been reported to increase char residue,⁸⁰ compression strength,^{71,72,80} biodegradation,¹⁴ while decreasing thermal conductivity,⁷² and water absorption.^{60,80,84} However, to the best of our knowledge, there is only one study using unmodified lignin on low-density rigid PUR/PIR foams.¹⁴⁶ That study¹⁴⁶ utilized 19 technical lignins to replace 30% of petroleum-based polyol in low-density rigid polyurethane/polyisocyanurate foams. The study reported that the lignin-based foams that failed in compression strength and/or closed-cell content testing were made with lignins that had lower pH, potassium, sodium, calcium, magnesium, and hydroxyl contents than lignin-based foams that passed all testing.¹⁴⁶

Comparatively, numerous works exist on lignin-based rigid PUR foams,^{14,86,87,147} mainly utilizing modified lignins, including oxypropylated,^{68–74} liquefied,^{71,72,75–81} and various other modification techniques^{21,49,107,148–150} like amination,¹⁴⁸ phenylation/epoxidation,¹⁵⁰ and hydroxymethylation.⁹⁴ Oxypropylation is one the most well-known techniques used to change the phenolic hydroxyl (OH) groups of lignin to aliphatic OH groups and prepare liquid lignin polyol for use in rigid foam.⁸⁴ The oxypropylation process is conducted at relatively high temperature (150-523 °C), pressure (0.24-1.75 MPa), time (9 min to 5 days), along with high solvent/propylene oxide (50-80%), and catalyst (2-10%) content to liquefy lignin.^{67–74,100,151} Though oxypropylation and other lignin modification techniques can increase the reactivity of

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lignin, the use of high-energy reaction conditions (high temperature and pressure) and petrochemically sourced solvents (propylene oxide) make these lignin polyols less desirable for commercialization. Lastly, due to the high percentage of propylene oxide/solvent and catalyst used in lignin polyol synthesis, the amount of lignin in the final polyol (10-30%)^{67,70} is often lower than or similar to unmodified lignin replacement.

The use of unmodified lignins as polyol replacement in low density rigid polyurethane foams has been reported at ~30% replacement due to the reduction of foam properties at higher lignin loadings.^{84,87} To the best of our knowledge, the maximum amount of unmodified lignin and its effect on foam properties in low-density lignin-based rigid PUR/PIR foams have not been studied. The goal of this work is to elucidate the maximum amount of lignin as polyol replacement in lignin-based polyurethane/polyisocyanurate foam while monitoring the effect of lignin loading on foam properties. To accomplish this, foams were formulated with 0, 25, 50, 75, and 100% lignin as polyol replacement in rigid PUR/PIR foam. The influence of percent lignin loading on polyol viscosity, foam reactivity, morphology, mechanical properties, and horizontal burn were studied.

3.3 Materials and Methods

Commercial Indulin AT kraft softwood lignin was provided by Ingevity and was used without further modification. Huntsman Polyurethanes (The Woodlands, TX, USA) graciously supplied all the foam raw materials.¹⁴⁶ Other reagents were purchased from Fisher Scientific (Hampton, NH, USA) and used as is.

The hydroxyl content of the lignin sample was determined according to previously published methods using ³¹phosphorus nuclear magnetic resonance spectroscopy (³¹ P NMR).^{122,146,152} In brief, lignin was dissolved in a solution of pyridine, deuterated chloroform, and dimethylformamide. Cyclohexanol solution consisting of anhydrous pyridine and deuterated chloroform was then added as an internal standard.^{122,146,152} Chromium (III) acetylacetonate solution (anhydrous pyridine and deuterated chloroform) was added as a relaxation reagent along with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane as phosphitylation reagent. Spectra were acquired using an Agilent DDR2 500 MHz NMR spectrometer (Billerica, MA, USA).¹⁴⁶ The hydroxyl value of lignin was then calculated by multiplying the measured total hydroxyl content of lignin by the mass of KOH (56.1).¹⁴⁶

The Polyurethane Foam Cup Test ASTM D7487-13¹²⁴ standard was used to formulate foams. The effect of steric hindrance from lignin hydroxyl groups and the increased viscosity of solid lignin addition was decreased by the adjustment of catalyst and viscosity reducer based on the percent weight of lignin (Table 3.1). Using a 237 mL cup, polyol, lignin, catalysts, surfactant, blowing agent, viscosity reducer, and flame retardant were mixed to create each B-side polyol blend. B-side polyol blends were mixed for about 15 seconds using a high-speed mixer (Camframo overhead mixer) at 3000 rpm.

Table 3.1. Foam Formulations in Grams

Foam Additive		Lignin polyol replacement (100% Polyol)							
		0%	25%	50%	75%	100%			
			Foam Additive (System %)						
100%	Polyol	29.28	21.3	12.3	5.19	0			
Polyol	Lignin	0	7.1	12.3	15.56	17.53			
Water		0.07	0.07	0.06	0.05	0.04			
Viscosity Reducer		2.93	3.55	6.15	15.56	23.37			
Surfactant		0.29	0.28	0.25	0.21	0.18			
Catalysts		1.84	1.83	1.86	1.83	1.76			
Blowing age	ent	6.44	6.25	5.41	4.56	4.67			
Flame retardant		2.93	2.84	2.46	2.07	1.75			
PMDI		56.21	56.77	59.2	54.96	50.69			
System % To	otal	100	100	100	100	100			

The viscosity of the B-side polyol blend was determined using a Discovery HR-1 rheometer (Waters TA Instruments Newcastle, DE, USA) with a 10 s⁻¹ shear rate, at 23°C, for 30 seconds. Viscosities were averaged and reported.

After mixing B-side polyol blends, the isocyanate was then added (3-second pour time) with a 270-isocyanate index and mixed until heat was felt on the outside of the cup (mix time). Foam reaction time was determined by measuring the following: mix, cream, string gel, top of cup, string gel, tack-free, and end of rise times as described in previous literature.^{124,146} The mix time indicates the start of the water and isocyanate reaction, cream time shows the onset of foaming, while top of cup time indicates blowing agent activity. Lastly, string gel, tack-free, and end of rise times and catalysis.^{124,146}

Foam samples were cut to size for each test at least 24 hours after foam formulation. Foams were then kept at room temperature for another 48 hours before being analyzed.

Apparent density was determined according to ASTM D1622¹²⁵ following previously published method.¹⁴⁶ Each sample was measured volumetrically to 0.01 significant figures (three times per side) using a digital caliper and weighed using a digital scale (0.0001). The average of at least five foam samples were used to calculate apparent density and results were reported in kg/m^3 .

A Meter TEMPOS TPA machine (Pullman, WA, USA) with glycerin as a calibration standard was used to measure the thermal conductivity of foam samples. Measurements were taken perpendicular to foam rise (in at least triplicate) using a 60 mm K3 probe.¹⁴⁶

Closed-cell content was determined using a micromeritics gas pycnometer (AccuPyc II 1340, Norcross, GA, USA)¹⁴⁶ according to ASTM D6226-15.¹²⁸ Following micromeritics method B¹²⁹ and previously published literature,¹⁴⁶ experimental conditions included nitrogen atmosphere with 10 purges, 10 cycles, 27.58 kPa purge, and cycle fill pressures at 0.03 kPa/min.

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The compression strength was determined using an Instron 5565 universal testing machine (Norwood, MA, USA) following ASTM D1621-16.¹²⁶ Twenty-five-millimeter cube samples were tested using a 2.5 mm/min strain rate (13% initial thickness) perpendicular to the foam rise direction.¹⁴⁶

The fire properties of control and lignin-based foams were determined according to ASTM D4986-18,¹⁵³ Standard Test Method for Horizontal Burning Characteristics of Cellular Polymeric Materials. In brief, at least ten 125 mm by 13 mm by 13 mm samples were burned for 30s in a laboratory fume hood free of induced/forced draft with a Bunsen burner (natural gas supply). The foams were marked at 25- and 100 mm lengths, then volume and weights were measured. After burning, the foam weights and burn lengths were remeasured and used to calculate burn length and percent weight loss of foam.

The morphology of polyurethane/polyisocyanurate foams were determined using scanning electron microscope (SEM) and digital light microscope. For SEM analysis, the foam samples were cut, flash-frozen in liquid nitrogen, and cut with a razor blade. Cut samples were then placed on double-sided carbon conductive tape attached to a metal stub and sputter-coated with gold using an EMSCOPE SC 500 (Emzer, Barcelona, Spain) with a 3-minute coat time and 20 mA dissociation. After mounting, the gold-coated samples were analyzed on a JEOL JSM 6610LV (Akishima, Tokyo, Japan) microscope using 10 kV accelerating voltage, 13 mm working distance, 30 spot size, at 200 x magnification. Each foam's cell size (diameter, strut width, and perimeter) was measured following a modified version of ASTM D3576-15¹²⁷ using three-millimeter foam slices cut 25mm below the top of the foam.¹⁴⁶ The average of at least 20

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cells from each set of foams (\geq 3) were averaged and analyzed perpendicular to foam rise using a Dino-Lite Edge digital microscope (Torrance, CA, USA).

3.4 Results and Discussion

Quantitative ³¹P NMR analysis was utilized to determine the hydroxyl content of lignin before incorporation into foam (Table 3.2). The industry recommended commercial polyester polyol, which was used in this study had a hydroxyl value (OHV) of ~248 mgKOH/g. In general, commercial polyols used in rigid foams typically have OHV between 200-550 mgKOH/g.^{1,2} The kraft softwood lignin used to in this study had a OHV of 327 mgKOH/g which was in acceptable range for rigid foam formulation (Table 3.2).

Tab	le .	3.2.	Н	[yċ	lroxyl	Content	of	Kraft	Lignin
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	Aliphatic	Condensed	Guaiacyl	P-Hydroxyphenyl	Carboxylic	Total OH*
		Phenolic			Acid	
Kraft Lignin	2.10 ± 0.03	1.11 ± 0.11	1.98 ± 0.17	0.24 ± 0.04	0.40 ± 0.06	5.83 ± 0.17
**** 1 1	1 207	WOIL!				

Hydroxyl content of lignin analyzed by ³¹ P NMR (mmol/g)

*Hydroxyl value 327 mgKOH/g

The viscosity of polyol systems determines mixing efficiency along with foam uniformity and quality.⁸⁸ To achieve sufficient mixing and dispensing in polyols for rigid foams, viscosity of polyol blends is recommended to be less than 20,000 cP. (20 Pa·s), with lower viscosities being more favorable.¹⁵⁴ The effect of unmodified lignin addition on polyol blend viscosity from 0-100% loading is reported for the first time (Table 3.3). Although polyol viscosity increased with lignin addition from 0 to 100% loading, it should be noted that viscosity measurements were performed at room temperature. Li et al.¹⁵⁵ reported that the viscosity of lignin-based polyols significantly decreased by heating the polyol blend to 50°C, a method often used in the foaming industry, turning a completely solid polyol into a liquid with a viscosity of 6.3 Pa·s.¹⁵⁵ This indicates that the viscosities of polyol blends containing 75% and 100% lignin polyol could easily meet the viscosity requirements by heating the polyol blends to a slightly higher temperature (50°C).

Ta	ble	3.3.	Polyo	I Blend	V1scos1ties	

Lignin (%)	0%	25%	50%	75%	100%
Polyol Blend Viscosity (Pa·s)	1.24ª	4.29ª	6.84ª	25.93 ^b	46.12 ^c

*Values with the same letter are not significantly different (p < 0.05)

Figure 3.1 shows the formulated lignin-based foams and control foam that has no lignin (made with entirely petroleum-based polyol). The foaming reactions of control and lignin-based foams represented by end of rise, tack free, string gel, top of cup, cream, and mix times are reported in Figure 3.2. Although the addition of lignin into foam increased reaction times, all the foams had suitable reaction times for rigid foam synthesis.^{4,124} The only other study incorporating unmodified lignin into low-density rigid PUR/PIR foams used 19 technical lignins to replace 30 wt.% of petrochemical polyol with lignin and found that foams with higher reaction times (~357 s) had significantly worse compression strengths, closed cell contents, and cell morphologies.¹⁴⁶ All control and lignin-based foams were well below this reaction time by 27-75%.





The 100% lignin-based foam outperformed various lignin-based low-density rigid PUR foams in foam reaction times. Haridevan et al.⁷⁹ dispersed up to 6% kraft lignin powder (356 hydroxyl value) in a 80/20 mixture of commercial aromatic polyester polyol/glycerol and formulated low-density rigid polyurethane foams.⁷⁹ The 6% lignin polyol dispersion based foam had a 240 s tack free time⁷⁹ while our 100% lignin-based foam was 70% lower (Figure 3.2). The cream and end of rise times of 100% lignin-based foam was even superior to liquefied lignin polyol by over 95% and 80% respectively.¹⁵⁵ Li et al.¹⁵⁵ fractionated miscanthus giganteus lignin using a multistep process and formulated foams with the resultant biopolyol at 50, 80, and 100% petrochemical polyol replacement.¹⁵⁵ Cream times for these foams ranged from 166-290 s and end of rise times ranged from 445-451 s.¹⁵⁵ Both of these studies incorporated less actual lignin as polyol replacement (6-40%) and used energy intensive lignin dispersion/modification methods (≥ 6 h processing times).^{79,155}





After foaming reactions characterization, foams were evaluated for apparent density (Table 3.4). The apparent density of rigid foams is known to correlate with, relate logarithmically, and significantly affect most foam properties outside of the 30-60 kg/m³ low-density range.^{3,4,7,146} The densities of lignin-based foams ranged from 41-59 kg/m³ (Table 3.4), successfully falling within the low-density foam range, making the effect of density on foam properties insignificant. The increased density, compared to the control (35 kg/m³), in lignin-based foams is likely caused by the use of solid lignin which can delay foaming times (Figure 3.2), increase polyol blend viscosity (Table 3.3), and increase the degree of foam crosslinking.^{70–72,79,80} Even so, all lignin-based foams had suitable apparent densities for rigid insulation and structural applications indicated by ASTM D7425 and E1730.^{138,156}

The thermal conductivity (and reciprocal R-Value) of rigid PUR and PUR/PIR foams depends on various factors, including: cell morphology, closed-cell content, and type of blowing agent(s) used.^{96,157} In general, smaller, more closed, and homogenous cells create foams with lower thermal conductivities.² Blowing agent choice also affects thermal conductivity; for example, the thermal conductivity of air (0.0249 W/mK) is higher than carbon dioxide (0.0153 W/mK) and n-pentane (0.0137 W/mK) measured at 10°C.² Low thermal conductivity in rigid foams ensures the foam will act as a good insulator and should be below 0.257 W/mK.¹³⁸ All foams met minimum requirements for thermal conductivity and closed cell content (Table 3.4) based on ASTM E1730-15¹³⁸ and D7425¹⁵⁶ respectively.

Lignin (%)	Apparent Density (kg/m³)	Thermal Conductivity (W/Mk)	R-Value (Km²/W)**	Closed Cell Content (%)
0%	35 ± 1^{a}	0.0101 ± 0.0002^{a}	6.02 ± 0.14ª	$99.7\pm0.03^{\text{a}}$
25%	41 ± 2^{ab}	$0.0106\pm0.0002^{\text{ab}}$	5.66 ± 0.16^{ab}	$99.6\pm0.04^{\text{ab}}$
50%	$48\pm4^{\text{bc}}$	$0.0116 \pm 0.0009^{\text{bc}}$	5.20 ± 0.48^{bc}	$99.4\pm0.02^{\rm b}$
75%	50 ± 2^{cd}	$0.0126\pm0.0001^{\text{cd}}$	4.78 ± 0.06^{cd}	$95.8\pm0.08^{\rm c}$
100%	59 ± 2^{d}	$0.0138\pm0.0012^{\text{d}}$	4.38 ± 0.50 ^d	$92.7\pm0.17^{\rm d}$
Standard	30-60 ⁴⁵	<0.257 ¹³⁸		>90 ¹³⁷

 Table 3.4. Measured Foam Properties

*Values with the same letter are not significantly different (p < 0.05) **Measured at 0.06m

Although, the thermal conductivity of foams increased with lignin addition, they still fell significantly below the standard insulation requirements by a wide margin (~95% lower than required).¹³⁸ Compared to other studies, the thermal conductivities of control and lignin-based PUR/PIR foams (Table 3.4) were better than oxypropylated lignin⁷⁰ and liquefied biomass¹⁵⁸ based rigid foams. The oxypropylated lignin polyols used varying amounts of lignin/propylene oxide/catalyst (30/70/2 or 20/80/5) to replace 50% and 100% of petrochemical polyol in rigid PUR foam.⁷⁰ Even though the resultant foams had extremely low densities (18-25 kg/m³) and used the same blowing agent as our formulation, the oxypropylated lignin-based rigid PUR foams still had higher thermal conductivities (~0.03 W/mK) than the 100% unmodified lignin-based PUR/PIR foam (~0.01 W/Mk, Table 4). Researchers¹⁵⁸ also used liquefied marine biomass at 20 and 30%

petrochemical polyol replacements for use in low-density rigid PUR/PIR foam; though the densities of those foams were higher (~50 kg/m³) foam thermal conductivities (~0.03 W/mK)¹⁵⁸ were similar to the oxypropylated lignin-based PUR foams.⁷⁰ The enhanced thermal conductivity properties of the unmodified lignin-based PUR/PIR foams in this study compared to the previous studies^{70,158} are likely due to increased closed cell content but, neither study measured nor reported those values. A reported knowledge gap for lignin-based rigid foams is the lack of foam testing based on industrial requirements.^{84,159} Researchers should incorporate a wider array of tests to ensure that formulated foams will be suitable for industrial applications.

The closed-cell content of foam is crucial in maintaining low thermal conductivity.^{2,4} Additionally, closed and more homogenous cells create foams with better mechanical strength and thermal conductivity properties.^{4,160,161} The industry-accepted method to measure foam closed cell content uses a gas pycnometer.¹⁶² For lignin-based rigid PUR foams, most researchers have utilized a combination of digital, light, or scanning electron microscopy to estimate closed cell content.^{80,163} To have a more accurate results, we used gas pycnometry for closed cell content analysis (Table 3.4). All control and lignin-based foams met the minimum 90% closed cell content requirement for thermal insulation¹³⁷ with foams up to 75% lignin loading meeting stricter 95% closed cell content requitements.¹³⁸ Even with the decrease in closed cell content with lignin addition, the 100% lignin-based foam not only met ASTM requirements but also outperformed various biobased polyols reported in the literature.^{17,89,164}

Tu et al.¹⁶⁴ used epoxidized soybean oil to replace 40% of petrochemical polyol in lowdensity rigid PUR foam but did not meet 90% closed cell content requirements¹³⁷ (~87% closed cells). Although lower 10, 20, and 30% soyoil replacements did meet minimum requirements (~95% closed cells),¹⁶⁴ they were all lower than control and lignin-based foams up to 50% lignin loading (Table 3.4). Unmodified wheat straw lignin and oxypropylated wheat straw lignin polyol were used as 15% filler and 15% polyol replacement respectively in rigid PUR foam.⁸⁹ Both lignin-based foams had lower closed cell contents $(92 \pm 3\%)^{89}$ than our PUR/PIR control and lignin-based foams (Table 4). Additionally, all foams in this study outperformed oxypropylated tannin as 75% polyol replacement in rigid PUR/PIR foam (92 ± 2) .¹⁷ Though these other studies used either liquefied lignin/biomass^{17,89,164} or lignins with higher hydroxyl contents (8.4 compared to 5.8 mmol/g in Table 3.2),⁸⁹ the lower closed cell contents compared to our control and unmodified lignin-based foams (Figure 3.2) is a combination of high string gel times (>200 s)⁸⁹ and end of rise times (100-180 s).¹⁷

Along with decreased foam reactivity in lignin-based foams, compression strength has also been reported as a limiting factor for lignin incorporation.^{84,146} Due to foam anisotropy, compression strength of foams almost doubles based on testing perpendicular to foam rise compared to parallel.^{2,165} Here (Figure 3.3), we evaluate compression strength perpendicular to foam rise to ensure we are meeting minimum requirements on the weakest side of the foam. The highest compression strength of control and lignin-based foams was obtained at 50% lignin loading (shown in Figure 3.3). Although compression strength negatively correlated with lignin loading percentage (r = -0.6), as expected due to the use of solid unmodified lignin, all control and lignin-based foams met the minimum compression strength requirement (>104 kPa) for type 1 rigid foams.¹³⁷ Lignin-based foams even outperformed oxypropylated lignin as 100% polyol replacement in low-density rigid PUR foam (90 kPa).⁶⁷ A similar result was found with the

compression strength of hydroxymethylated lignin used as 2-30% polyol replacement in lowdensity rigid PUR foam (~40 kPa).⁶⁵



Figure 3.3. Compression strength of formulated foams. The dashed red line denotes ASTM minimum requirement. Values with the same letter are not significantly different (p < 0.05).

The horizontal burn flammability test was used to determine the flammability rating (HF1 and HF2) of the foams.¹⁵³ This test can ensure the safety and trustworthiness of products by elucidating relative burn rate, time, and extent of burn.^{153,166} Longer flame times to the 25 mm mark and lower values for burn time, percent loss, and burn length indicate better fire behavior.¹⁵³ On average, the flame did not reach the 25 mm burn mark for lignin-based foams and had significantly shorter burn times than the control (Table 3.5). The flame time to the 25 mm mark
had a positive correlation (r = 0.7) with the percentage of lignin loading and increased compared to the control by over 72% (Figure 4). Burn time after flame removal decreased by over 242% in 100% lignin-based foams compared to the control. All burn time values for control and ligninbased foams were below 30 s, meeting the HF1 fire characterization.¹⁵³ The weight change and burn length of lignin-based foams, compared to the control, decreased by over 24% and 55%, respectively. All specimens had less than 60 mm burn length and did not ignite the cotton indicator, meeting the HF1 material classification.¹⁵³ In general, lignin has been reported to increase the char yield of rigid PUR foams (analyzed via thermal gravimetric analysis at 10°C/min) due to its aromatic structure and creating an insulation layer to further prevent the spread of flame.⁸⁰

Lignin (%)	Flame time to 25 mm mark (s)	Burn Time After Flame Removal (s)	Percent Weight Loss (%)	Burn Length (mm)
0%	5 ± 1^{a}	$4.6\pm0.5^{\text{a}}$	$\textbf{-5.6}\pm0.6^{a}$	35 ± 14^{a}
25%	18 ± 9^{a}	$2.2\pm0.3^{\text{b}}$	$\textbf{-4.5}\pm0.7^{ab}$	$22\pm8^{\text{a}}$
50%	19 ± 10^{a}	$1.6\pm0.8^{\text{b}}$	$\textbf{-4.3}\pm0.6^{ab}$	$20\pm9^{\text{a}}$
75%	b**	$1.3\pm0.6^{\rm b}$	$\textbf{-4.1}\pm0.5^{ab}$	17 ± 5^{a}
100%	b**	$1.3\pm0.3^{\mathrm{b}}$	-3.7 ± 0.6^{b}	15 ± 4^{a}

Table 3.5. Fire Behavior of Foam

*Values with the same letter are not significantly different (p < 0.05)

**Flame removed after 30 seconds because flame did not reach 25 mm mark

Though fire properties in rigid foam are generally enhanced via the use of reactive flame retardants, active flame retardants, or flame-retardant coatings;¹⁶⁷ higher density foams and the use of PUR/PIR over PUR formulations will increase fire retardant behavior due to a more compact burn layer¹⁶⁸ and the presence of more thermally stable polyisocyanurate bonds,² respectively. Since all of our foams were within the low-density range for rigid polyurethane foams, 30-60 kg/m³, the effect of density should not be significant.^{4,146} This is confirmed by the low correlations between apparent density and fire properties: burn time after flame removal (r = -0.3), percent weight loss (r = 0.5), and burn length (r = -0.5). The addition of unmodified kraft lignin as a polyol replacement and its ability to act as a flame retardant further increases the value proposition of lignin for use in rigid PUR and PUR/PIR foams.



Figure 3.4. Charring of control and lignin-based foams. Uncharred samples on left and charred samples on the right.

Scanning electron and digital light microscope images (Figure 3.5) show the increase in cell diameter and perimeter (Figure 3.6) with lignin addition (r = 1). Up to 50% loading, no significant difference was found for lignin-based foams compared to the control for cell perimeter

and diameter, while the cell strut width showed no significant difference from the control at any lignin loading percentage. Overall, the cell diameter of our control and lignin-based foams (~0.2 mm) were smaller than previous studies using 0-6% lignin loading in low-density rigid PUR foam (~0.5 mm).⁷⁹ All cell size results were comparable to other biobased polyols used in low-density rigid PUR/PIR foam formulations,¹⁵⁸ our previous research,¹⁴⁶ and ASTM specifications.¹⁶⁹





Figure 3.5. Scanning electron microscope^S and digital light microscope^L images of formulated foams



Figure 3.6. Cell Sizes of Formulated Foams. Values with the same letter are not significantly different (p < 0.05). All cell strut widths were within 0.05 ± 0.01 mm.

3.5 Conclusion

This paper is the first to report 100% petrochemical polyol substitution with unmodified commercially available solid lignin in low-density rigid polyurethane/polyisocyanurate foams. The kraft softwood lignin was incorporated into foam by replacing 0-100% of petroleum-based polyol in 25% increments. All lignin-based foams outperformed the control in fire testing by over 56% while meeting the minimum ASTM required closed-cell content, compression strength, and thermal conductivity/R-Value for rigid foam applications. This work shows the feasibility of using an unmodified commercial lignin to fully replace fossil fuel-based polyols while formulating low density rigid polyurethane/polyisocyanurate foams that meet the standard requirements for type 1 insulation applications. This is a significant step toward using more sustainable foams with superior fire performance for building construction applications, while simultaneously creating value-added opportunity for lignin as an underutilized portion of biomass. Future research should

focus on further optimization of lignin-based foams for industrial scale up and the tuning of lignin properties like hydroxyl content and molecular weight to further enhance and evaluate their effects on foam properties.

CHAPTER 4 EFFECT OF 0-100% LIGNIN POLYOL LOADING ON RIGID POLYURETHANE FOAM FORMULATIONS

4.1 Abstract

This study focused on fabricating and testing low-density rigid polyurethane foam using unmodified kraft lignin to replace 0-100% of conventional petroleum-based polyol. Foams were formulated for insulative applications and tested for density, compression strength, closed cell content, thermal conductivity, water absorption, and cell morphology using various ASTM standard methods. Fire properties of formulated foams were evaluated via furnace testing. Up to 50% lignin loading, all foams also met or exceeded minimum requirements for thermal conductivity, water absorption, compression strength, and closed cell content. Overall, the incorporation of lignin significantly improved the fire performance of formulated foams at all lignin loadings.

4.2 Introduction

The preparation of green polyurethanes and other polymeric products have recently drawn lots of attention due to petrochemical dependence and increased usage around the world. Since their inception in 1937, polyurethanes and their production has grown exponentially, with 18 million tons produced worldwide in 2016.¹² Polyurethane foams account for almost half of this market value, with rigid foams set to outpace all other polyurethane products until 2026 due to their increased use in the construction industry.¹⁷⁰

As the second most abundant natural polymer on earth after cellulose, lignin has been widely studied as a polyol replacement in polyurethanes.⁸⁴ Not only does lignin make up 15-35% of the dry mass of wood/woody plants, it is also produced as an industrial byproduct at over 150

million tons per year.¹⁷¹ Most of this lignin byproduct is incinerated as low-value fuel, but the numerous hydroxyl groups of lignin available to react with isocyanate make it a viable alternative for petrochemically sourced polyols.¹⁴⁶ Replacing the polyol portion of rigid foam with lignin is an important step in formulating greener polyurethanes while simultaneously improving the life cycle impacts of the final polyurethane product.

The incorporation of unmodified lignin into rigid polyurethane foams has been reported to increase sorption capacity for oil spills,⁹¹ decrease water absorption,⁹ and increase color stability.⁹⁰ Other researchers report that unmodified lignin is limited to ~6-30% replacement in rigid PUR foams due to a decrease in foam properties like compression strength and increased polyol viscosity.^{79,84} Aside from the solid state of lignin increasing polyol blend viscosity and decreasing foam reactivity, the poor compressive properties of lignin-based foams are also due to the presence of impurities in lignin like potassium, sodium, calcium, and magnesium which can cause isocyanate trimerization (PIR), creating brittle foams.⁴ The most popular way to get around these issues is lignin modification like liquefaction,^{14,16,81,96,71,72,75-80} and oxypropylation.^{68–74}

Though lignin modifications can decrease foam reaction times and enhance the mechanical properties of foam, their increased energy expenditure, elevated temperatures, high-pressure reaction conditions, and use of toxic chemicals (like propylene oxide) make it ill-favored by industry. Our study uses an optimized foam formulation that favors the PUR over the PIR reaction, decreases polyol viscosity, and increases unmodified lignin loading percentage above 30% while meeting minimum ASTM requirements for rigid foam applications. Lignin was first characterized for hydroxyl content and molecular properties, then incorporated in 25% increments to replace up to 100% of petrochemical polyol in low-density rigid PUR foams for

the first time. Formulated foams were evaluated and tested for polyol blend viscosity, density, cell morphology, volumetric change, thermal conductivity, compression strength, and fire behavior. Lignin-based foams were then compared to a control foam with no lignin along with ASTM standard minimum requirements for rigid foam applications.

4.3 Materials and Methods

Foam raw materials were supplied by Huntsman Polyurethanes (The Woodlands, TX, USA). Polyurethane (PUR) foam formulations are shown in **Table 1**. Other reagents were purchased from Fisher Scientific and used as is. Commercial Indulin AT lignin was obtained from Ingevity and dried at 80°C until constant weight.

Hydroxyl content was determined according to previously published works using an Agilent DDR2 500 MHz NMR spectrometer (Billerica, MA, USA).^{146,172}

Molecular properties of lignin were determined using gel permeation chromatography (GPC). Lignin was first acetylated according to literature,¹⁷², then analyzed on a Waters GPC e2695 Separation Module. Experimental conditions used 35°C column temperature, 1 mL/min flow rate, refractive index detector (2414), and three columns (Styragel HR 4 THF, Styragel HR 3 THF, and Ultrastyragel THF). Monodisperse polystyrene were used as calibration standards and Empower GPC software was utilized to analyze data.

The Polyurethane Foam Cup Test ASTM D7487-13¹²⁴ standard was used to formulate foams. Foams were formulated based on a predetermined additive ratio (Table 4.1) using a 237 mL cup. B-side polyol blends were prepared by mixing specified amounts of polyol, lignin, catalysts, surfactant, blowing agent, and flame retardant in a predetermined ratio for thirty

seconds using a high-speed mixer (Camframo overhead mixer) at 3000 rpm. Isocyanate was then added and mixed until heat was felt on the outside of the cup (mix time). Foam reaction time was determined by measuring the following: mix, cream, top of the cup, tack-free, and end of rise times as described in the previous literature.¹⁴⁶

B-side polyol blend viscosity was determined using a 10s-1 shear rate for 30 s at 23°C (Discovery HR-1 rheometer; Waters TA Instruments; Newcastle, DE, USA).

			Percent			
PUR Additive		0	25	50	75	100
				g		
100%	Polyol	15.00	11.25	7.50	3.75	0
Polyol	Lignin	0.00	3.75	7.50	11.25	15
Water		0.04	0.04	0.04	0.04	0.04
Viscosity	Reducer	1.50	1.88	3.75	5.63	15
Surfactan	t	0.15	0.15	0.15	0.15	0.15
Catalysts		0.49	0.49	0.68	0.94	1.05
Blowing A	lgent	3.00	3	3	3	3
PMDI		16.61	16.99	17.37	17.75	18.13

Table 4.1. Foam Formulations in system percent

Foam samples were prepared for each test at least 24 hours after formulation, then cut to size (bandsaw and razor blade) based on the test procedure. After cutting, foams were left at room temperature for at least 48 hours before analysis.

Apparent density was determined according to ASTM D1622¹²⁵ following previously published literature.¹⁴⁶ Each sample was measured volumetrically to 0.01 significant figures (three times per side) using a digital caliper and weighed using a digital scale (0.0001).

The cell size (diameter, strut width, and area) of each foam was measured following a modified version of ASTM D3576-15¹²⁷ using three-millimeter foam slices cut 25mm below the top of the foam.¹⁴⁶ The average of at least 20 cells from each slice were averaged and analyzed perpendicular to foam rise using a Dino-Lite Edge digital microscope (Torrance, CA, USA).¹⁴⁶

Closed-cell content was determined according to ASTM D6226-15¹²⁸ using a micromeritics gas pycnometer (AccuPyc II 1340, Norcross, GA, USA). Following previously published literature,¹⁴⁶and micromeritics method B¹²⁹ experimental conditions included nitrogen atmosphere with 10 purges and 10 cycles, along with 27.58 kPa purge and cycle fill pressures at 0.03 kPa/min.

Water absorption/volumetric change was determined according to ASTM D2842¹⁷³ (reduced sample size). Twenty-five-millimeter cube samples were measured volumetrically before and after 72 hours of water submersion. The change in volume was averaged and calculated from the absolute value of each sample in at least triplicate.

A Meter TEMPOS TPA machine (Pullman, WA, USA) was used to measure the thermal conductivity of foam samples. Measurements were taken perpendicular to foam rise (in at least triplicate) with glycerin as a calibration standard and a 60 mm K3 probe.

The compression strength of each foam sample was determined via ASTM D1621-16¹²⁶ using an Instron 5565 universal testing machine (Norwood, MA, USA). Twenty-five-millimeter cube samples were tested perpendicular to the foam rise, in at least triplicate, using a 2.5mm/min strain rate (13% initial thickness).

The muffle furnace char test procedure was performed following a modified method reported by Rogers et al.¹⁵⁴ In brief, 12.5 mm³ samples were measured volumetrically and

weighed. Then, each sample was wrapped in aluminum foil and placed inside a lidded ceramic crucible. The sample was then placed in a 450°C-muffle furnace for 5 minutes. After cooling, samples were remeasured, and percent change was calculated.

4.4 Results and Discussion

Quantitative ³¹ P NMR analysis was utilized to determine the hydroxyl content of lignin (Table 4.2) in line with previously published work .^{146,174} The results show that the hydroxyl content of lignin is suitable for polyols used for rigid foam formulation (>200 mg KOH/g)² and is comparable to the control (~361 mg KOH/g). These lignin hydroxyl content results are also within 10% of other researchers (6.15 and 6.42 mmol/g total),¹⁷⁵ and the modest difference in these values can be attributed to producer batch variations and ³¹P NMR method differences.⁶¹

	Total OH (mmol/g)	Hydroxyl Value (mg KOH/g)	Mn (Da)	Mw (Da)	PDI
SW-K	5.66	318	1500	6200	4.15

The molecular properties of lignin determined via gel permeation chromatography (GPC) are summarized in Table 4.2. In general, lower molecular weight and higher functionality polyols create foams with better mechanical strengths due to increased crosslinking.¹⁷⁶ Additionally, lower molecular weight polyols have been reported to have better reactivity due to decreased polyol blend viscosities.⁶⁷ Since the molecular properties of lignin can vary greatly between and within lignin sources, more work needs to be done to determine the direct effect of lignin molecular weight on foam properties.

The mix, cream, top of the cup, and string gel times of lignin-based foams were all significantly lower than the control (Figure 4.1), likely due to the optimized formulations in Table 4.1. As expected, from 25% to 100% lignin loading, the reaction times of lignin-based foams increased due to steric hindrance effects of lignin hydroxyl groups (i.e., guaiacyl)⁸⁴ and the increase in polyol blend viscosity (Table 4.3). The increase in reaction time using unmodified lignin has been reported by several studies even at lower lignin loading.^{10,146};





Up to 50% lignin loading, polyol blend viscosities were below the acceptable 20 Pa·s maximum (Table 4.3).¹⁵⁴ Other researchers have reported that the viscosity of polyol blends can be significantly reduced by heating to 50°C, turning solid polyol blends into liquids that are well below the maximum requirement.¹⁵⁵ The apparent densities of control and lignin-based foams ranged from 32-82 kg/m³ (Table 4.3), with foams with up to 75% lignin loading falling within

the range for low-density foams $(30-60 \text{ kg/m}^3)$.⁴⁹ In general, the addition of lignin increased foam density (r = 0.9) as reported by other researchers.^{71,72,80} This increase in apparent density is easily adjusted by using physical¹⁰² or chemical blowing agent.⁸⁸

Foam Label	Polyol Blend Viscosity (Pa·s)	Apparent Density (kg/m³)	Thermal Conductivity (W/mK)	Closed Cell Content (%)	Furnace Testing Weight Change (%)
0% KL	0.26 ± 0.03 ª	$32\pm1^{\text{a}}$	0.010 ± 0.0008 $^{\rm a}$	95.3 ± 0.07 $^{\circ}$	-60 \pm 6 a
25% KL	0.83 ± 0.06 ª	36 ± 1^{a}	$0.011\pm0.0004~^{\text{ab}}$	$94.5\pm0.02^{\text{b}}$	$\text{-49}\pm3^{\text{b}}$
50% KL	4.51 ± 0.02 ª	45 ± 2^{b}	$0.012\pm0.0004~^{\text{bc}}$	96.6 ± 0.06^{c}	-41 \pm 2 ^{bc}
75% KL	**	50 ± 2^{b}	0.014 ± 0.0009 c	$88.0\pm0.08{}^{\text{d}}$	-41 \pm 1 ^{bc}
100% KL	**	82 ± 6^{c}	$0.021\pm0.0007~^{\text{d}}$	6.20 ± 0.10^{e}	$-32\pm1^{\circ}$

Table 4.3. Foam Properties

*Values with the same letter are not significantly different (p < 0.05)

**Too high to test

Low thermal conductivity in foam ensures that the foam will act as a good insulator. All foams met the minimum requirements for thermal conductivity (Figure 4.2) with values far lower than the 0.257 W/mK maximum.¹³⁸ In general, lignin incorporation caused an increase in thermal conductivity (r = 0.8), though no significant difference was found between the control and lignin-based foams up to 50% lignin loading. Since apparent density increased outside of the low-density range (>30-60 kg/m³) for the 100% lignin-based foam formulation, the effect of density is significant for these foams. This significant increase in apparent density outside the acceptable low-density range from 75% to 100% lignin loading caused a significant positive correlation

between foam's apparent density and thermal conductivity (r = 1). Even with the increased density with lignin addition, all foams met the minimum requirements for thermal conductivity.



Figure 4.2. Thermal conductivity of foams. ASTM maximum is 0.25 W/mK.

The closed cell content of foam (Table 4.3) is crucial in maintaining a low thermal conductivity and must be at least 90% for insulative applications.¹³⁷ The highest closed-cell content was found at 50% lignin loading (~97%), outperforming the control and meeting more rigorous 95% closed-cell content requirements.¹³⁸ Above 50% loading, lignin-based foams did not meet the minimum closed cell content requirements for insulative applications. The decrease in closed cell content with lignin addition above 50% is reportedly caused by a combination of decreased compression strength, increased density, decreased reactivity, and cell inhomogeneity.⁴ This is the first study to evaluate the effect of lignin addition on closed cell content of low-density lignin-based PUR foam.

Compression strength (Figure 4.3) of foam should be ≥ 104 kPa for use in rigid foam¹³⁷ and has been reported as a limiting factor for lignin incorporation into polyurethane foams.^{84,146} All foams met the minimum requirement for compression strength up to 50% lignin loading. The 100% lignin-based formulation also met the minimum compression strength requirement but had significantly higher density (Table 4.2) than control and other lignin-based foams. Though not significant, the lignin-based foam outperformed the control at 25% lignin loading. This is the first study to successfully replace 50% of a petrochemical polyol with unmodified lignin while meeting minimum requirements for viscosity, compression strength, and closed cell content for low-density polyurethane foams.



Figure 4.3. Compression strength of formulated foams. Line denotes 104 kPa minimum. Darker colors denote higher lignin loading.

The cell morphology of formulated foams is shown in Figure 4.4. Cell diameter and perimeter of PUR foams increased with the addition of lignin (r = 0.6 and 0.7, respectively), while no significant difference was found between the cell diameter of lignin-based PUR foams compared to the control foam. Up to 75% lignin loading in PUR foams, no significant difference was found between the cell perimeter of control and lignin-based PUR foams. All control and lignin-based foams were comparable to ASTM requirements for cell diameter (~0.33 mm).¹²⁷



Figure 4.4. Cell sizes of formulated foams

The volumetric change/water absorption volume of foam is an important property because it can predict changes in thermal conductivity over the service life of the foam.¹⁷³

Because of this, the volumetric change of rigid foams should be below 5%.¹⁷³ All Foams were below the 5% maximum volumetric change for rigid foam, and below 50% loading, lignin-based foams outperformed the control (Figure 4.5). Above 50% lignin-loading, volumetric change increased compared to the control but still met minimum requirements. This increase in volumetric change with lignin loading over 50% is in line with the increase in cell perimeter (r =0.7) and apparent density (r = 0.7).



Figure 4.5. Volumetric change of formulated foams. Line denotes 5% maximum. Darker colors denote higher lignin loading.

Furnace testing determines char formation and mass loss differences in foam which can be useful in evaluating the suitability of foam in fire applications.^{154,177} All lignin-based PUR foams had significantly lower weight loss compared to the control foam (Figure 4.6 and Table 4.3), with the 100% lignin-based foam performing best. As the percentage of lignin increased in PUR foams, the weight loss of heated samples decreased (r = -1), proving the enhanced fire properties with lignin addition. Other researchers have utilized 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide and lignin¹⁷⁸ to enhance the fire properties of polyurethane, but here, we see that unmodified kraft lignin can have similar effects without the use of flame retardant.



Figure 4.6. Image of formulated foams pre and post-furnace test

4.5 Conclusion

Low-density lignin-based rigid polyurethane foams were formulated using 0-100% unmodified kraft lignin as petrochemical polyol replacement. Up to 50% lignin loading, all lignin-based foams met the minimum compression strength, thermal conductivity, closed cell content, and volumetric change requirements for insulative applications, while all lignin-based foams significantly outperformed the control foam in furnace testing without the use of flame retardant. This work successfully increases the unmodified lignin loading percentage from ~30% to 50% and proves that lignin can act as not only a polyol but flame retardant as well, increasing the

value proposition of lignin in polyurethanes. Future work should focus on the effect of lignin molecular weight on foam performance.

CHAPTER 5 ULTRACLEAN HYBRID POPLAR LIGNIN AS POLYOL REPLACEMENT IN RIGID POLYURETHANE/POLYISOCYANURATE FOAM

5.1 Abstract

Low-density polyurethane/polyisocyanurate (PUR/PIR) rigid foams were prepared by replacing 80% petrochemical polyol with feed hybrid poplar and aqueous lignin purification using hot agents (ALPHA) fractionated hybrid poplar lignin. Both feed and ALPHA fractionated hybrid poplar lignins were characterized to determine hydroxyl content, molecular properties, and pH. After characterization, lignins were used to formulate rigid PUR/PIR foam and were then compared to a control foam with no lignin. Foams were tested based on industrial ASTM standards for foaming, mechanical, and physical properties. All control and lignin-based foams met the minimum requirements for rigid foams in closed cell content, compression strength, and thermal conductivity testing. The ALPHA fractionation process successfully reduced molecular weight, molecular number, and polydispersity index of lignin and increased lignin pH. ALPHA lignin-based foams significantly improved foam reaction time, closed cell content, and cell diameter compared to feed lignin-based foams. Compared to the control, the incorporation of ALPHA modified lignin into foam enhanced closed cell content and increased compression strength of foam.

5.2 Introduction

Polyurethane (PUR) foams were first developed in the 1800s and are still derived from fossil fuel-based polyols and isocyanates.² Flexible polyurethane foams are the largest product category of polyurethanes but, due to increased use in construction, rigid foams are set to outpace all other polyurethane sectors in production over the coming years.¹⁷⁰ Rigid

polyurethane foams are formulated by reacting isocyanate and polyol along with various additives (most importantly blowing agent) at an isocyanate index above 100.² Isocyanate indexes above 250 create polyurethane/polyisocyanurate (PUR/PIR) foams which improve fire and compression properties due to isocyanate trimerization (isocyanurate formation).⁴ Rigid polyurethane and polyurethane/polyisocyanurate foams are used in construction, refrigeration, and structural applications due to their low density to high strength ratio.² Although rigid foams and other polyurethanes have been used for decades, the deleterious impacts of petroleum-derived polyols have created a call to action.

Lignin, the most abundant natural polymer second to cellulose, contains multiple types of naturally occurring hydroxyl functional groups that can act as polyol replacements, reacting with isocyanate to form polyurethane.^{67,84} Lignin polyols have been incorporated into rigid PUR foams as unmodified solids/fillers, chemically modified liquids/solids, and fractionated solids. The incorporation of unmodified lignin into rigid PUR foams has been limited to ~30% due to steric hinderance effects, increased polyol viscosity, high impurity content, and polydispersity of lignin. Because of this, lignin is often modified before being incorporated into foam. Chemical modification is the most popular method for lignin used in rigid PUR foam synthesis because it enhances these natural hydroxyl groups by converting phenolic hydroxyl groups to aliphatic, modifies molecular weight/polydispersity index and lowering glass transition temperature of lignin.^{21,49,107,148,67–74} Though chemical modification of lignin can improve lignin-based foam properties, the use of petrochemical solvents, high temperatures and pressure make these methods more environmentally taxing.^{21,49,107,148,67–74}

Solvent fractionation has been reported as an efficient method for enhancing lignin properties for use in polyurethanes.¹⁷⁹ Lignin fractionation reportedly increases homogenization, decreases dispersity, and increases compatibility between lignin and polyurethane.⁹² Multiple research groups have fractionated lignin using combinations like ethanol/butanone/methanol/acetone¹⁸⁰ and ethyl-acetate/ethanol/acetone⁹² to effectively reduce the lignin polydispersity index. Thies et al.¹⁸¹ discovered that kraft lignin splits into two liquid phases when mixed with aqueous acetic acid at relatively low solvent-to-lignin ratios (9:1 – 3:1).¹⁸¹ This behavior was further exploited by Tindall et al.¹⁸² to develop a process for purifying and fractionating biorefinery-type hybrid poplar lignin with controlled molecular weights using ethanol-water solutions.¹⁸²

To the best of our knowledge, the effect of lignin fractionation and the use of fractionated lignin in low-density rigid PUR/PIR foam has not been studied. In this work, we modify a feed hybrid poplar (HP) lignin using the aqueous lignin purification using hot agents (ALPHA) process,¹⁸² characterize it using various analytical techniques, then use it to replace 80% of petrochemical polyol in low-density rigid polyurethane/polyisocyanurate foam for the first time. The effect of feed and ALPHA lignin addition on foam properties like reaction time, closed cell content, thermal conductivity, and compression strength is determined by comparing both feed and ALPHA lignin-based foams to a control foam with no lignin; along with ASTM International standards for rigid foams used in structural/insulative applications.

5.3 Materials and Methods

Lignin Preparation

Hybrid Poplar (HP) feed lignin was extracted from HP wood chips with the following mild alkaline pretreatment procedure: *Populus nigra* var. *charkowiensis* × *P. nigra* var. *caudina* cv. NE19 wood chips were added to a 20-L digester (model AU/E-20, RegMed, Osasco, Brazil) along with NaOH at an 18 wt% loading on biomass. Water was then added to create a liquor-to-wood ratio of 5:1 wt/wt. The digester was then heated to 150 °C and held at this temperature for 3 h. After the 3-h period, the vessel was allowed to cool below 100 °C prior to opening. The resulting alkaline liquor was decanted from the residual solids and allowed to cool to room temperature before further processing. Next, this alkaline liquor was acidified to a pH of 2.0 by the addition of 96.6 wt% sulfuric acid. This resulted in the precipitation of lignin solids from the solution. This slurry was centrifuged to ensure the completed disengagement of the lignin particles from the residual brine solution. The lignin solids were then twice resuspended in deionized water (at a ratio of 1:5 lignin: water by mass), centrifuged, and the supernatant decanted to remove any excess salt residue. Finally, the still-damp lignin solids were dried, under ambient conditions for 24 h, then in a vacuum oven at 50°C for 24 h.

Fractionation of this lignin was achieved by using an 'ALPHA Solvent' of 80 wt% ethanol / 20 wt% water at a solvent-to-lignin ratio of 3:1 by mass. The solvent and lignin were added to a 2-L Parr reactor with a custom-made conical bottom. While at room temperature (measured to be 24.5 °C), the contents were mixed with a helical ribbon impeller at 60 RPM for 90 min. This resulted in a pliable lignin-rich (LR) phase at the bottom of the reactor, with a darkcolored solvent-rich (SR) phase atop the LR phase. The SR phase was vacuum filtered through

Whatman Grade 4 (20-25µm) filter paper to remove any insoluble contaminates. After the feed of the SR phase had been filtered, the LR phase was also added atop the filter paper to disengage any trapped solvent-rich phase from this viscous mass. The resulting filtrate was then added to a new vessel, and water was added to the SR phase at a ratio of 1:3, water-to-SR phase. This decreased the ethanol composition (on a lignin-free basis) of the SR phase from ~80% to ~60% and caused the precipitation of a new pliable, and cohesive LR phase. This LR phase, of higher molecular weight and purity than the feed, was set aside for further investigation. The SR phase that formed (after water addition) was dried to a solid and labeled as 'AHP' for further discussion. For reference, the AHP fraction was found to have a yield of 68.7% compared to the initial feed lignin.

Lignin Characterization

Hydroxyl content was measured in accordance with previous literature using an Agilent DDR2 500 MHz NMR spectrometer (VnmrJ 3.2 A: Billerica, MA, USA).^{26,122,123,146} In brief, 40 mg of lignin was dissolved in a mixture of pyridine, deuterated chloroform, and dimethylformamide. After this, 100 μ L of pyridine, deuterated chloroform, and cyclohexanol was added as internal standard.¹⁴⁶ Then, 50 μ L of pyridine, deuterated chloroform, and chromium (III) acetylacetonate was added as a relaxation reagent. Finally, Phosphitylation reagent (100 μ L 20chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane) was added in the last step. A 5 mm tube, 5 s relaxation delay, 90° pulse angle flip, and 128 scans were used to obtain data.¹⁴⁶

Number average molecular weight, weight average molecular weight, and polydispersity index of lignin samples were determined using gel permeation chromatography. To ensure lignin

solubility in the tetrahydrofuran mobile phase, lignin samples were first acetylated, according to previously published work .¹⁸³ Lignin acetylation was carried out by mixing 1 g lignin, 20 mL pyridine, and 20 mL of acetic anhydride and mixed for 24 hours at room temperature (600 rpm). Then the acetylated lignin was precipitated with 150 mL 0.1 M hydrochloric acid. Precipitated lignin was separated from the solution under vacuum filtration, washed three times with 0.05 M HCL and deionized water, and vacuum dried at 40°C for 16 hours.

After acetylation, lignin was then dissolved in THF (5mg/mL) and syringe filtered (PTFE, 0.45 μ m). The filtrate (25 μ L) was then analyzed on a Waters GPC (e2695 Separation Module) using a 1 mL/min flow rate and three 300 x 7.8 mm columns in series (Styragel HR 4 THF, Styragel HR 3 THF, and Ultrastyragel THF) at a constant column temperature of 35°C. A 2414 refractive index detector was used to detect peaks and monodisperse polystyrene (162, 370, 580, 945, 1440, 1920, 3090, 4730, 6320, 9590, 10,400, and 16,200) were used for calibration. Lastly, Empower GPC Software was used to collect and analyze data.

The pH of lignin was determined according to previously published literature.¹⁴⁶ About 0.1 g lignin was dispersed into 10 mL deionized water and stirred for 5 minutes at 350 rpm. Then, pH was measured after 30 seconds using a Fisher brand Mettler Toledo SevenCompact pH/Ion meter (Columbus, OH, USA).¹⁴⁶

Foam Preparation and Characterization

Foams were formulated according to ASTM D7487-13¹²⁴ and previously reported literature.¹⁴⁶ B-side polyol blend (polyol, lignin, additives) were mixed at 3000 rpm in a 237 mL cup at a predetermined ratio (Table 5.1). After this, isocyanate was added and mixed until the onset of the

exothermic isocyanate and water reaction (mix time), where heat was felt on the outside of the cup. Cream, top of cup, tack free, and end of rise times were observed.

Table 5.1. Foan	n Formulation	Components
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	Control	80% HP	80% AHP			
Foam Component	Foam Raw Material (%)					
Polyol	29.67	4.74	4.73			
Lignin	-	18.95	18.91			
Viscosity Reducer	2.97	9.48	9.45			
Water	0.07	0.06	0.06			
Surfactant	0.30	0.24	0.24			
Catalysts	1.85	2.14	2.14			
Flame Retardant	2.97	2.37	2.36			
Blowing Agent	6.53	5.21	5.20			
Isocyanate	55.64	56.81	56.92			

Closed Cell Content was determined using a Micromeritics Gas Pycnometer (AccuPyc II 1340, Norcross, GA, USA) according to ASTM D6226-15¹⁶² following Micromeritics Method B.¹²⁹

Foam thermal conductivity was measured using a Meter TEMPOS TPA (Pullman, WA, USA) with a 60 mm KS-3 probe. Measurements were taken according to previous literature using glycerin as the calibration standard.¹⁴⁶

The average cell diameter of foams was determined using a Dino Lite Edge Digital Microscope (Torrance, CA, USA) following ASTM D3576-15¹²⁷ and previously reported literature.¹⁴⁶

Apparent Density of formulated foams were determined following ASTM D1622¹²⁵ and previously published literature.¹⁴⁶ In brief, 25 mm cube samples were measured volumetrically, in triplicate using a digital caliper, and averaged. The weight of each sample was determined (0.0001g) and used to calculate the apparent density in kg/m³.

Foam compression strength was measured using an Instron 5565 Universal Testing Machine (Norwood, MA, USA) according to ASTM D1621-16¹²⁶ and published literature.¹⁴⁶

5.4 Results and Discussion

Unlike in previous applications of the ALPHA process to kraft lignin^{184,185}, the asrecovered HP lignin in this work did not readily form liquid-liquid equilibrium upon contact with an 'ALPHA Solvent' at any temperature between ambient and the boiling point of the solvent. As detailed in previous work,¹⁸⁶ the presence of high levels of salts and insoluble polysaccharides appear to have disrupted the formation of a lignin-rich phase. To combat this issue, a solvent composition (80/20 EtOH/water as mentioned in the methods section) was chosen to dissolve as much of the lignin as possible while leaving the undesired impurities behind as solids. At a relatively low ratio of solvent to lignin, we were able to dissolve more than 80% of the starting lignin solids. After dissolving the lignin, fractionation was then carried out by water addition, which resulted in the precipitation of liquid, lignin-rich phases of controlled molecular weight.

As the primary benefits of incorporating lignin into polyurethane foams are its costeffective and sustainably sourced nature, one may be concerned about the process complexity described so far. We want to clarify that, while the fractionation process splits one stream into several complementary purity and molecular weight, all of these lignin fractions can still be used to create individual value-added products.

Lignin Characterization

The physio-chemical properties of feed hybrid poplar (HP) and ALPHA HP (AHP) lignin samples are summarized in tables 5.2 and 5.3. The lignin hydroxyl values obtained via ³¹ P NMR (Table 5.2) were used to calculate the amount of isocyanate and additives to maintain a 270isocyanate index (Table 5.1) prior to their incorporation into foam (Figure 5.1). The acceptable hydroxyl content for rigid polyurethane foam is >200 ², with the commercial polyol having a hydroxyl value of ~227 mg KOH/g. Both HP and AHP lignins met the hydroxyl value requirement and had higher hydroxyl values than the commercial polyol. The ALPHA process was found to not significantly affect the hydroxyl content of lignin though a slight decrease in aliphatic, syringyl, and total hydroxyl values were observed while guaiacyl, p-hydroxyphenyl, and carboxylic acid hydroxyl groups increased with the ALPHA process.

Lignin Property	HP	AHP
Aliphatic (mmol/g)	2.18	2.05
Syringyl (mmol/g)	1.54	1.48
Condensed (mmol/g)	0.43	0.43
Guaiacyl (mmol/g)	0.87	0.88
P-Hydroxyphenyl (mmol/g)	0.20	0.28
Carboxylic (mmol/g)	0.83	0.89
Total OH (mmol/g)	6.05	6.01
Hydroxyl Value (mg KOH/g)	339	337

Table 5.2. Hydroxyl Content Determination of Feed and ALPHA Hybrid Poplar Lignin

 Samples



Figure 5.1. Image of Formulated Foams. A is the control foam with no lignin, B is the 80% feed HP lignin-based foam, and C is the 80% ALPHA HP fractionated lignin-based foam.

The pH and molecular properties of the two lignin samples are reported in table 5.3. The ALPHA process significantly decreased the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI), while also increasing the pH of lignin by 14% (p < 0.05). The increase in lignin pH has been reported to create lignin-based foams with better properties^{132,146}, while the direct effect of molecular properties on rigid foam have yet to be reported. Lignin extraction and modification processes have been proven to have a major impact on the structure of lignin,¹⁷⁴ and our pH and molecular weight results (Table 5.3) affirm this finding.

Label	Feed HP	ALPHA HP
Mn (Da)	1400	1300*
Mw (Da)	10400	4000*
PDI	7.2	3.1*
рН	5.7 ± 0.2	6.5 ± 0.1*

Table 5.3. Molecular Weight Distribution and pH Data of Lignins

*Significantly different from feed (p<0.05)

Foam Preparation and Characterization

The addition of HP lignin significantly increased all foam reaction times (Table 5.4) compared to the control, while AHP lignin-based foams were comparable to the control and ASTM D7487 estimated values.¹²⁴ Since hydroxyl contents of feed and ALPHA lignins were comparable (Table 5.2), the increased reactivity of AHP lignin-based foams compared to the feed HP lignin-based foams is likely due to the decreased molecular weight (Table 5.3) of AHP lignin. Polyols with lower molecular weight have lower polyol blend viscosities and higher mobility when mixed with isocyanate.⁸⁶ Higher mobility combined with lower polyol blend viscosities increase foam reactivity and create foams with more uniform cells, improved compression strength, and greater closed cell content.^{4,86}

Label	Mix Time (s)	Cream Time (s)	Top of Cup Time (s)	Tack Free Time (s)	End of Rise Time (s)
Control	4.3 ± 0.5 ª	6.3 ± 0.5 ª	8.3 ± 0.5 ª	19.7 ± 1.2 ª	34.7 ± 2.1ª
80% HP	5.7 ± 0.5 ^b	7.7 ± 0.5 ^b	13.3 ± 2.6 ^b	55.0 ± 0.8 ^b	69.0 ± 2.9 ^b
80% AHP	4.0 ± 0.1 ª	6.0 ± 0.1 ª	9.7 ± 0.5 ^{ab}	42.7 ± 2.5 °	49.3 ± 2.1 °
ASTM D7487 ¹²⁴	-	6.8 ± 0.85	21.9 ± 1.6	47.6 ± 7.5	62.1 ± 6.9

 Table 5.4.
 Foam Reaction Time

*Numbers with the same letter are not significantly different

Cell morphology was evaluated via closed cell content, cell diameter, and thermal conductivity (Table 5) analysis. All control and lignin-based foams met or exceeded the minimum requirements for closed cell content (>95%),¹³⁸ thermal conductivity (<0.25 W/mK), and were within the low-density range for rigid foams (30-60 kg/m³). The AHP lignin-based foam had significantly higher closed cell content than the control and HP lignin-based foams. The decreased closed cell content and increased thermal conductivity of HP lignin-based foams is likely due its significantly higher cell diameter (Table 5.5). For the AHP lignin-based foam, the improvements in thermal conductivity and closed cell content are a combination of increased cell size (Table 5.5) and enhanced reactivity (Table 5.4) compared to the control and HP lignin-based foams, based foams, respectively.

Table 5.5. Foam Properties

Label	Closed Cell Content (%)	Thermal Conductivity (W/mK)	Apparent Density (kg/m ³)	Cell Diameter (mm)	Compression Strength (kPa)
Control	98.29 ± 0.07 ª	0.0105 ± 0.001 ª	35 ± 1.2 ª	0.14 ± 0.01 ª	226 ± 23 ª
80% HP	95.74 ± 0.04 ^b	0.0136 ± 0.001 ^b	57 ± 2.1 ^b	0.33 ± 0.02 ^b	200 ± 35 °
80% AHP	99.34 ± 0.06 °	0.0132 ± 0.001 ^b	56 ± 3.2 ^b	0.26 ± 0.01 ^c	260 ± 35 °
ASTM/Range	>90-95 137,138	<0.25 138	30-60 ⁴	~0.33	≥172 ¹³⁸

*Numbers with the same letter are not significantly different

Though the apparent density (Table 5.5) of both feed and ALPHA lignin-based foams significantly increased compared to the control foam, all foams still fell within the acceptable range for low-density rigid foam (30-60 kg/m³).⁴ Additionally, all control and lignin-based foams met the minimum compression strength requirements for rigid foams (172 kPa) based on ASTM E1730-15.¹³⁸ The AHP lignin-based foam outperformed feed HP lignin-based foams in compression strength testing, likely due to a combination of decreased reaction times (Table 4), and decreased cell diameter (Table 5.5) compared to the feed HP lignin-based foam. The decreased molecular weight and reduction in reaction time (likely caused by increased catalytic activity with the isocyanate groups) are creating a more crosslinked and thus stronger final foam.⁶⁷

5.5 Conclusion

Lignin-based low-density rigid polyurethane/polyisocyanurate foams were successfully formulated using feed hybrid poplar (HP), and aqueous lignin purification using hot agents (ALPHA) modified HP lignin to replace 80% of petrochemical polyol. The ALPHA fractionated lignin displayed significantly decreased molecular weight and polydispersity index (PDI) and a more neutral pH. The incorporation of this ALPHA processed hybrid poplar lignin into foam increased compression strength and closed cell content compared to control and feed HP ligninbased foams. This work suggests that decreasing the molecular weight and/or PDI of a lignin precursor will positively impact the thermal and mechanical properties of resulting polyurethane/ polyisocyanurate foam. To better understand this connection, future investigations should attempt to decouple the molecular weight reduction and PDI reduction to better understand their individual impact on foam performance. Additionally, lignins from other biomass sources and extraction methods should be investigated to determine the role that lignin chemistry plays in foam formulation.

CHAPTER 6 CONCLUSIONS AND FUTURE WORK

6.1 CONCLUSIONS

The expansion of applications and growth in the polyurethane foam market has motivated industry and researchers to find more sustainable raw materials for polyurethane synthesis. One way to meet sustainability goals and decrease the cost of polyurethane foams is to replace polyol with lignin. Lignin is currently created in mass as a byproduct of multiple industries, specifically pulp and paper and changes within this industry specifically makes lignin valorization more important than ever.

Lignin has multiple hydroxyl functional groups that can react with isocyanate to form polyurethane. But the incorporation of unmodified lignin in high-density rigid PUR foam is limited to ~40% polyol replacement due to decreased foam performance above these loading percentages. Researchers have modified lignins to replace over 70% of commercial polyol but these techniques often utilize petrochemical raw materials and intense synthesis parameters. Our study was the first that was focused on closing the following gaps that exist in this field.

- 1. Study the effect of lignin properties (hydroxyl content, pH, impurity content, and molecular weight) on rigid polyurethane/polyisocyanurate foam performance
- Incorporation of unmodified lignin as polyol replacement in low-density rigid PUR foam formulations while ensuring that the developed foams meet the minimum ASTM International standard requirements (compression strength, closed cell content, volumetric change, and thermal conductivity) for insulation applications.

In this work, lignin-based low-density rigid polyurethane/polyisocyanurate and polyurethane foams were prepared by substituting up to 100% of the petroleum-based polyol with unmodified lignins. We found that unmodified corn stover lignin from the enzymatic hydrolysis process performed the best in low-density rigid PUR/PIR foam testing when used to replace 30% of petroleum-based polyols. Overall, our results showed that lignins with higher pH, sodium, potassium, calcium, and aliphatic/p-hydroxyphenyl contents were more suitable for PUR/PIR rigid foam applications, regardless of lignin source and isolation process.

One hundred percent of petrochemical polyol was replaced with unmodified lignin in low-density rigid PUR/PIR foam while meeting ASTM International standards for the first time. This value in low-density rigid PUR foams was found to be 50% while the incorporation of lignin into PUR and PUR/PIR foams significantly enhanced the fire properties of formulated foams at all lignin loadings compared to control foams. Additionally, lignin with reduced bulk molecular properties (isolated via ALPHA fractionation, at Clemson University) significantly improved foam reactivity compared to with the foam made with unfractionated feed lignin. The foams made with this lower molecular weight lignin also had higher compression strength and closed cell content compared to control foam with no lignin.

6.2 FUTURE WORK

Future works should focus on:

1. Expanding testing of lignin-based foams to ensure they meet minimum ASTM requirements in basic (already achieved in this study) and advanced testing:
- a. Basic testing: apparent density, closed cell content, compression strength, and thermal conductivity.
- b. Advanced testing: adhesion, response to thermal/humid aging, pH, water absorption, dimensional stability, volatile organic compound content, and fire.
- Exploration of modified lignins as polyol replacement in rigid PUR/PIR foam formulations.
- Developing lignin liquefaction/modification techniques that do not contain toxic raw materials.
- 4. Utilizing lignin to synthesize isocyanate to further increase the value proposition of lignin in polyurethane foam while exploring non-isocyanate lignin-based PUR foam
- 5. Incorporating more lignin source and isolation process combinations in lignin characterization and rigid foam formulation
- 6. Modeling lignin properties and foam performance to further understand the effect of lignin properties on foam performance along with subsequent life cycle and technoeconomic assessments to inform cost benefit analyses
- Scale-up production of lignin-based rigid PUR and PUR/PIR foams to determine enhancements needed at the industrial scale

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